$[FCO]^+$ ion. From a CO/Br_2 mixture and SbF_5 no evidence for $[BrCO]^+$ was obtainable. It is concluded that the $[FCO]^+$ ion is a stronger electrophile than the $[ClCO]^+$ ion, while the $[BrCO]^+$ ion is less thermally stable than the $[ClCO]^+$ ion.

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[1] F. Grandinetti, F.Pepi, A. Ricci, *Chem. Eur. J.* **1996**, *2*, 495–501.
[2] T. J. Buckley, R. D. Johnson III, R. E. Huie, Z. Zhang, S. C. Kuo, R. B. Klemm, *J. Phys. Chem.* **1995**, *99*, 4879–4885.
[3] T. Kotiaho, B. J. Shay, R. G. Cooks, M. N. Eberlin, *J. Am. Chem. Soc.* **1993**, *115*, 1004–1014.
[4] O. Bortolini, S. S. Yang, R. G. Cooks, *Org. Mass Spectrom.* **1993**, *28*, 1313–1322.
[5] P. Botschwina, P. Sebald, M. Bogey, C. Demuynck, J.-L. Destombes, *J. Mol. Spectrosc.* **1992**, *153*, 255–275.
[6] J. M. Dyke, N. Jonathan, A. Morris, M. J. Winter, *J. Chem. Soc. Faraday Trans. 2* **1981**, *77*, 667–672.
[7] K. A. Peterson, R. C. Mayrhofer, R. C. Woods, *J. Chem. Phys.* **1991**, *94*, 431–441.
[8] Y. Pak, R. C. Woods, *J. Chem. Phys.* **1997**, *107*, 5094–5102.
[9] G. K. S. Prakash, J. W. Bausch, G. A. Olah, *J. Am. Chem. Soc.* **1991**, *113*, 3203–3205.
[10] K. O. Christe, B. Hoge, J. A. Sheehy, W. W. Wilson, X. Zhang, *Abstr. Pap. 216th ACS National Meeting* (Boston, MA) **1998**, Div. of F_2-chem. 036.
[11] B. Hoge, J. A. Sheehy, G. K. S. Prakash, G. A. Olah, K. O. Christe, *Abstr. Pap. 12th European Symposium of Fluorine Chemistry* (Berlin) **1998**, B39.
[12] B. Hoge, J. A. Sheehy, J. A. Boatc, G. K. S. Prakash, G. A. Olah, *J. Am. Chem. Soc.*, submitted.
[13] B. Bley, H. Willner, F. Aubke, *Inorg. Chem.* **1997**, *36*, 158–160.
[14] B. Bley, Dissertation, Universität Hannover, **1997**.
[15] E. Bernhardt, B. Bley, R. Wartchow, H. Willner, F. Aubke, E. Bill, P. Kuhn, unpublished results.
[16] C. Bach, H. Willner, C. Wang, S. J. Rettig, J. Trotter, F. Aubke, *Angew. Chem.* **1996**, *108*, 2104–2106; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1974–1976.
[17] J. G. Ballard, T. Birchall, *Can. J. Chem.* **1978**, *56*, 2947–2950.
[18] W. J. Casteel, P. Kolb, N. LeBlond, H. P. A. Mercier, G. J. Schrobilgen, *Inorg. Chem.* **1996**, *35*, 929–942.
[19] M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, *Gaussian 94*, *Manual Version 5.0*, Gaussian, Inc., Pittsburgh, PA, **1995**.
[20] A. Saouli, I. Dubois, J. F. Blavier, H. Bredohl, G. Blanquet, C. Meyer, F. Meyer, *J. Mol. Spectrosc.* **1994**, *165*, 349–357.
[21] A. Foord, J. G. Smith, D. H. Whiffen, *Mol. Phys.* **1975**, *29*, 1685–1704.
[22] T. Sundius, *J. Mol. Struct.* **1990**, *218*, 321.
[23] D. H. Rank, D. P. Eastman, B. S. Rao, T. A. Wiggins, *J. Opt. Soc. Am.* **1961**, *51*, 929.
[24] E. Hirota, Y. Endo, *J. Mol. Spectrosc.* **1988**, *127*, 527–534.
[25] H. Willner, F. Aubke, *Angew. Chem.* **1997**, *109*, 2506–2530; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2402–2405.
[26] D. McNaughton, *Struct. Chem.* **1992**, *3*, 245–252.
[27] G. S. H. Chen, J. Passmore, *J. Chem. Soc. Dalton Trans.* **1979**, 1257–1261.

The Critical Importance of Water in the Asymmetric Allylboration of *N*-Trimethylsilylbenzaldimines with *B*-Allyldiisopinocampheylborane

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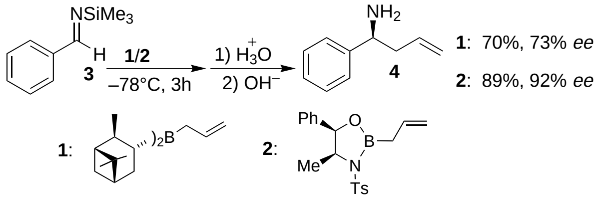
Dedicated to Professor Heinrich Nöth on the occasion of his 70th birthday

Among the several α-pinene-based asymmetric synthetic methods[1] that we have developed over the last ten years, the allylboration of aldehydes with *B*-allyldiisopinocampheylborane (**1**, D-Ipc_2BAll)[2] has been adopted in numerous syntheses.[3] Recently, we reported an efficient synthesis of C_2-symmetric diols with very high diastereoselectivity (*de*) and enantioselectivity (*ee*) by the allylboration of various dicarboxaldehydes with **1**.[4]

On the contrary, there are only a few reports on the allylboration of aldimines, probably owing to the inherent instability of such imines and the lack of reactivity of the more stable N-substituted imines.[5] Recently, Itsuno and co-workers reported the asymmetric allylboration of various N-masked benzaldimines with a variety of allylborating agents, including **1** (Scheme 1).[6] They concluded that *N*-trimethylsilylaldimine is the most reactive species for such allylborations. The reaction can be carried out at −78 °C to give the corresponding homoallylamines with up to 92 % *ee* upon use of the norephedrine derivative **2** as the chiral auxiliary. Villieras and co-workers adopted Itsuno's methodology for the allylboration of *N*-trimethylsilylaldimines with a 2-ethoxycarbonyl-substituted allylboronate.[7]



Scheme 1. Asymmetric allylboration of **3** with **1** or **2**.

We previously established that the rate of allylboration of aldehydes with **1** is exceptionally fast at −78 °C, and fast even at −100 °C.[8] It appeared desirable to obtain comparable information about the allylboration of imines, especially trimethylsilylaldimines, which Itsuno had reported to be very facile. Accordingly, we mixed *N*-trimethylsilylbenzaldimine (**3**) and **1** in THF at −78 °C and followed the rate of reaction by ^{11}B NMR spectroscopy. To our great surprise, we observed no reaction after several hours, not even after a week at room temperature! Clearly there is a discrepancy with the literature

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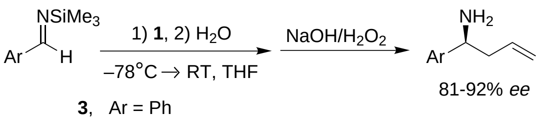
report of a reaction time of 3 h at −78 °C in the case of **1**.[6] The ^1H NMR spectrum also supported this observation, revealing only the unchanged starting materials. Interestingly, the aqueous workup of this reaction mixture led to a strongly exothermic reaction which provided the product amine in 95 % yield. Apparently, the reaction takes place during the aqueous workup. It might have proceeded by rapid liberation of the aldimine intermediate from the *N*-trimethylsilylaldimine derivative following the addition of water, with a fast reaction of the aldimine with **1**.

Consequently, we repeated the reaction with dropwise addition of a molar equivalent of water in THF to the solution of **3** and **1** at −78 °C (Table 1). Indeed, we obtained product amine **4** with 92 % *ee* and in 90 % yield (Scheme 2), which is considerably better than the 73 % *ee* and 70 % yield realized previously.[6] Lowering the reaction temperature to −100 °C improved the chiral induction to 94 % *ee*. In Itsuno's case, it is possible that the exothermic reaction during the aqueous workup raised the reaction temperature rapidly, resulting in an inferior enantioselectivity.



3, Ar = Ph
5, Ar = 2-Cl-C$_6$H$_4$
6, Ar = 4-MeO-C$_6$H$_4$
7, Ar = 2-furyl
8, Ar = 2-thienyl

Scheme 2. Asymmetric allylboration of **3** as well as **5**–**8** with **1**.

We then examined the allylboration of 2-chloro- (**5**) and 4-methoxybenzaldimines (**6**), and obtained the products with 82 and 92 % *ee*, respectively (Table 1), in contrast to the values of 46 and 52 % *ee* reported earlier.[6] In addition, the reaction of 2-furfuraldimine (**7**) and 2-thiophenealdimine (**8**) with **1** furnished the corresponding homoallylamines with 86 and 81 % *ee*, respectively. Thus, we have shown that in the presence of one molar equivalent of H_2O, **1** is an excellent reagent for the allylboration of aldimines.

N-Trimethylsilylimines are not reactive toward **1**. However, our observation suggests that the reactive aldimines can be generated in situ from *N*-trimethylsilylimines in a controlled manner upon addition of one equivalent of water, and then captured by the allylborating agent. We believe that this observation is significant for imine chemistry and should find wide applications in organic synthesis, extending considerably the range of applicability of the allylboration reaction.

Table 1. Asymmetric allylboration of some aromatic aldimines with D-Ipc$_2$BAll.

Imine[a]	*T* [°C]	Yield [%][b]	Product homoallylamines *ee* [%][b,c]	config.[d]	$[\alpha]_D^{22}$ (*c*, CHCl$_3$)
3	−78	90 (73)	92 (73)	*S*	−43.2 (1.9)
3	−100	87	94	*S*	−44.0 (1.3)
5	−78	69 (62)	82 (46)	*S*	−71.3 (1.5)
6	−78	74 (65)	92 (52)	*S*	−34.7 (1.2)
7	−78	86	86	*S*	−30.4 (1.5)
8	−78	72	81	*S*	−20.2 (1.5)

[a] The *N*-trimethylsilylaldimines were prepared in 75–87 % yield based on the literature procedure.[9] [b] The values in parentheses are from ref. [6]. [c] Determined by HPLC analysis of product amines on a Chiralcel OD-H column with hexanes/*i*PrOH/Et$_2$NH (95/5/0.05) as eluent. [d] Determined either by comparison with the rotation value reported in the literature,[10] or by analogy.

Experimental Section

Representative example: asymmetric allylboration of **3** with **1**. All of the operations were conducted under a nitrogen atmosphere: To a stirred solution of **3** (0.89 g, 5.0 mmol) and **1** (1.79 g, 5.5 mmol) in THF (5 mL) at −78 °C, was added dropwise H_2O (0.100 g, 5.5 mmol) in THF (0.50 mL). The mixture was stirred for 0.5 h, warmed to room temperature, and worked up with NaOH (6.0 mmol), H_2O_2 (12 mmol), and diethyl ether (20 mL). The product was extracted with 3 N HCl (3 × 10 mL). The combined aqueous layer was washed with diethyl ether (2 × 10 mL), neutralized with Na_2CO_3, extracted with diethyl ether (3 × 10 mL), washed with brine (2 × 10 mL), and dried over anhydrous $MgSO_4$. Removal of the solvent provided a crude product, which was purified by column chromatography (hexanes/*i*PrOH/Et$_2$NH 80/20/0.5) to afford the product, 1-phenyl-3-butenamine, as a colorless liquid (0.66 g, 90 % yield). HPLC analysis of the amine on a Chiralcel OD-H column revealed it to be the *S* isomer (92 % *ee*); $[\alpha]_D^{22} = -43.2°$ ($c = 1.9$ in CHCl$_3$; $[\alpha]_D^{22} = -42.6°$ ($c = 0.5$ in CH$_2$Cl$_2$)[10a]).

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[1] a) H. C. Brown, P. V. Ramachandran, *Advances in Asymmetric Synthesis, Vol. 1* (Ed.: A. Hassner) JAI, Greenwich, CT, **1995**, chap. 5; b) H. C. Brown, P. V. Ramachandran, *J. Organomet. Chem.* **1995**, *500*, 1–19.

[2] H. C. Brown, P. K. Jadhav, *J. Am. Chem. Soc.* **1983**, *105,* 2092.

[3] Examples of such applications: a) S. D. Rychnovsky, U. R. Khire, G. Yang, *J. Am. Chem. Soc.* **1997**, *119*, 2058–2059; b) A. B. Smith, S. S.-Y. Chen, F. C. Nelson, J. M. Reichert, B. A. Salvatore, *J. Am. Chem. Soc.* **1995**, *117*, 12013–12014; c) K. C. Nicolaou, M. E. Bunnage, K. Koide, *J. Am. Chem. Soc.* **1994**, *116*, 8402–8403.

[4] P. V. Ramachandran, G.-M. Chen, H. C. Brown, *Tetrahedron Lett.* **1997**, *38*, 2417–2420.

[5] a) Y. Yamamoto, W. Ito, K. Maruyama, *J. Chem. Soc. Chem. Commun.* **1985**, 1131–1132; b). Y. Yamamoto, T. Koshiaki, K. Maruyama, *J. Org. Chem.* **1985**, *50*, 3115–3121; c) Y. Yamamoto, S. Nishi, K. Maruyama, T. Komatsu, W. Ito, *J. Am. Chem. Soc.* **1986**, *108*, 7778–7786.

[6] a) K. Watanabe, K. Ito, S. Itsuno, *Tetrahedron: Asymmetry* **1995**, *6*, 1531–1534; b) S. Itsuno, K. Watanabe, K. Ito, A. A. El-Shehawy, A. A. Sarhan, *Angew. Chem.* **1997** *109,* 105–107; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 109–110.

[7] I. Chataigner, F. Zammattio, J. Lebreton, J. Villieras, *Synlett* **1998**, 275–276.

[8] H. C. Brown, U. S. Racherla, P. J. Pellechia, *J. Org. Chem.* **1990**, *55*, 1868–1874.

[9] D. J. Hart, K. Kanai, D. G. Thomas, T.-K. Yang, *J. Org. Chem.* **1983**, *48*, 289–294.

[10] a) T. Basile, A. Bocoum, D. Savoia, A. Umani-Ronchi, *J. Org. Chem.* **1994**, *59*, 7766–7773; b) S. Liu, A. Mi, L. Wu, Y. Jiang, *Synth. Commun.* **1993**, *23*, 2485–2488.