

# Lewis acid mediated domino allylation of diallylsilane to $\alpha,\beta$ -unsaturated ketones

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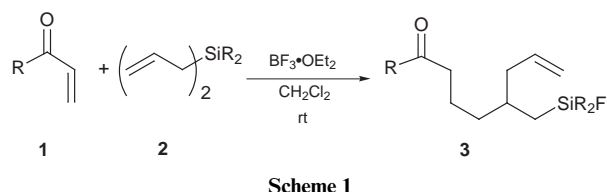
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On treatment of diallyldiisopropylsilane and  $\alpha,\beta$ -unsaturated ketones with  $\text{BF}_3 \cdot \text{OEt}_2$ , 1,4-addition of an allyl moiety and subsequent intramolecular allylation onto the  $\beta$ -silyl carbocation intermediate furnished domino allylation products. Oxidative cleavage of the carbon–silicon bond furnished bis-homoallylic alcohols in good yields.

Lewis acid mediated 1,4-addition of allylsilane to  $\alpha,\beta$ -unsaturated ketones, the Hosomi–Sakurai reaction,<sup>1</sup> has been established as a useful synthetic method for the introduction of an allyl moiety.<sup>2</sup> Although this reaction proceeds by desilylation of the  $\beta$ -silyl carbocation intermediate, nucleophilic attack onto the carbocation intermediate has recently attracted attention as a novel method for the formation of carbon–carbon bonds<sup>3,4,5</sup> as well as carbon–heteroatom bonds.<sup>6,7</sup> It is well recognized that use of a sterically demanding silyl group suppresses the desilylation and facilitates the attack onto the carbonium ion. Thus, both 5-membered and 4-membered carbocycles as well as heterocycles have been synthesized stereoselectively.

As part of our continuing interest in the development of novel synthetic methods based on  $\beta$ -silyl carbocation intermediates,<sup>5,7,8</sup> we have found a novel type of Lewis acid mediated tandem allylation reaction of diallylsilane with  $\alpha,\beta$ -unsaturated ketones. Thus, on treatment of diallyldiisopropylsilane **2** with  $\alpha,\beta$ -unsaturated ketones **1** in the presence of  $\text{BF}_3 \cdot \text{OEt}_2$ , 1,4-addition of an allyl moiety followed by intramolecular allylation proceeded smoothly to afford domino allylation products **3** (Scheme 1).

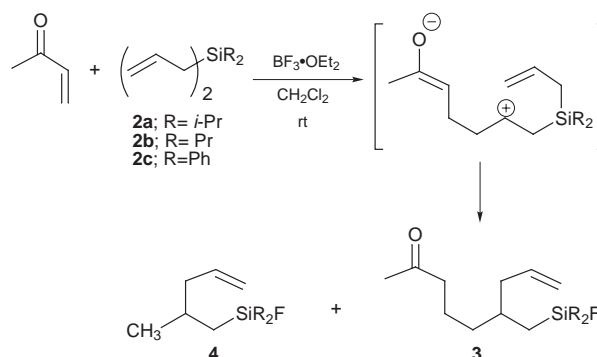


Treatment of methyl vinyl ketone with diallyldiisopropylsilane (**2a**; R = *i*-Pr) in the presence of  $\text{BF}_3 \cdot \text{OEt}_2$  (1.1 equiv) in  $\text{CH}_2\text{Cl}_2$  at room temperature for 30 min afforded 62% of **3a** (R = *i*-Pr) and 15% of **4**.<sup>9</sup> Formation of **3** could be rationalized by Michael addition of one of the allyl groups of **2** and subsequent intramolecular allylation of another allyl moiety onto the  $\beta$ -silyl carbocation intermediate. The effects of the silyl substituents were examined and the results are shown in Table 1. As expected, increasing the bulkiness of the silyl group suppressed the cleavage of the carbon–silicon bond thus increasing the yield of **3**.

Other metal fluorides were found to be less effective for the formation of **3a**; the yields of **3a** were 23% with  $\text{TiF}_4$ , 0% with both  $\text{Ph}_3\text{SnF}$  and  $\text{SnF}_2$ .

The results of the tandem allylation with other  $\alpha,\beta$ -unsaturated ketones are shown in Table 2. In the case of  $\alpha$ -substituted ketones, 1:1 mixtures of diastereomers were obtained (Entries 3 and 4). A  $\beta$ -substituted ketone did not afford the adduct (Entry 5).

Next oxidative cleavage of the carbon–silicon bond was studied. We have already disclosed that fluorodiisopropylsilyl group



**Table 1** Effect of silyl substituent

Entry	R	Yield of <b>3</b> (%)	Yield of <b>4</b> (%)
1	<i>i</i> -Pr	62	15
2	Pr	22	0
3	Ph	19	5

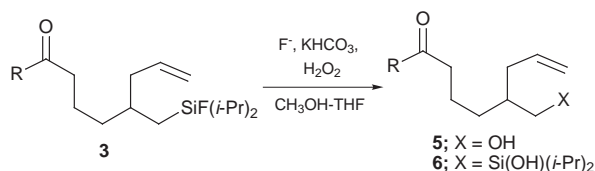
**Table 2** Reaction with various  $\alpha,\beta$ -unsaturated ketones

Entry	Enone	Time/h	Product	Yield (%)
1	<b>1b</b>	0.3	<b>3b</b>	63
2	<b>1c</b>	1.5	<b>3c</b>	32
3	<b>1d</b>	6	<b>3d</b>	52 <sup>a</sup>
4	<b>1e</b>	3.5	<b>3e</b>	46 <sup>a</sup>
5	<b>1f</b>	2.5	<b>3f</b>	0

<sup>a</sup> 1 : 1 Mixtures of diastereomers were obtained.

could be oxidatively cleaved to afford a hydroxy group.<sup>5,10</sup> Thus, on treatment of **1a** with  $\text{KF}$ ,  $\text{KHCO}_3$ , and  $\text{H}_2\text{O}_2$  under Tamao conditions<sup>11</sup> at 60 °C, the corresponding alcohols **5** were obtained in fairly high yields as shown in Table 3. It is note-





**Table 3** Oxidative cleavage of the carbon–silicon bond

Entry	R	F <sup>-</sup>	T/°C	Yield of 5 (%)	Yield of 6 (%)
1	CH <sub>3</sub>	KF	60	89	10
2	CH <sub>3</sub>	KF	50	35	47
3	CH <sub>3</sub>	<i>n</i> -Bu <sub>4</sub> NF	60	80	0
4	CH <sub>3</sub> CH <sub>2</sub>	KF	60	80	0

worthy that silanol **6** was obtained preferentially at lower temperatures.

In summary, we have found a novel type of domino allylation reaction, in which diallyldiisopropylsilane **2** played the role of the synthetic equivalent of **7** (Scheme 2).

## Notes and references

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- A typical experimental procedure for the preparation of **3a** is described (Entry 1, Table 1). To a solution of methyl vinyl ketone (18.2 mg, 0.20 mmol) and diallyldiisopropylsilane (66.1 mg, 0.4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.3 ml) was added BF<sub>3</sub>·OEt<sub>2</sub> (35.5 μl, 0.289 mmol) at room temperature. After being stirred at that temperature for 30 min, the reaction mixture was quenched by addition of 5% KHSO<sub>4</sub> solution. The aqueous layer was extracted with ethyl acetate and the combined organic layers were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated to dryness. Purification of the crude mixture by column chromatography (SiO<sub>2</sub>, hexane–ethyl acetate = 15 : 1, v/v) gave **3a** (46.4 mg, 62%) and **4** (6.5 mg, 15%).
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