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o-Bis(allyldimethylsilyl)benzene as a Remarkably Effective Allylation Agent for Carbonyl Compounds with Bu_4NF Catalyst

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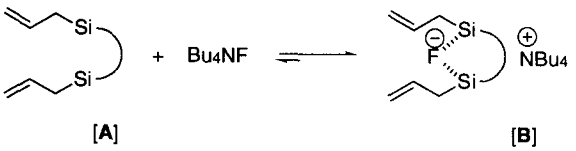
Abstract: A new type of fluoride ion catalyzed allylation agent, *o*-bis(allyldimethylsilyl)-benzene (**1a**) and bis(allyldimethylsilyl)methane (**1b**), can be successfully utilized for various carbonyl substrates. The rate acceleration is ascribable to the shift of equilibrium to complex with Bu_4NF by the favorable chelation of bis(silane) toward the fluoride ion.

Fluoride ion displays an extremely high affinity toward silicon atoms in organosilicone compounds as expected from the high homolytic bond energy (132 Kcal/mol) of the Si-F linkage,[1,2] and the utilization of this characteristic property was initially demonstrated in protonolysis of the Si-O bond.[3] The synthetic potential of the fluoride-mediated generation of nucleophiles has been exploited by the desilylation of alkynylsilanes,[4] allylic silanes,[5,6] silyl enol ethers,[7,8] and silyl ketene acetals.[9] Among these, the desilylation condition of allylic silanes is not mild enough (THF reflux) for sensitive functional group compatibility within a molecule. This is mainly due to the mobile equilibrium between the parent allylic silanes and their unfavorable complexes with Bu_4NF (eq 1). In this context, we have been interested for some time in the possibility of generating allyl anion species from certain allylic silanes with Bu_4NF catalyst under mild reaction conditions without affecting other sensitive functional groups. Here, we wish to report that some bis(allyl)silanes of type [**A**] are highly effective for generating allyl anion species *via* a chelate formation [**B**] with Bu_4NF (eq 2), thereby allowing the hitherto unattainable mild allylation with carbonyl compounds.[10]

(1)



(2)

o-Bis(allyldimethylsilyl)benzene (**1a**) was initially selected to observe any chelation effect with Bu_4NF catalyst. It was synthesized by treatment of *o*-bis(dimethylsilyl)benzene with Br_2 (2 equiv) followed by

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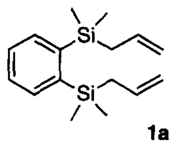
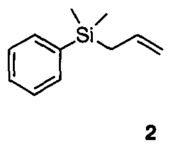
allylmagnesium bromide (2.2 equiv) in 75% yield. Reaction of **1a** with benzaldehyde in the presence of 5 mol% of Bu_4NF in THF at 0 °C proceeded smoothly within 1 h to furnish allylation product **3** quantitatively (eq 3). In contrast, the corresponding monosilyl derivative, allyldimethylphenylsilane **2** upon reaction with benzaldehyde under similar reaction conditions afforded **3** in only 4% yield.[11,12] Clearly, the rate acceleration with bis(silyl) compound **1a** is ascribable to the shift of equilibrium to the complex [**B**] with Bu_4NF by the favorable chelation of bis(silane) toward the fluoride ion as shown in eq 2.[13]



1a



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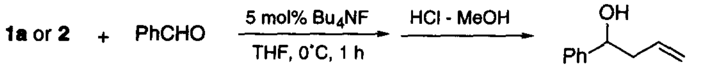
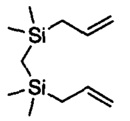


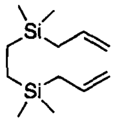
(3)

3 >99% with **1a**
4% with **2**

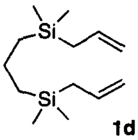
We then synthesized a series of bis(allyl)silane compounds, **1b-h** possessing other spacers between two silyl groups, and evaluated their chelation effect with Bu_4NF catalyst by allylating benzaldehyde under the above conditions. The results, summarized in Table 1, showed bis(allyl)silane **1a** and **1b** to be most satisfactory (entries 1-2). Notably, switching one allyldimethylsilyl group in **1a** by the trimethylsilyl group significantly lowered the yield of allylation product **3** (entry 8). Due to the two allylsilyl groups, **1a** probably has higher affinity toward the fluoride ion than **1h**.



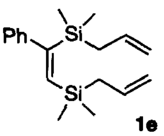
1b



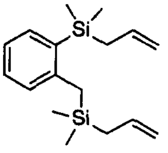
1c



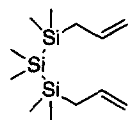
1d



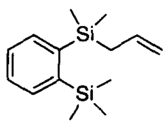
1e



1f



1g



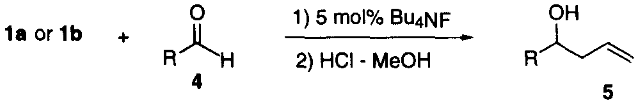
1h

With this information at hand, the allylation reactions of *o*-bis(allyldimethylsilyl)benzene (**1a**) and bis(allyldimethylsilyl)methane (**1b**) with several aldehydes **4** were then carried out as listed in Table 2. Allylations of aromatic aldehydes proceeded smoothly at 0 °C to room temperature to give the corresponding homoallyl alcohol **5** in high yield (entries 1-4). However, reactions of aliphatic and α,β-unsaturated aldehydes were sluggish under similar conditions (entries 5-7).

Table 1. Allylation of benzaldehyde with bis(silyl) compounds, **1a-h** in the presence of 5 mol% Bu_4NF.[a]

entry	bis(silyl) compound	% yield of **3**[b]
1	**1a**	100
2	**1b**	100
3	**1c**	53
4	**1d**	25
5	**1e**	53
6	**1f**	60
7	**1g**	0
8	**1h**	33

[a] The reaction was carried out using bis(allyldimethylsilyl) compound (1.1 equiv) and benzaldehyde (1.0 equiv) at 0°C for 1h. [b] Isolated yield.



(4)

Table 2. Allylation of various aldehydes **4** with bis(allyl)silane **1a** and **1b** in the presence of 5 mol% Bu_4NF in THF.[a]

entry	bis(allyl)silane R	aldehyde **4**	condition (°C, h)	% yield of **5**[b]
1	**1a**	p-$MeOC_6H_4$	0, 4	85
2	**1a**	p-FC_6H_4	rt, 0.6	99
3	**1b**	p-FC_6H_4	0, 2	89
4	**1a**	β-naphtyl	rt, 0.3	98
5	**1a**	$CH_3(CH_2)_5$	rt, 4	32
6	**1b**	$CH_3(CH_2)_5$	rt, 3	34
7	**1a**	C_6H_{11}	0, 4	35
8	**1a**	PhCH=CH	0, 4	40
9	**1b**	PhCH=CH	rt, 3	49

[a] The reaction was carried out using bis(allyldimethylsilyl) compound (**1a** or **1b**) (1.1 equiv) and aldehydes **4** (1.0 equiv). [b] Isolated yield.

The allylation of benzaldehyde with **1a** is representative: To a solution of **1a** (0.32 ml, 1.1 mmol) and benzaldehyde (0.10 mL, 1.0 mmol) in THF (2 mL) was added a 1 M THF solution of Bu_4NF (0.05 mL, 0.05 mmol) at 0°C under argon. After stirring for 1h at this temperature, the reaction was quenched by a mixture of 1N HCl and MeOH (1 : 9) at 0°C. Ether was added and the mixture was washed with satd $NaHCO_3$ and brine. The organic layer was dried, filtered, and concentrated. The residue was purified by column chromatography on silica gel using a mixture of hexane and EtOAc (5:1) as eluant to give 1-phenyl-3-buten-1-ol (**3**) (148 mg, 100% yield) as a colorless oil.

In summary, we have developed a new type of fluoride ion-catalyzed allylation agent, *o*-bis(allyldimethylsilyl)benzene (**1a**) and bis(allyldimethylsilyl)methane (**1b**). The allylation proceeds much faster than those with monosilyl counterparts due to the preferable formation of the chelate complex [**B**] (eq 2) by the chelation effect of two neighboring silicon atoms. A more appropriate choice of nucleophilic substituents on silicon atoms and a more sophisticated design of bis(silyl) compounds possessing the high chelation effect with fluoride ion are subjects of our ongoing study.

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11. The reaction of allyltrimethylsilane with benzaldehyde under similar conditions gave 14% yield.
12. Reaction of allyltrimethylsilane with various carbonyl substrates in the presence of 5 mol% of Bu_4NF in refluxing THF is reported to produce allylation products in high yields (ref. 5). In our hands, treatment of allyltrimethylsilane with the same carbonyl substrates (*e.g.*, hydrocinnamaldehyde, cyclohexanone...) gave the allylation products in quite low yield. We used commercially available Bu_4NF from Aldrich Chemical Co. by drying it with molecular shieves 4Å. On the other hand, Hosomi and Sakurai prepared Bu_4NF by themselves, thereby causing the different outcome (Private communication by Prof. Hosomi).
13. The existence of the chelate complex of **1a** with fluoride ion like [**B**] was also supported by ^{19}F NMR analysis. The spectra of Bu_4NF and a mixture of Bu_4NF and **2** in $CDCl_3$ did not show any noticeable difference in chemical shifts. The original F signal in Bu_4NF appeared at δ -81.98 and, upon addition of 1 equivalent of **2**, the signal shifted slightly to δ -82.01 (ethyl trifluoroacetate as external standard). However, the spectrum of the mixture of **1a** and Bu_4NF showed two peaks at δ -81.75 and -77.67, respectively (integration ratio = ~9:1). The large signal corresponds to the original peak of Bu_4NF and the small one might be ascribed to the chelate complex [**B**] between **1a** and Bu_4NF.