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

Naoki Asao, Atsushi Shibato, Yoshifumi Itagaki, Fabrice Jourdan, and Keiji Maruoka*

Department of Chemistry, Graduate School of Science,
Hokkaido University, Sapporo 060, Japan

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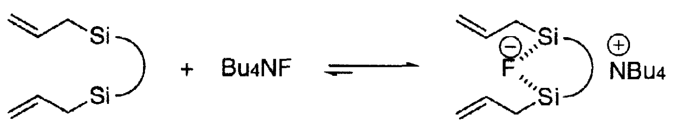
Abstract: **A new type of fluoride ion catalyzed allylation agent, o-bis(allyldimethylsilyl)-benzene (1a) and bis(allyldimethylsilyl)methane (1b), can be successfully utilized for various carbonyl substrates. The rate acceleration is ascribable to the shift of equilibrium to complex with Bu_4NF by the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

[**A**] [**B**]

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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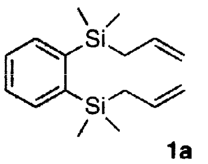
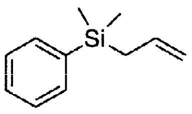
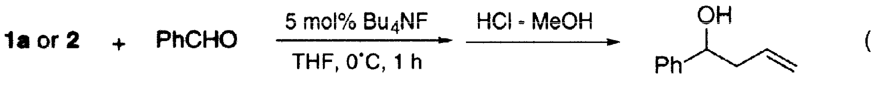
allylmagnesium bromide (2.2 equiv) in 75% yield. Reaction of **1a** with benzaldehyde in the presence of 5 mol% of Bu_4NF in THF at 0 °C proceeded smoothly within 1 h to furnish allylation product **3** quantitatively (eq 3). In contrast, the corresponding monosilyl derivative, allyldimethylphenylsilane **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



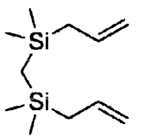
2



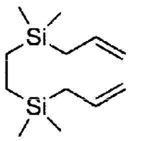
(3)

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

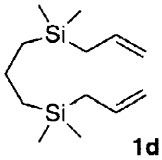
We then synthesized a series of bis(allyl)silane compounds, **1b-h** possessing other spacers between two silyl groups, and evaluated their chelation effect with Bu_4NF catalyst by allylating benzaldehyde under the above conditions. The results, summarized in Table 1, showed bis(allyl)silane **1a** and **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**.



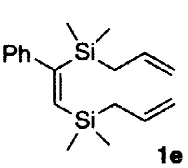
1b



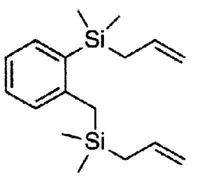
1c



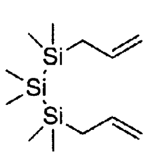
1d



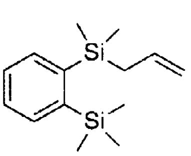
1e



1f



1g



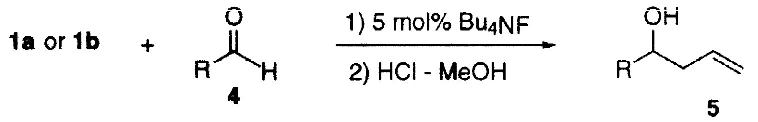
1h

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	aldehyde **4**	condition	% yield of **5** [b]
	R		(°C, h)	
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.