Allallylsilane compounds opens a new facet in the widely used allyl organometallic reagents,\textsuperscript{1} reaction,\textsuperscript{6g} has been extensively studied and applied successfully in organic synthesis.\textsuperscript{6} In contrast to the as the Sakurai catalyzed allylation of carbonyl compound with allyl silane is known\textsuperscript{1982}, \textsuperscript{1985}.

**Introduction**

The allylation of carbonyl compound is one of the most important C–C bond forming reactions.\textsuperscript{1} In addition to the widely used allyl organometallic reagents,\textsuperscript{1–4} the use of allylsilane compounds opens a new facet in the allylation reaction.\textsuperscript{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,\textsuperscript{69} has been extensively studied and applied successfully in organic synthesis.\textsuperscript{6} In contrast to the reaction with a C=O bond, little is known about its azalike 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,\textsuperscript{7} excess fluorides 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**

1. **Synthesis of Homoaallylamines 3.** To cleave the C–Si bond efficiently, several fluoride compounds, CsF, NH\textsubscript{4}F, and n-Bu\textsubscript{4}NF, 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 homoaallylamine 3a was afforded when 10 mol % of NH\textsubscript{4}F was used. According to the yields of homoaallylamine 3a, TBAF is the most efficient and suitable reagent for the allylation of aldimines in comparison with CsF and NH\textsubscript{4}F (vide infra). The solubility of fluoride in THF may be a decisive factor.

Various homoaallylamines 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 conditions, and the mild conditions reported above are a great advantage over other methods. In addition, 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, ref 16a); here we further extended the name of this reaction to include the fluoride-triggered reaction.
The reaction of allylsilane with an imine bears close
in the presence of a catalytic amount of TBAF (Table 1).
Lane and imines can proceed smoothly with high yields
contrary, we found that the reaction of allyltrimethylsi-
an and allytrimethylsilane is an unprecedented reaction, but
Isolated yields based on aldimine.

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.

The authors, however, did not preclude the possibility of the participation of a hypervalent silicon
intermediate \[\text{CH}_2=\text{CH}_2\text{Si(}\text{F})\text{Me}_3\] . These two mecha-
nisms appear in the authors’ review article as two possible alternatives,\textsuperscript{a,b,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$_3$SiF 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).\textsuperscript{11}
So the metathesis between Me$_3$SiF and the alkoxy anion is not favorable thermodynamically even if Me$_3$SiF 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.\textsuperscript{11} To clarify
this point, we synthesized the high-boiling triethylsilicon
fluoride\textsuperscript{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$_3$SiF 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. Fur-
thermore, 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.\textsuperscript{13}
Therefore, the autocatalytic reaction seems to be the most probable
mechanism. Up to this point, we may extrapolate this
catalytic mechanism to the aza analogue of the
Sakurai–Hosomi reaction. But one still may argue as to

(9) Sakurai, H.; Hosomi, A.; Saito, M.; Sasaki, K.; Iguck, H.; Sasata,
(10) Pauling, L. The Nature of the Chemical Bond, 3rd ed.; Cornell
(11) For the fluoride-catalyzed Aldol reaction of enol silyl ethers with
aldehydes, see: (a) Noyori, R.; Nishida, I.; Sakata, J. J.; Am. Chem.
(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 alkoxy-induced reaction between an imine and a benzylsilane derivative, see: Shimizu, S.; Ogata, M. Synth.
Commun. 1989, 19, 2219.
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-Bu4NCl 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-Bu4NF. 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 Me3SiF and the $\pi$-allyl species A-1, the countercation being tetra-n-butylammonium. $\pi$-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 $\pi$-allylic anion A-6 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 nucleophilicity 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 allyltrimethylsilyl 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 Et3N. 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 $\gamma$-attack product in the reaction with cinnamyl- or crotyltrimethylsilane. Therefore, cinnamyltrimethylsilane17 was subjected to a reaction with PhCH=...
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-butynyltrimethylsilane with benzaldehyde in a catalytic amount of TBAF: a mixture of α- and γ-attack was obtained. The exclusive α-attack in our case did not support the pentacoordinated silicon mechanism.

In conclusion, allylation of aldimines with allyltr trimethylsilane 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-


(18) Sakurai, H. Synlett 1989, 1.
Allylation of Imines with Allyltrimethylsilane

mediately prior to use from sodium/benzophenone ketyl under nitrogen, and the other solvents were treated according to standard methods. Et₂SiF₂ and N-sulfonylimines were prepared according to literature methods in reasonable yields. All imines were prepared according to reported procedures. Proton magnetic resonance spectra were recorded on a Brucker AMX-300 (300 MHz) spectrometer. 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 tetrabutylammonium tetrabutylammonium chloride was added under nitrogen and the reaction mixture was stirred for 6 h at room temperature. The concentration of the resulting solution is 1 M.

Allylation of Imines 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 30 μL of 1 M tetrabutylammonium chloride 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 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).

Regiochemistry of Fluoride-Triggered Reactions of Allylic Silanes. To a solution of o-nitroallyltrimethylsilane (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 chromatographed on a silica 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.

N-(Phenyl)-α-2-propenylbenzethanamine (3a): ¹H NMR (CDCl₃) 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-propenylbenzethanamine (3b): ¹H NMR (CDCl₃) 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-propynylfurfurylbenzethanamine (3c): ¹H NMR (CDCl₃/TMS) δ 7.30 (m, 1H), 6.75 (m, 2H), 6.55 (m, 2H), 6.30 (dd, J₁ = 1.77 Hz, J₂ = 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-propenylbenzethanamine (3d): ¹H NMR (CDCl₃) 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-β-chlorobenzethanamine (3e): ¹H NMR (CDCl₃) 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 Hz, 1H), 1.80 (br, 1H), 1.35 (d, J = 6.65 Hz, 2H). Isomer 2: ¹H NMR (CDCl₃) 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 Hz, 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 mixture was stirred for 6 h at room temperature. The concentration of the resulting solution is 1 M.

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