Allylation of Imines with Allyltrimethylsilane and Experimental Evidences for a Fluoride-Triggered Autocatalysis Mechanism of the Sakurai−Hosomi Reaction

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This article reports the reaction of allyltrimethylsilane **1** with aldimines **2** in the presence of tetra-*n*-butylammonium fluoride to give the corresponding homoallylamines **3** in moderate to excellent yields. The allylation mechanism of imines as well as that of aldehydes can be reasonably interpreted by a fluoride-triggered autocatalytic procedure.

Introduction

The allylation of carbonyl compound is one of the most important C−C bond forming reactions.[1] In addition to the widely used allyl organometallic reagents,[1−4] the use of allylsilane compounds opens a new facet in the allylation reaction.[5] The reaction of an allylsilane with a carbonyl compound under Lewis acid conditions or in the presence of fluoride ions, known as the Sakurai−Hosomi reaction,[6g] has been extensively studied and applied successfully in organic synthesis.[6] In contrast to the reaction with a C═O bond, little is known about its aza analogue, that is, the reaction between allylsilane and aldimine. Although the reactions of allyltrifluorosilane and allyltrimethylsilane with imines mediated by fluorides were reported by Sakurai and very recently by DeSheng, respectively,[7] excess florides have to be used (3−4 equiv of CsF and 10 equiv of tetrabutylammonium triphenyldifluorosilicate was used respectively). To our knowledge the reactions of allylsilane with imines in the presence of a catalytic amount of fluoride anion has never been reported. In this paper, we disclose our research results for this problem: the facile synthesis of homoallylamines from allyltrimethylsilane and imines under mild conditions triggered by a catalytic amount of fluoride ion and the experimental evidences for its mechanism.

Results and Discussion

I. Synthesis of Homoallylamines 3. To cleave the C−Si bond efficiently, several fluoride compounds, CsF, NH_4F, and *n*-Bu_4NF, were tested as catalysts for the reaction of allyltrimethylsilane (**1**) with benzylideneaniline (**2a**). The reaction gave no allylation product in the presence of 10 mol % of CsF while a 40% yield of homoallylamine **3a** was afforded when 10 mol % of NH_4F was used. According to the yields of homoallylamine **3a**, TBAF is the most efficient and suitable reagent for the allylation of aldimine in comparison with CsF and NH_4F (vide infra). The solubility of fluoride in THF may be a decisive factor.

Various homoallylamines **3** can be prepared by the reaction of allyltrimethylsilane **1** with aldimines **2** in the presence of 1 mol % of TBAF (Scheme 1), and the results are summarized in Table 1. The addition of allylsilane **1** to the simple aldimines **2**, which derive from aryl aldehydes and aryl amines (entries 1 and 3−5) proceeded very smoothly under reflux in the presence of as little as 1 mol % of TBAF or even 0.1 mol % (entries 1 and 3, respectively). Many organometallic reactions used in organic syntheses require strictly anhydrous reaction

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[1] For recent reviews, see: (a) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207. (b) Roush, W. R. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds. (Vol. 2 editor C. H. Heathcock); Pergamon Press: Oxford, 1991; pp 1−53. (c) Fleming, I. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I. Eds.(Vol. 2 editor C. H. Heathcock); Pergamon Press: Oxford, 1991; pp 563−593. (d) Masse, C. E.; Panek, J. S. *Chem. Rev.* **1995**, *95*, 1293. (e) Nishigaichi, Y.; Takuwa, A.; Naruta, Y.; Maruyama, K. *Tetrahedron* **1993**, *49*, 7395.

[2] (a) Yasuda, M.; Fujibayashi, T.; Shibata, I.; Baba, A.; Matsuda, H.; Sonada, N. *Chem. Lett.* **1995**, 167. (b) Jephcote, V. J.; Thomas, E. J. *Tetrahedron Lett.* **1985**, *26*, 5327. (c) Yamamoto, Y.; Maruyama, K.; Naruta, Y.; Yatagai, H. *J. Am. Chem Soc.* **1980**, *102*, 7101. (d) Yamamoto, Y.; Yatagai, H.; Ishihara, Y.; Maeda, N.; Maruyama, K. *Tetrahedron* **1984**, *40*, 2239. (e) Jephcote, V. J.; Pratt, A. J.; Thomas, E. J. *J. Chem. Soc., Chem. Commun.* **1984**, 800. (f) Yanngisawa, A.; Morodome, M.; Nakashima, H.; Yamamoto, H. *Synlett* **1997**, 1309. (g) Yanagisawa, A.; Inoun, H.; Morodome, M.; Yamamoto, H. *J. Am. Chem. Soc.* **1993**, *115*, 10356 and references therein.

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[4] For some leading references, see: (a) Roush, W. R.; Ando, K.; Powers, D. B.; Palkowitz, A. D.; Halterman, R. L. *J. Am. Chem. Soc.* **1990**, *112*, 6339. (b) Roush, W. R.; Palkowitz, A. D.; Ando, K. *J. Am. Chem. Soc.* **1990**, *112*, 6348. (c) Corey, E. J.; Yu, C. M.; Kim, S. S. *J. Am. Chem. Soc.* **1989**, *111*, 1, 5495. (d) Corey, E. J.; Huang, H. C. *Tetrahedron Lett.* **1989**, *30*, 5235 and references therein.

[5] For reviews, see: (a) Furin, G. G.; Vyazankina, O. A.; Gostevsky, B. A.; Vyazankin, N. S. *Tetrahedron* **1988**, *44*, 2675. (b) Sakurai, H. *Pure Appl. Chem.* **1985**, *57*, 1759. (c) Sakurai, H. *Pure Appl. Chem.* **1982**, *54*, 1. (d) Hosomi, A. *Acc. Chem. Res.* **1988**, *21*, 200.

[6] (a) Hosomi, A.; Shirahata, A.; Sakurai, H. *Tetrahedron Lett.* **1978**, *19*, 3043. (b) Sarker, T. K.; Andersen, N. H. *Tetrahedron Lett.* **1978**, *19*, 3513. (c) Deleris, G.; Dunogues, J.; Calas, R.; Pisciotti, F. *J. Organomet. Chem.* **1974**, *69*, C 15. (d) Deleris, G.; Dunogues, J.; Calas, R.; Pisciotti, F. *J. Organomet. Chem.* **1975**, *93*, 43. (e) Able, E. W.; Rowley, R. J. *J. Organomet. Chem.* **1975**, *84*, 199. (f) Hosomi, A.; Sakurai, H. *Tetrahedron Lett.* **1976**, 1295. (g) Generally, the Lewis acid-catalyzed allylation of carbonyl compound with allyl silane is known as the Sakurai−Hosomi reaction (Majetich suggested to name this reaction as Hosomi reaction, see ref 16a); here we further extended the name of this reaction to include the fluoride-triggered reaction.

[7] (a) Kira, M.; Hino, T.; Sakurai, H. *Chem. Lett.* **1991**, 277. They suggested that the pentacoordinate allylsilicate complexes might be involved when the following molar ratio of reagents was used: crotyltrifluorosilane/aldimine/CsF = 2/1/3−4. (b) Pilcher, A. S.; DeShong, P. *J. Org. Chem.* **1996**, *61*, 6901.

10.1021/jo980767y CCC: $18.00

Scheme 1

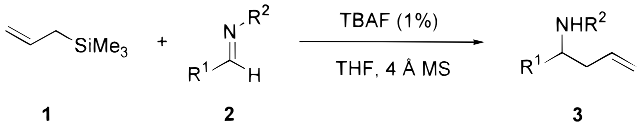

Table 1. Addition of Allyltrimethylsilane to Aldimines in the Presence of a Catalytic Amount of TBAF[a]

entry	R^1	R^2	reaction conditions	yield (%)[b]
1	Ph	Ph	1 mol % TBAF, 5 h	92 (**3a**)
2	Ph	Ph	1 mol % TBAF, 5 h	0[c]
3	Ph	Ph	0.1 mol % TBAF, 9 h	85 (**3a**)
4	*p*-MeOPh	Ph	1 mol % TBAF, 3 h	91 (**3b**)
5	furyl	*p*-MeOPh	1 mol % TBAF, 3 h	93 (**3c**)
6	Ph	Me	1 mol % TBAF, 2 d	74 (**3d**)
7	*p*-ClPh	$CH(CH_3)$-Ph (*R*)	1 mol % TBAF, 2 d	30 (60:40) (**3e**)[d]
8	Ph	*tert*-butyl	1 mol % TBAF, 2 d	
9	Ph	Ts	1 mol % TBAF, 2 d	

[a] The reaction was run on a 0.5 mmol scale, the ratio of reagents was allylsilane/aldimine = 1.2:1, and 200 mg of 4 Å MS was added. [b] Isolated yields based on aldimine. [c] No 4 Å MS was added. [d] Ratio of diastereoisomers (300 MHz ^{1}HNMR analysis) was obtained and is shown in parentheses. The configuration of the homoallylamine was not determined.

conditions, and the allylation reaction of allylsilane with imines is not an exception especially due to the easy hydrolysis of imines. Since the commercially available TBAF contains a certain amount of water, the addition of 4 Å MS was invoked. In the presence of anhydrous 4 Å MS, the reaction can take place efficiently. None of the desired product could be obtained in the absence of 4 Å MS (entry 2). In the cases of aldimines derived from alkyl amines, the reactions gave lower chemical yields (entries 6 and 7) even under reflux for an appropriate period of time. When a hindered aldimine (entry 8) and an *N*-electron deficient aldimine (entry 9) were used, no addition took place under the same conditions, even for a prolonged time period.

II. Mechanism of the Addition of Allylsilane with C=O and C=N Double Bonds. As DeShong reported in his paper,[7b] fluoride-promoted condensation of imines and allytrimethylsilane is an unprecedented reaction, but the reaction is not catalytic in the silicate salt. On the contrary, we found that the reaction of allyltrimethylsilane and imines can proceed smoothly with high yields in the presence of a catalytic amount of TBAF (Table 1). The reaction of allylsilane with an imine bears close analogy to that of the reaction with a carbonyl compound. For the later reaction, the so-called Sakurai−Hosomi reaction,[5,6] two possible mechanisms have been proposed.

The first mechanism is a fluoride ion catalyzed reaction[5c,6a] (Scheme 2). The released trimethylsilyl fluoride reacts again with the tetrabutylammonium alkoxide **5** to regenerate tetrabutylammonium fluoride in the catalytic cycle. This same author expressed concern about this mechanism due to the low boiling point of Me_3SiF (16.4 °C) which might not exist in the reaction system at the refluxing temperature. However, this mechanism is mentioned even in a recent monograph review book.[8a] The reviewer adopted this mechanism and modified it by the assumption that a pentacoordinated silicon species may also be involved. Recently, Bottoni and Tagliavini[8b] reported computational and experimental evidence for the mechanism of the Sakurai−Hosomi reaction in the presence of BF_3. They found that the reaction of aldehydes with allyltrimethylsilane promoted by BF_3 afforded fluorotrimethylsilane and a borylated homoallylic alcohol in a noncatalytic fashion, but they did not study the mechanism of fluoride-catalyzed allylation of aldehydes.

An alternative autocatalytic mechanism was proposed[9] for an isopropenylation reaction of benzophenone, which took place quantitatively at 50 °C (Scheme 3). In this mechanism, the fluoride ion just served as an initiator of the reaction and was not involved in the catalytic cycle. The strongly basic alkoxide **6** reacted with allylsilane and then regenerated the active species and completed the catalytic cycle. The intermediate **6** acted as a key species in the catalytic cycle, and autocatalysis was named for this mechanism. The authors, however, did not preclude the possibility of the participation of a hypervalent silicon intermediate $[CH_2{=}CHCH_2Si(F)Me_3]^-$. These two mechanisms appear in the authors' review article as two possible alternatives,[5b,c] and no further validation has appeared.

We deem that the first fluoride-catalyzed reaction probably does not occur, not only because of the low boiling point of Me_3SiF but also since the bond energy of Si−F (561 kJ/mol) is much higher than that of the Si−O bond (442 kJ/mol) and the Si−N bond (~316 kJ/mol).[10] So the metathesis between Me_3SiF and the alkoxy anion is not favorable thermodynamically even if Me_3SiF could exist as a solvent complex in the reaction mixture. In other words, we doubt that the fluoride ion could be regenerated under the reaction conditions.[11] To clarify this point, we synthesized the high-boiling triethylsilicon fluoride[12] and the key intermediate alkoxy anions **7** and **8** which were included in both the fluoride-catalyzed mechanism and the autocatalytic mechanisms and tried to find further evidence about the mechanism of this reaction.

First, when Et_3SiF and tetrabutylammonium alkoxy anion salt were mixed together in THF, no triethylsilyl alkyl ether formed even on refluxing for a prolonged period of time (eq 1 in Scheme 4). This indicates that the trimethylsilyl fluoride formed in the reaction cycle could not be regenerated to TBAF as shown in Scheme 2. Furthermore, when a catalytic amount of alkoxy anion (10 mol %) in place of fluoride ion was used for the Sakurai−Hosomi reaction (eq 2 in Scheme 4) and the reaction of allylsilane with imine **2a** (eq 3 in Scheme 4), both homoallyl alcohol and homoallylamine **3a** could be obtained in 76% and 65% yields, respectively.[13] Therefore, the autocatalytic reaction seems to be the most probable mechanism. Up to this point, we may extrapolate this autocatalytic mechanism to the aza analogue of the Sakurai−Hosomi reaction. But one still may argue as to

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(8) (a) For a recent book, see: Majetich, G. In *Organic Synthesis Theory and Application*; Hudlicky, T., Ed.; JAI Press Ltd.: 1989; Vol. 1, p 173. (b) Bottoni, A.; Costa, A. L.; Tommaso, D. D.; Rossi, I.; Tagliavini, E. *J. Am. Chem. Soc.* **1997**, *119*, 12131.

(9) Sakurai, H.; Hosomi, A.; Saito, M.; Sasaki, K.; Iguck, H.; Sasata, J.; Araki, Y. *Tetrahedron* **1983**, *39*, 883.

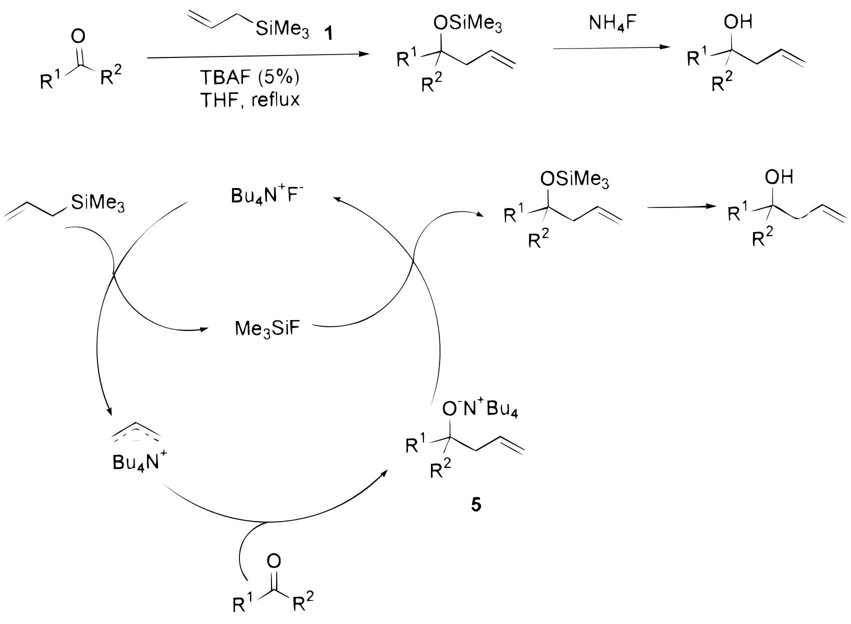
(10) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: New York, 1960; Chapter 3.

(11) For the fluoride-catalyzed Aldol reaction of enol silyl ethers with aldehydes, see: (a) Noyori, R.; Nishida, I.; Sakata, J. *J. Am. Chem. Soc.* **1981**, *103*, 2106. (b) Nakmura, E.; Shimizu, M.; Kuwajima, I.; Sakata, J.; Yokoyama, K.; Noyori, R. *J. Org. Chem.* **1983**, *48*, 932.

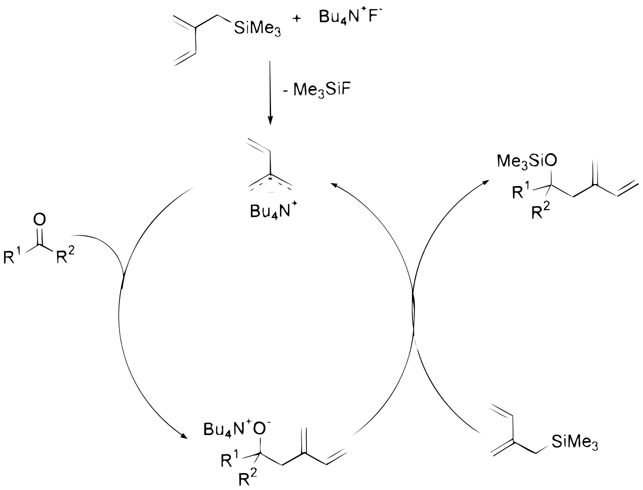
(12) DiGiorgio, P. A.; Strong, W. A.; Sommer, L. H.; Whitmore, F. C. *J. Am. Chem. Soc.* **1946**, *68*, 1380.

(13) For an example of an alkoxide-induced reaction between an imine and a benzylsilane derivative, see: Shimizu, S.; Ogata, M. *Synth. Commun.* **1989**, *19*, 2219.

Scheme 2



Scheme 3



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whether the amide anion intermediate **8** (analogue to **7**) is basic enough to do the same job. Similarly, with a catalytic amount of amide anion **8** (10 mol %) used instead of an alkoxy anion to catalyze this reaction, homoallylic amine could be obtained in 80% isolated yield (eq 3 in Scheme 4). Accordingly, a catalytic amount of amide anion generated in situ from the reaction product **3a**, NaH, and n-Bu$_4$NCl can also initiate this reaction (eq 4 in Scheme 4) in a one-pot manner, and no fluoride ion is further invoked.

The above experimental evidences showed that the fluoride ion only served as a trigger in these reactions and could not act as a catalytic species to regenerate n-Bu$_4$NF. It also showed that the autocatalytic cycle formed by the alkoxide ion or the amide anion is the most probable mechanism and the fluoride-catalyzed mechanism for the Hosomi−Sakurai reaction should be rejected. On the basis of this argument, a possible mechanism of the allylation of imine with allyltrimethylsilane **1** is proposed (Scheme 5), which confirmed the autocatalytic mechanism proposed by Sakurai and Hosomi.[9]

According to this mechanism, the interaction of allylsilane and fluoride ion leads to the evolution of Me$_3$SiF and the π-allyl species **A-1**, the countercation being tetra-n-butylammonium. π-Allyl species **A-1** then reacts with imine to afford intermediate **A-2**. The key species **A-2** then reacts with allylsilane again to regenerate active species **A-1** and a catalytic cycle is complete.

Interaction between **A-2** and allylsilane **1** gives the π-allylic anion **A-1** and the silyl homoallylamine. When the substituents on the nitrogen atom are bulky alkyl groups, such as *tert*-butyl (entry 7 of Table 1) or secondary alkyl (entry 6), the hindered structure causes the addition of **A-1** to be difficult. When the substituent was a strongly electron withdrawing tosyl group, it stabilized and reduced the nucleophlicity of the intermediate **A-2**, and hence stopped the catalytic cycle (entry 9).

According to the current pentacoordinated silicon chemistry,[14] probably a pentacoordinated species may also be involved during the reaction of **A-2** with allyltrimethylsilane **1** (from **A-2** to **A-1**). To probe the existence of this pentacoordinated species, a model reaction was carried out (Scheme 6). The tetrabutylammonium alkoxide of benzyl alcohol was prepared (eq 5) and subjected to a reaction with allyltrimethylsilane **1** at room temperature in THF (eq 6). After 1 h, the ^{29}Si NMR showed only two peaks at 0.06 and 17.25 ppm. The former one belongs to the chemical shift of allyltrimethylsilane **1** and the downfield one is the signal of the silyl ether which was confirmed by comparison with an authentic sample prepared by the reaction of benzyl alcohol and TMSCl in the presence of Et$_3$N. There was no signal indicating the presence of a pentacoordinated species in the background of the glass Si of the NMR tube (−70 to −200 ppm) as expected. However, this phenomenon does not exclude the presence of a transient formation of a pentacoordinated silicon intermediate.

It is claimed that a pentacoordinated silicon species could explain the γ-attack product in the reaction with cinnamyl- or crotyltrimethylsilane. Therefore, cinnamyltrimethylsilane[17] was subjected to a reaction with PhCH═

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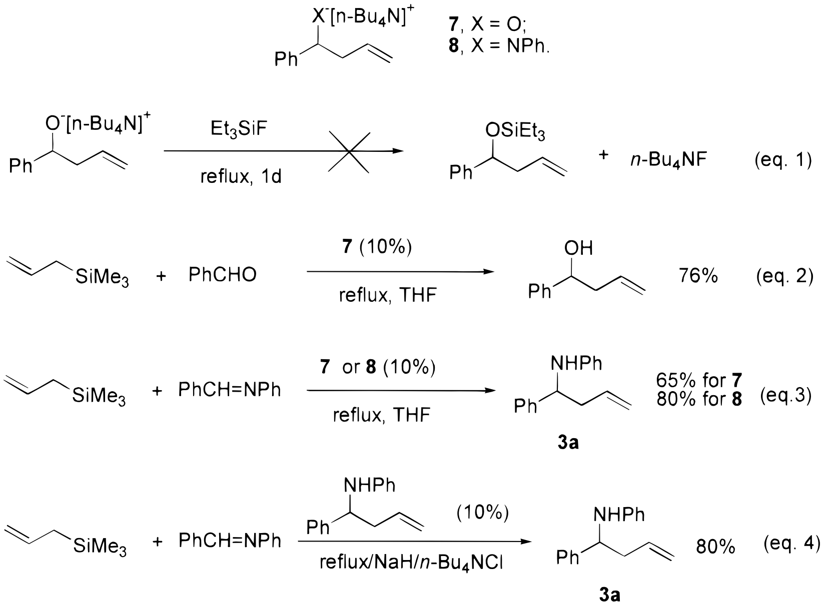
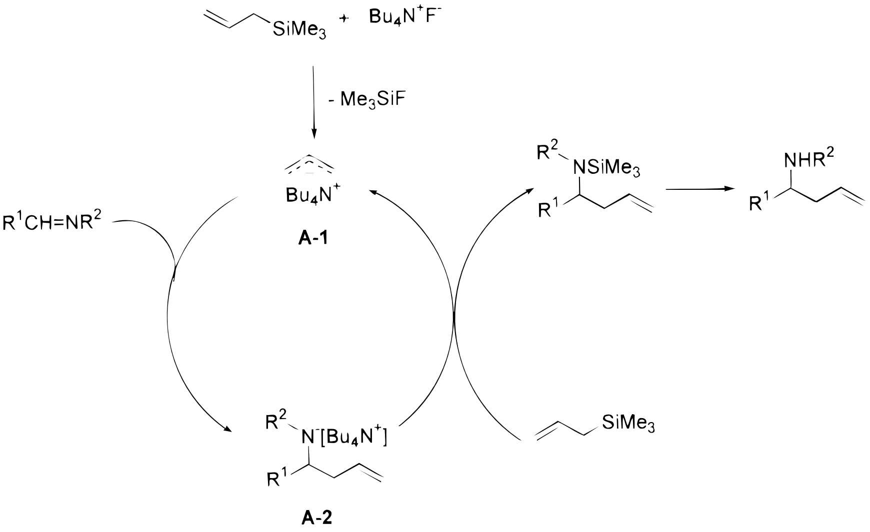
(14) For an excellent review on reactivity of pentacoordinate silicon compounds, see: Chuit, C. C.; Corriu, R. J.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371 and references therein.

(15) Love, B. E.; Raje, P. S.; Williams, T. C., II. *Synlett* **1994**, 493.

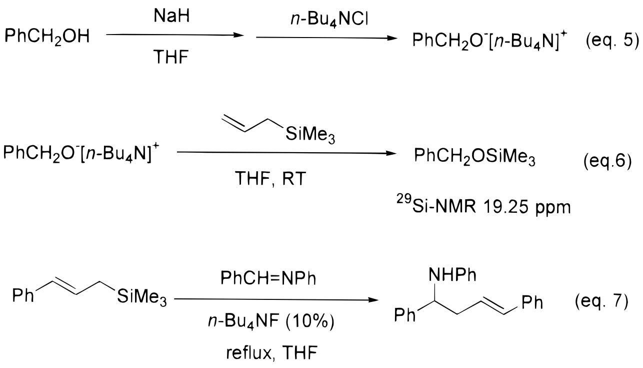
Scheme 4



Scheme 5



Scheme 6



NPh under the same conditions, and an almost linear product (>95:5) was obtained in 83% isolated yield (eq 7 in Scheme 6). Furthermore, Sakurai reported the reaction of 3-methyl-2-butenyltrimethylsilane with benzaldehyde in a catalytic amount of TBAF: a mixture of α- and γ-attack was obtained.[18] The exclusive α-attack in our case did not support the pentacoordinated silicon mechanism.

In conclusion, allylation of aldimines with allyltrimethylsilane triggered by a catalytic amount of TBAF under mild conditions is realized. Furthermore, experimental evidences also supported the fluoride-triggered autocatalytic mechanism of the Sakurai–Hosomi reaction as well as its aza analogue. This method represents the first example of a catalytic allylation of imines by allylsilane, which is a non-Lewis acid mediated allylation of aldimines and can be used for homoallylamine synthesis.

Experimental Section

Materials and General Procedure. All reactions were performed in oven-dried glassware under an atmosphere of nitrogen unless otherwise stated. THF was distilled im-

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(16) (a) Campbell, K. N.; Sommers, A. H.; Campbell, B. K. *J. Am. Chem. Soc.* **1944**, *66*, 822. (b) Castello, J. A.; Goldmacher, J. E.; Barton, L. A.; Kane, J. S. *J. Org. Chem.* **1968**, *33*, 3501.

(17) Slutsky, J.; Kwart, H. *J. Am. Chem. Soc.* **1973**, *95*, 8684.

(18) Sakurai, H. *Synlett* **1989**, 1.

mediately prior to use from sodium/benzophenone ketyl under nitrogen, and the other solvents were treated according to standard methods. Et_3SiF[12] and *N*-sulfonylimine[15] were prepared according to literature methods in reasonable yields. All imines were prepared according to reported procedures.[16] Proton magnetic resonance spectra were recorded on a Brucker AMX-300 (300 MHz) spectromer. *J* values are in hertz.

General Procedure for Fluoride-Triggered Allylation of Imines. To a solution of allyltrimethylsilane (0.6 mmol) and imine (0.5 mmol) in THF (2 mL) were added 200 mg of 4 Å molecular sieves and 30 μL of 1 M TBAF (in THF). The reaction mixture was refluxed. After reaction was complete according to TLC, the reaction mixture was filtered on a short silica gel column and the filtrate was concentrated and chromatographied on a silica gel column with a mixture of light petroleum ether (60−90 °C) and ethyl acetate (10:1) as the eluent to give pure homoallylamines (showed identical spectroscopic properties to those previously reported, see lit.[7b,19a,b]).

***N*-(Phenyl)-α-2-propenylbenzemethanamine (3a):**[7b] ^{1}H NMR ($CDCl_3$) δ 7.30 (m, 5H), 7.07 (t, $J = 8.84$ Hz, 2H), 6.66 (t, $J = 7.20$ Hz, 1H), 6.50 (m, 2H), 5.75 (m, 1H), 5.15 (m, 2H), 4.40 (m, 1H), 2.55 (m, 2H).

***N*-(*p*-Methoxyphenyl)-α-2-propenylbenzemethanamine (3b):**[19b] ^{1}H NMR ($CDCl_3$) δ 7.20 (m, 5H), 6.55 (d, $J =$ 9.01 Hz, 2H), 6.30 (d, $J = 9.10$ Hz, 2H) 6.00−5.65 (m, 1H), 5.20 (m, 2H), 4.25 (t, $J = 9.00$ Hz, 1H), 3.65 (s, 3H), 2.50 (d, J $= 9.00$ Hz, 2H), 1.30 (br, 1H).

***N*-(*p*-Methoxyphenyl)-α-2-propenylfurylmethanamine (3c):**[19b] ^{1}H NMR ($CDCl_3$/TMS) δ 7.30 (m, 1H), 6,75 (m, 2H), 6.55 (m, 2H), 6.30 (dd, $J_1 = 1.77$ Hz, $J_2 = 3.15$ Hz, 1H), 6.10 (d, $J = 3.15$ Hz, 1H) 5.70 (m, 1H), 5.15 (m, 2H), 4.45 (t, $J = 6.35$ Hz, 1H), 3.36 (s, 3H), 2.60 (t, $J = 6.78$ Hz, 2H), 2.00 (br, 1H).

***N*-Methyl-α-2-propenylbenzemethanamine (3d):**[19c] ^{1}H NMR ($CDCl_3$) δ 7.30 (m, 5H), 5.70 (m, 1H), 5.05 (m, 2H), 3.60 (t, $J = 6.90$ Hz, 1H), 2.45 (m, 2H), 2.30 (s, 3H).

***N*-(α-Methylbenzyl)-α-2-propenyl-*p*-chlorobenzemethanamine (3e).**[19b] Isomer 1: ^{1}H NMR ($CDCl_3$) δ 7.25 (m, 9H), 5.65 (m, 2H), 5.00 (m, 1H), 3.70 (m, 1H), 3.50 (t, $J = 6.72$ Hz, 2H), 2.45 (q, $J = 6.65$, 1H), 1.80 (br, 1H), 1.35 (d, $J = 6.65$ Hz, 2H). Isomer 2: ^{1}H NMR ($CDCl_3$) δ 7.25 (m, 9H), 5.65 (m, 2H), 5.00 (m, 1H), 3.70 (m, 1H), 3.40 (t, $J = 6.72$ Hz, 2H), 2.25 (q, $J =$ 6.65, 1H), 1.80 (br, 1H), 1.30 (d, $J = 6.65$ Hz, 2H).

Synthesis of Tetrabutylammonium Alkoxide 7 and Amide 8. To a solution of alcohol or amine (5 mmol) in THF (5 mL) was added NaH (5 mmol) in three portions, and after 30 min, 1.40 g (5 mmol) tetrabutylammonium chloride was added under nitrogen and the reaction miture was stirred for 6 h at room termperature. The concentration of the resulting solution is 1 M.

Allylation of Imine and Aldehyde Catalyzed by the Tetrabutylammonium Salt. To a solution of allyltrimethylsilane (0.6 mmol) and imine or aldehyde (0.5 mmol) in THF (2 mL) were added 200 mg of 4 Å molecular sieves and 60 μL of 1 M tetrabutylammonium alkoxide **7** or amide **8** (in THF). The reaction mixture was refluxed after reaction was complete according to TLC. The reaction mixture was filtered on a short silica gel column, and the filtrate was concentrated and chromatographed on a silical gel column with a mixture of light petroleum ether (60−90 °C)/ethyl acetate (10:1) as the eluent to give pure homoallylamines or homoallyl alcohols.

Regiochemistry of Fluoride-Triggered Reactions of Allylic Silanes. To a solution of cinnamyltrimethylsilane[17] (0.6 mmol) and imine (0.5 mmol) in THF (2 mL) were added 200 mg of 4 Å molecular sieves and 30 μL of 1 M TBAF (in THF). The reaction mixture was refluxed. After reaction was complete according to TLC, the reaction mixture was filtered on a short silica gel column, and the filtrate was concentrated and chromatographied on a silica gel column with a mixture of light petroleum ether (60−90 °C) and ethyl acetate (10:1) as the eluent to give pure homoallylamines.

***N*-(Phenyl)-α-(3-phenyl-2-propenyl)benzemethanamine:** ^{1}H NMR ($CDCl_3$) δ 2.72 (m, 2H), 4.48 (dd, $J = 7.6$, 5.4, 1H), 6.13 (dt, $J = 15.8$, 7.2, 1H), 6.50 (m, 3H), 6.64 (m, 1H), 7.06 (m, 2H), 7.30 (m, 10H); MS m/z 300 (M + 1, 19), 299 (M^+, 71), 207 (56), 182 (100), 91 (7); IR 3412, 3026, 1602, 1505, 693; HRMS calcd for $C_{22}H_{21}N$ (M^+) 299.1674, found 299.1650.

Spectroscopic Investigations. ^{29}Si NMR: $BnOSiMe_3$ (or allyltrimethylsilane) was directly dissolved in anhydrous THF at room termperature, the chemical shift of allyltrimethylsilane is 0.06 ppm, $BnOSiMe_3$ is 19.25 ppm. The exchange of tetrabutylammonium alkoxide BnON(n-Bu)$_4$ with allyltrimethylsilane was performed in an NMR tube under nitrogen at room termperature in anhydrous THF (Me_4Si as the inner standard); after 30 min, the NMR tube was transferred into the NMR instrument set at room termperature. Recording of ^{29}Si NMR spectra showed the signals of allyltrimethylsilane (0.06 ppm) and $BnOSiMe_3$ (19.17 ppm).

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