Pergamon

Tetrahedron 58 (2002) 8227–8235

TETRAHEDRON

Remarkable enhancement of Lewis acidity of chlorosilane by the combined use of indium(III) chloride

Yoshiyuki Onishi, Takeshi Ito, Makoto Yasuda and Akio Baba*

Department of Molecular Chemistry and Handai Frontier Research Center, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

Received 2 May 2002; accepted 28 May 2002

Abstract—A combination of $InCl_3$ and R_3SiCl provided a strong Lewis acid catalyst for such reactions as allylation, hydrosilation and Friedel–Crafts alkylation. Especially, catalytic Sakurai–Hosomi-type allylation was accomplished with high yield and selectivity. The silicon atom is assumed to be the acidic center of the combined system, and the catalytic activity largely depends on the substituents on the silicon center.

1. Introduction

In the area of synthetic chemistry, main group XIII metal salts have long been used as prominent Lewis acids. For example, aluminum and boron salts are known to be excellent promoters for the Friedel–Crafts, Diels–Alder and Mukaiyama-aldol reactions, rearrangement and so on.[1] On the other hand, less attention has been focused on indium salts, because of their low Lewis acidity compared with that of aluminum or boron salts.[2]

In this decade, the utilization of indium salts has been dramatically expanded due to their characteristic properties: (i) they easily provide carbon nucleophiles by transmetallation,[3] and (ii) can be used in water.[4–6] The low Lewis acidity of the indium salts, however, considerably limits the scope of applicable substrates.

We have recently reported several indium-catalyzed reactions such as reductive Friedel–Crafts reaction,[7] deoxygenative allylation,[8] Clemmensen-type reduction[9] and deoxygenation of alcohols[10] using chloro-hydrosilanes. In these reactions, the interaction between chlorosilanes and indium(III) chloride ($InCl_3$) is assumed to play an important role in the C–O bond cleavage as shown in Scheme 1. Mukaiyama also reported that the $InCl_3$–*t*-$BuMe_2SiCl$ and $InCl_3$–Me_3SiCl systems affected the Mukaiyama-aldol reaction and nucleophilic addition toward *S*–*O* acetals.[11] In this context, we felt that an $InCl_3$–chlorosilane system could possess high Lewis acidity. Here we wish to report on the enhancement manner of Lewis acidity and synthetic applications of the combined $InCl_3$–chlorosilane catalyst to various nucleophilic additions and Freidel–Crafts alkylation.

2. Results and discussion

2.1. Catalytic Sakurai–Hosomi reaction

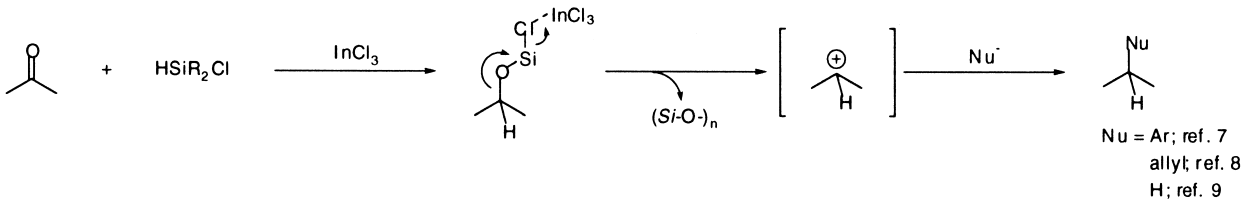
Lewis acid-promoted allylation of carbonyl compounds using allyltrimethylsilane (Sakurai–Hosomi reaction) is an important method for C–C bond formation and has been extensively studied.[12] Although valuable methods have been reported,[13] the catalytic modification of this reaction is still a challenging target because the catalyst is hardly regenerated from the produced homoallylic metaloxide **A** by transmetallation with Me_3SiCl (Scheme 2).

We have recently demonstrated that the Sakurai–Hosomi reaction is promoted by a catalytic amount of the $InCl_3$–Me_3SiCl combined system.[14,15] The allylation of *p*-chlorobenzaldehyde (**1a**) was investigated under various conditions, and the results are summarized in Table 1. Neither Me_3SiCl nor $InCl_3$ alone is active (Table 1, entries 2 and 3). The combination of Me_3SiCl and $InCl_3$ increased the yield of the adduct **2a** up to 87%. The direct bonding between silicon and chlorine is virtually essential because the employment of the chloromethyl moiety only minimally enhanced the yield (entries 3 and 7). Consequently, others than the chlorine atom showed no effect (entries 7–9). Tributyltin chloride could not take its place (entry 10). Even the use of equimolar amounts of $InCl_3$ resulted in the recovery of **1a** (entry 11). This result clearly reveals the low Lewis acidity of $InCl_3$. Then we rule out the possibility that

Keywords: indium and compounds; silicon and compounds; silicon halides; allylation; catalysts.

* Corresponding author. Tel.: +81-6-6879-7386; fax: +81-6-6879-7387; e-mail: baba@chem.eng.osaka-u.ac.jp

0040–4020/02/$ - see front matter
PII: S0040-4020(02)00972-9



Scheme 1. Plausible Si–Cl–In interaction in the key-step of deoxygenative reactions.

Me_3SiCl works merely as the assistant for the catalyst regeneration by trapping indium alkoxide **A** (Mt=In in Scheme 2). Equimolar amounts of Me_3SiCl also gave no reaction (entry 12).

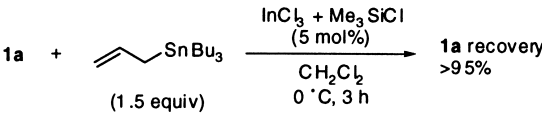
2.2. Investigation of interaction between $InCl_3$ and Me_3SiCl

The relationship between the yield of homoallyl alcohol **2a** and reaction time under five varying types of chorosilanes is illustrated in Fig. 1. The yield apparently depends on the size of substituents on chlorosilane. The reaction of **1a** with allyltrimethylsilane was complete after 5 min when Me_3SiCl or Et_3SiCl was used with $InCl_3$. On the other hand, bulkier chlorosilanes gave lower reaction rates; in the case of Ph_3SiCl, 180 min was required for completion, and *t*-$BuPh_2SiCl$ gave only 34% yield after 180 min.

To investigate the Lewis acidity of the combined catalyst, the chemical shifts δ (^{13}C) of carbonyl carbon of benzaldehyde (**1b**) in $CDCl_3$ in the presence of $InCl_3$ and/or Me_3SiCl were measured and the results are shown in Fig. 2.[16] When no $InCl_3$ was used, almost no shift was observed by varying the amounts of Me_3SiCl. In contrast, a low-field shift was detected by increasing $InCl_3$ in the absence of Me_3SiCl. It is noted that the degree of low-field shift was enhanced when Me_3SiCl was loaded, and this enhancement showed saturation at the point of $[InCl_3]/[Me_3SiCl]=1$ (marked by circles in Fig. 2). These results clearly show that (i) the Lewis acidity of $InCl_3$ is stronger than that of Me_3SiCl (ii) the combined use of $InCl_3$ and Me_3SiCl activates carbonyl compounds more effectively than their sole use and (iii) the combined catalyst readily forms active intermediate from 1:1 ratio of $InCl_3$ and Me_3SiCl with aldehydes.[17]

Among three types of activation of carbonyl moieties shown in Fig. 3, type **E** in which indium-coordinated oxygen interacts with Me_3SiCl can be easily excluded from the candidates because Me_3SiCl hardly accepts the direct coordination from the oxygen even in the absence of $InCl_3$ as shown in Fig. 2. The possibility of type **C** cannot be ruled out. However, we think type **D** would be the most plausible because (i) substituents on the silicon atom strongly affected the reaction rate and (ii) chlorosilylether is activated by the coordination of chlorine on the silicon atom toward $InCl_3$ as shown in Scheme 1. Unfortunately, no direct proof for the formation of type **D** was obtained by ^{29}Si NMR in any combinations between $InCl_3$, Me_3SiCl and benzaldehyde.

The participation of an allylindium species by the transmetallation between $InCl_3$ and allyltrimethylsilane can be ruled out by the fact that no Me_3SiCl was detected by ^{29}Si NMR when $InCl_3$, allyltrimethylsilane and *t*-$BuMe_2SiCl$ were mixed in dichloromethane.[18] In addition, the use of an allyltributylstannane instead of allyltrimethylsilane gave no adduct (Eq. (1)),[19] in which facile formation of allylindium species from the allystannane is plausible.[7]



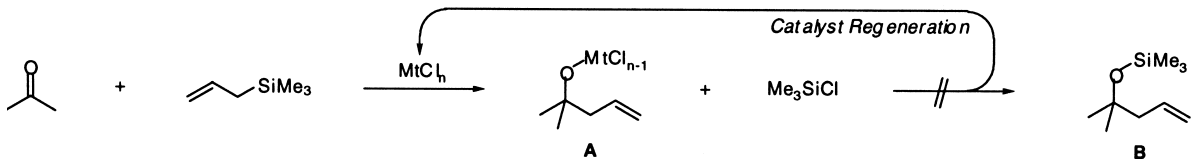
(1)

2.3. Allylation of imines

This catalyst system is also found to be applicable to the allylation of imines in nitromethane solvent in preference to dichloromethane (Table 2).[20] While the allylation of *N*-benzylideneaniline (**3a**) resulted in low yield (entry 1), active amines bearing a sulfonyl group furnished the corresponding homoallylamine in satisfactory yields (entry 3). *N*-Sulfonyl aliphatic imine **3c** also afforded the homoallyl amine **4c** in high yield.

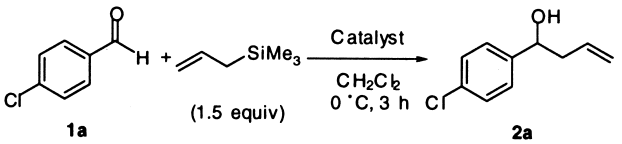
2.4. Chelation-controlled allylation of benzoin and its derivatives

Benzoin (**5a**) was allylated with the combined catalyst system to afford only *syn*-diol **6** selectively (Table 3). However, side products **8** and **9**, which are formed by phenyl rearrangement of the allylation adduct and its successive allylation, were increased in a period over 6 h, so that the yield of **6** could not be improved by prolonged reaction time (entries 3 and 4). In the allylation of α-hydroxypropiophenone (**5b**), stereoselective formation of the *syn*-product took place without rearrangement,[21,22] to give bis-trimethylsilylether **7** even after treatment with TBAF (entry 5). From this result, the selective allylation is suggested to follow the silation of the hydroxy group.[23]



Scheme 2. Concept scheme of Lewis Acid promoted Sakurai–Hosomi reaction.

Table 1. Combined effect of indium and silicon on catalytic Sakurai–Hosomi reaction



Entry	Catalyst (mol%)	Yield (%)[a]	Recovery (%)[a]
1[b]	None	0	99
2	Me_3SiCl (5)	0	98
3[b]	$InCl_3$ (5)	9	84
4[b]	$InCl_3$ (5)+Me_3SiCl (5)	87	0
5	$InCl_3$ (5)+$HSiMe_2Cl$ (5)	91	0
6	$InCl_3$ (5)+Me_2SiCl_2 (5)	80	0
7	$InCl_3$ (5)+Me_3SiCH_2Cl (5)	12	82
8	$InCl_3$ (5)+Me_4Si (5)	0	99
9	$InCl_3$ (5)+Me_3SiOEt (5)	5	85
10	$InCl_3$ (5)+Bu_3SnCl (5)	5	84
11	$InCl_3$ (100)	0	95
12	Me_3SiCl (100)	0	91

Reactions were quenched by TBAF.
[a] Determined by GLC.
[b] Previously reported data in Ref. 14.

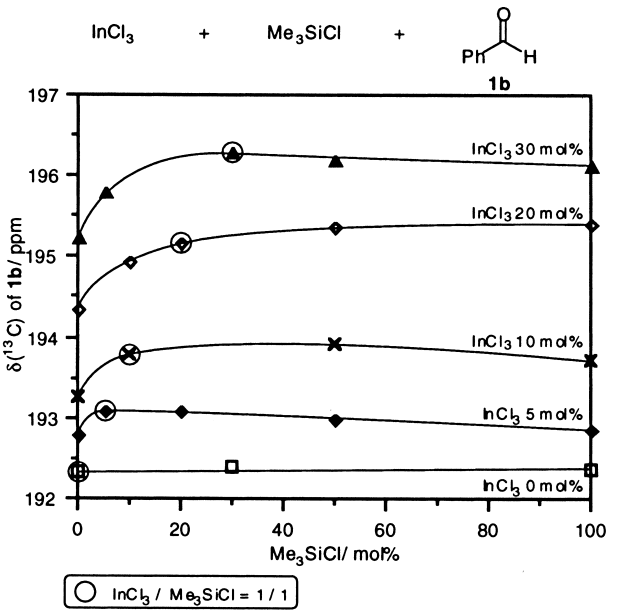
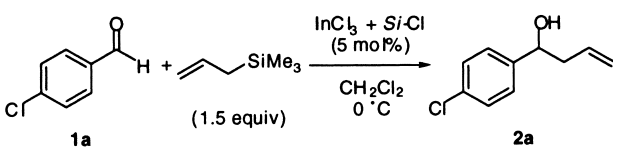


Figure 2. Chemical shift δ (^{13}C) of carbonyl carbon of **1b** in the presence of $InCl_3$ and/or Me_3SiCl.

In fact, benzoin trimethylsilyl ether (**10a**) afforded *syn*-diol **6** in a higher yield without rearrangement even after 6 h (Table 4, entries 2 and 3).[24] It was a little surprising that no allylation of benzoin methyl ether (**11**) took place although effective chelation had been expected by the methoxy moiety (Eq. (2)). Furthermore, the allylation of benzoin trimethylsilyl ether (**10a**) was completely suppressed by the addition of **11**, where both **10a** and **11** were unreacted as shown in Eq. (3). It is apparent that **11** disturbs the allylation of **10a**. The stronger coordination of the methoxy moiety perhaps impedes effective interaction between $InCl_3$ and Me_3SiCl.[25] This result did not conflict with the suppression by using THF as the solvent. On the other hand, the triethylsilyl moiety hardly coordinates due to its steric hindrance (Table 4, entry 4). Two possible chelation models are illustrated in Fig. 4, in which the nucleophilic attack of allyltrimethylsilane from the less hindered site gives *syn*-isomers. Chelation of two oxygens toward silicon atom of the combined catalyst (type **F**) is plausible. However, we cannot exclude the possibility that the silicon atom of the silylether moiety is coordinated by carbonyl oxygen (type **G**).



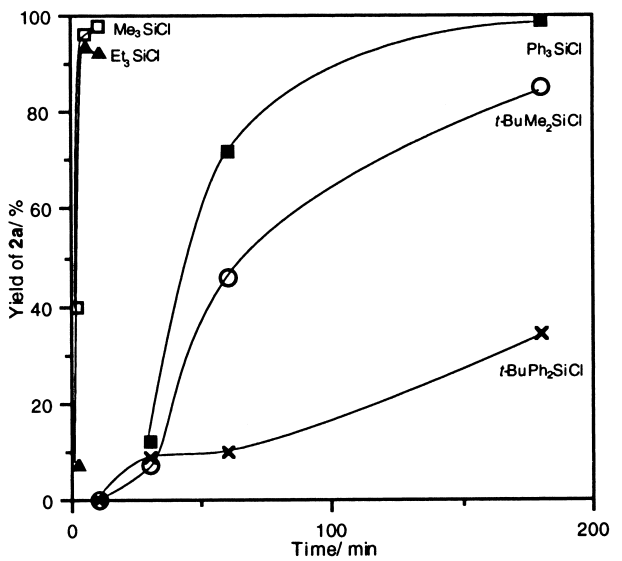
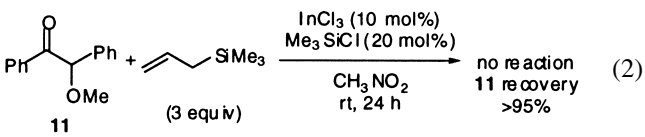


Figure 1. Effect of the size of chlorosilanes on the reaction rate of **1a** with allyltrimethylsilane.



(2)

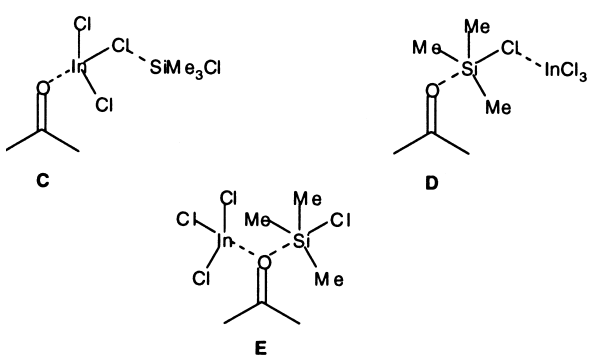
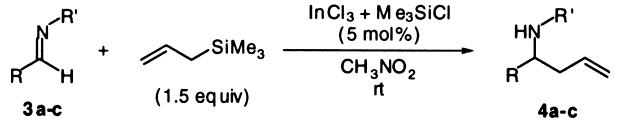


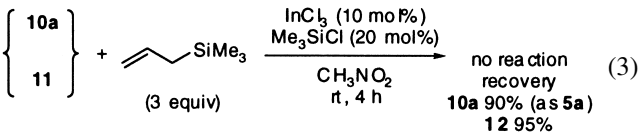
Figure 3. Carbonyl activation by $InCl_3$–Me_3SiCl system.

Table 2. Allylation of imines **3** with allyltrimethylsilane



Entry	R	R′	Time (h)	Yield (%)[a]
1	Ph	Ph (**3a**)	24	24[b]
2[c]	Ph	Ph (**3a**)	24	0[d]
3	Ph	$PhSO_2$ (**3b**)	6	74[e]
4[c]	Ph	$PhSO_2$ (**3b**)	24	56[e]
5	n-C_5H_{11}	p-$TolSO_2$ (**3c**)	3	87

Reactions were quenched by TBAF.
[a] Determined by NMR.
[b] Benzylphenylamine was obtained in 24% yield.
[c] Dichloromethane was used as solvent.
[d] Benzylphenylamine was obtained in 19%.
[e] Homoallylalcohol was obtained in 8% yield.

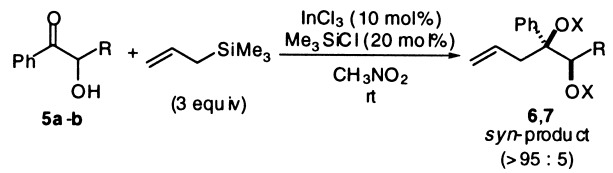


(3)

2.5. Allylation of ketones

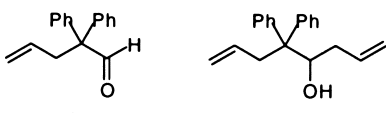
The results of allylation of simple ketones are summarized in Table 5. Cyclohexanone (**1c**) gave the corresponding Sakurai–Hosomi product **2c** in 47% yield (entry 2). However, acetophenone (**1d**) gave diallylation product **12d** predominantly (entry 3). The allylation of carbocation species **G**, which is generated via leaving of the $OSiMe_3$ group from the silylether **13**, is a plausible course to **12**, in which the stability of the tertiary benzylic cation is essential for the second allylation.[26] The yield of **12d** was improved to 64% by increasing the amount of allyltrimethylsilane to 3 equiv. (entry 4). Propiophenone (**1e**) and *p*-chloroacetophenone (**1f**) afforded the corresponding diallylated products in 49 and 55% yields, respectively, under similar conditions (entries 5–7).

Table 3. Diastereoselective allylation of α-hydroxyketones



Entry	R	Time (h)	X	Product	Yield (%)[a]	Recovery (%)[a]
1	Ph (**5a**)	2	H	**6**	31	64
2	Ph (**5a**)	4	H	**6**	55[b]	20
3	Ph (**5a**)	6	H	**6**	56[c]	16
4	Ph (**5a**)	24	H	**6**	29	0
5[d]	Me (**5b**)	4	$SiMe_3$	**7**	51	0

Reaction was quenched by saturated $NaHCO_3$ aq.
[a] Determined by ^1H NMR.
[b] Byproducts **8** and **9** were obtained in 4 and 9% yields, respectively.
[c] Byproducts **8** and **9** were obtained in 3 and 22% yields, respectively.
[d] Reaction was quenched by TBAF.



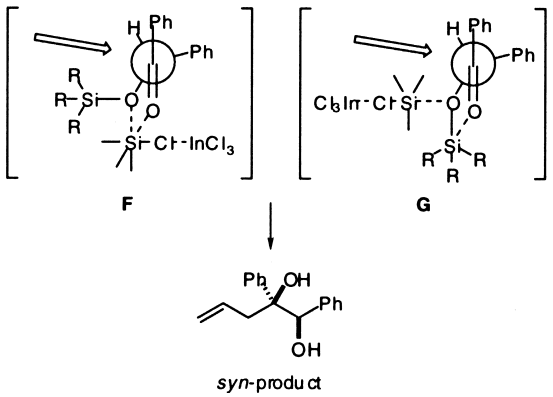


Figure 4. Chelation controlled allylation.

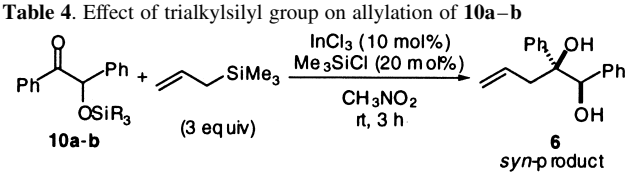
2.6. Friedel–Crafts reaction

We applied this system to Friedel–Crafts benzylation (Table 6). Similar to the Sakurai–Hosomi reaction, catalytic activity was observed only when $InCl_3$ and silyl halides or triflate were combined (entries 6–8). The sole use of $InCl_3$ showed no activity, while good yield was observed by a representative Friedel–Crafts catalyst, $AlCl_3$. This is also a proof of the low Lewis acidity of $InCl_3$. The effect of the combined system, however, is comparable to that of $AlCl_3$, and in particular, with Me_3SiOTf as the most effective partner. Lewis acidity enhancement of the silicon compound by $AlCl_3$ was not observed (entries 9 and 10).

2.7. Reduction of α,β-unsaturated ketone

The reaction of triethylsilane with α,β-unsaturated ketone was found to be promoted by the combined catalyst, $InCl_3$–Me_3SiCl (Scheme 3). This type of hydrosilation is well

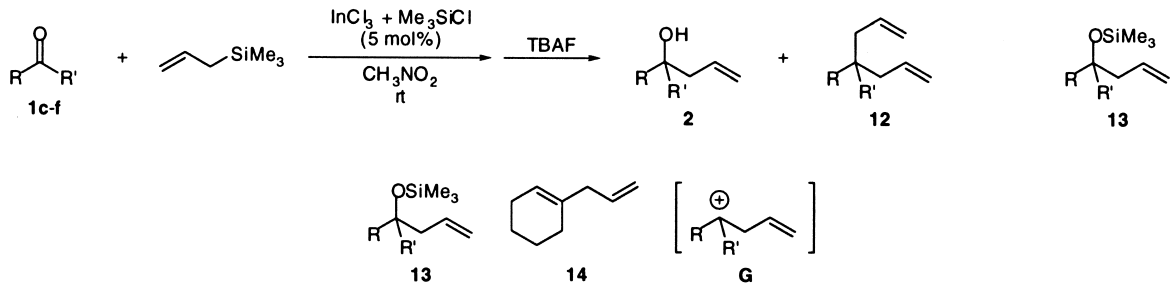
Table 4. Effect of trialkylsilyl group on allylation of **10a–b**



Entry	R	Time (h)	Yield (%)[a]	Recovery (%)[a,b]
1[c]	Me (**10a**)	3	0	77
2	Me (**10a**)	3	53 (>95:5)	28[d]
3	Me (**10a**)	6	73 (>95:5)	15[d]
4	Et (**10b**)	3	9[e]	80

Reaction was quenched by saturated $NaHCO_3$ solution.
[a] Determined by ^1H NMR.
[b] Recovered as **5a**.
[c] Without Me_3SiCl.
[d] Trace amounts of **8** was detected.
[e] Diastereoselectivity was not exactly determined owing to low yield (*syn*-predominantly).

Table 5. Allylation of ketones



Entry	R	R′		Allylsilane (equiv.)	Conditions	Yield (%)[a]	
						2	**12**
1	$-(CH_2)_5-$		(**1c**)	1.5	rt, 24 h	0[b]	0
2	$-(CH_2)_5-$		(**1c**)	1.5	−20°C, 2 h	47 (**2c**)	0
3	Ph	Me	(**1d**)	1.5	rt, 2 h	0	47 (**12d**)
4	Ph	Me	(**1d**)	3.0	rt, 2 h	0	64 (**12d**)
5	Ph	Et	(**1e**)	3.0	rt, 1.5 h	0	49 (**12e**)
6	*p*-Cl−C_6H_4	Me	(**1f**)	3.0	rt, 72 h	0	24 (**12f**)
7[c]	*p*-Cl−C_6H_4	Me	(**1f**)	3.0	rt, 12 h	0	55 (**12f**)

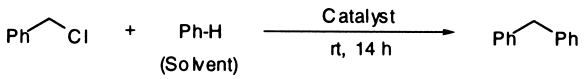
[a] Determined by GLC.
[b] Dehydrated product **14** was obtained in 11% yield.
[c] Reaction was carried out under 10 mol% of $InCl_3$ and 20 mol% of Me_3SiCl.

promoted by transition metal catalysts.[27] No effect was observed by the sole use of $InCl_3$ in this case, too. When chlorodimethylsilane was employed instead of triethylsilane, no addition of Me_3SiCl was required. Dimethylchlorosilane can act as both hydride donor and a catalyst partner to give the ketone **16** from chalcone (**15**), although it is a weaker hydride donor than triethylsilane. This result again indicates the importance of the combination of $InCl_3$ and a silyl chloride.

3. Conclusion

We have found the combination of $InCl_3$ and a silyl chloride catalytically promoted some useful and basic reactions such as allylation of aldehydes, ketones, imines, Friedel–Crafts alkylation and conjugate reduction. ^{13}C NMR studies revealed effective interaction between the combined catalyst and a carbonyl moiety. We expect that this mild and efficient catalyst system will be applied to other Lewis acid-promoted reactions.

Table 6. Friedel–Crafts reaction catalyzed by indium–silicon combined system



Entry	Catalyst (mol%)	Yield (%)[a]
1	None	0
2	Me_3SiCl (10)	0
3	$HSiMe_2Cl$ (10)	0
4	Me_3SiOTf (10)	0
5	$InCl_3$ (10)	4
6	$InCl_3$ (5)+Me_3SiCl (10)	58
7	$InCl_3$(5)+$HSiMe_2Cl$ (10)	79
8	$InCl_3$(5)+Me_3SiOTf (10)	90
9	$AlCl_3$ (5)	79
10	$AlCl_3$ (5)+Me_3SiOTf (10)	77

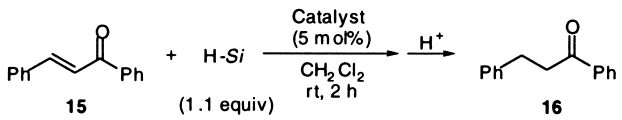
[a] Determined by GLC.

4. Experimental

4.1. General information

IR spectra were recorded as thin films on a HORIBA FT-720 spectrophotometer. ^1H and ^{13}C NMR spectra were obtained with a JEOL JNM-GSX-270 (270 and 67.9 MHz) spectrometer, respectively, with TMS as internal standard. Mass spectra were recorded on a JEOL JMS-DS303 spectrometer. GLC analyses were performed on a Shimadzu GC-14A with FID using a 15 m×0.25 mm column packed with TC-1701. Column chromatography was performed on silica gel (Fuji Silysia BW 200). Bulb-to-bulb distillation (Kugelrohr) was accomplished in a Sibata GTO-250RS at the oven temperature and pressure indicated. Yields were determined by GLC or ^1H NMR using internal standards.

Dichloromethane was distilled after the removal of H_2O by CaH_2. Benzene was distilled after the removal of H_2O by



H-*Si*	Catalyst	Yield/ %
$HSiEt_3$	$InCl_3$ + Me_3SiCl	73
$HSiEt_3$	$InCl_3$	0
$HSiMe_2Cl$	$InCl_3$	55

Scheme 3. 1,4-Reduction of chalcone.

sodium metal. Nitromethane was purchased from Aldrich and used without purification. $InCl_3$, Me_3SiCl, $HSiMe_2Cl$, Me_2SiCl_2, Me_3SiCH_2Cl, Me_4Si, Me_3SiOEt, Me_3SiOTf, allyltrimethylsilane, Bu_3SnCl, allyltributyltin, carbonyl compounds **1a**–**1f**, functionalized carbonyl compounds **5a**, **b**, **11** and **15**, imines **3a** and **b**, benzyl chloride, $NaHCO_3$ and TBAF (1.0 M solution in THF) were commercially available reagents.

4.1.1. Preparation of *N*-hexylidene-4-methylbenzenesulfonamide (3b). 1-Heptanal (1.5 g, 15 mmol), sodium *p*-toluenesulfonate (2.67 g, 15 mmol) and formic acid (22.5 mmol) were dissolved in water (45 mL). To this solution was added *p*-toluenesulfonamide (2.57 g, 15 mmol), and the solution was stirred at ambient temperature for 16 h under N_2 stream. After removing the liquid phase by filtration, the resulting white solid (6.1 g) was then dissolved in saturated $NaHCO_3$ aqueous solution, and the mixture was extracted with dichloromethane (2×50 mL). The organic layers were combined, dried over $MgSO_4$ and concentrated under reduced pressure. The crude residue was subjected to recrystallization to afford white solid **3b** (1.8 g, 47% yield).

4.1.2. Preparation of 2-hydroxy-1-phenyl-1-propanone (5b). To a solution of propiophenone (45 mL) and sodium hydroxide (450 mmol) in methanol (90 mL) was added iodobenzenediacetate (45.3 mmol), and the mixture was stirred at 0°C for 4 h under N_2 stream with irradiation of ultra sonic wave. After being quenched with aqueous HCl solution, and the mixture was extracted by chloroform (2×100 mL). The organic layers were combined, dried over $MgSO_4$ and concentrated under reduced pressure. The crude residue was subjected to chromatography (eluted by hexane/ethylacetate=4:1 solution) to afford **5b** (1.5 g, 22%).

4.1.3. Preparation of benzoin trimethylsilylether (10a). To a solution of Me_3SiCl (13.0 g, 120 mmol) in benzene (60 mL) was added dropwise a benzene (40 mL) solution of pyridine (11.0 g, 155 mmol) and benzoin (17.0 g, 80 mmol) for 40 min, and the mixture was stirred at 50°C for 4 h. The resulting pyridinium salt was filtered off and concentrated under reduced pressure. The crude residue was subjected to recrystallization to afford **10a** (15.84 g, 70%).

4.1.4. Preparation of benzoin triethylsilylether (10b). To a solution of benzoin (4.24 g, 20 mmol) and pyridine (2.51 g, 31 mmol) in benzene (20 mL) was added dropwise a benzene (20 mL) solution of Et_3SiCl (3.82 g, 25 mmol) for 30 min, and the mixture was stirred at 80°C for 4 h. The resulting pyridinium salt was filtered off and concentrated under reduced pressure. The crude residue was subjected to distillation (0.11 mm Hg, 120°C) to afford **10b** (3.75 g, 55%).

4.1.5. General procedure for catalytic Sakurai–Hosomi reaction. To a mixture of dried $InCl_3$ (0.1 mmol), Me_3SiCl (0.1 mmol) and allyltrimethylsilane (3.0 mmol) in the solvent (4 mL) was added carbonyl compounds (2.0 mmol). After stirring for representative hours, reaction was quenched by 1 M solution of TBAF (tetra-*n*-butylammonium fluoride) in THF (2 mL, 2 mmol) or saturated $NaHCO_3$ solution, after confirming the disappearance of the carbonyl compounds by GLC. The homoallylic alcohols were isolated by silica gel column chromatography followed by distillation.

4.1.6. ^{13}C NMR study on the interaction with benzaldehyde (1b) with catalysts. As a typical treatment; to a mixture of dried $InCl_3$ (0.044 g, 0.2 mmol), chlorotrimethylsilane (0.022 g, 0.2 mmol) in chloroform-*d* (4 mL) was added benzaldehyde (**1b**, 0.106 g, 1.0 mmol) at ambient temperature. After stirring for 1.5 h, 0.75 mL of the solution was sampled with a needle for ^{13}C NMR measurement at room temperature. The chemical shift of the carbonyl carbon of benzaldehyde was monitored.

4.1.7. Typical procedure for Friedel–Crafts reaction. Benzylchloride (0.25 g, 2.0 mmol) was added to a solution of $InCl_3$ (0.011 g, 0.1 mmol) and Me_3SiCl (0.022 g, 0.2 mmol) in benzene (10 mL). The reaction was quenched by saturated aqueous $NaHCO_3$ after stirring for 14 h at ambient temperature. Products were extracted by ether and the organic layer was dried and concentrated in vacuo. Diphenylmethane was obtained by silica gel column chromatography followed by distillation.

4.1.8. Typical procedure for 1,4-reduction of chalcone (15). Triethylsilane (0.26 g, 2.2 mmol) was added to the solution of $InCl_3$ (0.011 g, 0.1 mmol), Me_3SiCl (0.011 g, 0.1 mmol), chalcone (**15**, 0.42 g, 2.0 mmol) in dichloromethane (4 mL) and stirred for 2 h at ambient temperature. Products were extracted by ethylacetate and the organic layer was dried and concentrated in vacuo. The corresponding ketone **16** was obtained by silica gel column chromatography followed by distillation.

4.2. Product data

The spectroscopic data of the products **2a**,[28] **2c**,[28] **4a**,[29] **6**,[30] **8**,[31] **12e**,[32] **14**[33] and **16**[34] are in excellent agreement with the reported data. Diphenylmethane was the commercially available product.

4.2.1. *N*-(1-Phenyl-3-butenyl)benzenesulfonamide (4b). Prepared by the typical procedure from *N*-benzylidenebenzenesulfonamide (4 mmol) and allyltrimethylsilane (6 mmol) in the presence of $InCl_3$ (0.2 mmol) and chlorotrimethylsilane (0.2 mmol) in dry CH_3NO_2 (8 mL). A white solid **4b** (0.45 g, 40%) was obtained, after chromatography (hexane/EtOAc, 8:2) and recrystallization. Mp 150°C. ^1H NMR (270 MHz, $CDCl_3$): 7.69–7.66 (m, 2H, aroma), 7.44–7.39 (m, 1H, aroma), 7.32–7.25 (m, 2H, aroma), 7.14–7.03 (m, 5H, aroma), 5.69 (d, J=7.33 Hz, 1H, NH), 5.60–5.44 (m, 1H, 3-H). 5.04–4.98 (m, 2H, 4-H_2), 4.40 (dt, J=7.33, 7.33 Hz, 1H, 1-H), 2.50 (dd, J=7.33, 7.33 Hz, 1H, 2-H_a), 2.40 (dd, J=7.33, 7.33 Hz, 1H, 2-H_b). ^{13}C NMR (67.9 MHz, $CDCl_3$): 140.40 (s, 1-Ph), 140.09 (s, 1-Ph), 133.06 (d, C-3), 132.13 (d, 4-Ph), 128.55 (d, aroma-CH), 128.20 (d, aroma-CH), 127.24 (s, 4-Ph), 126.92 (d, aroma-CH), 126.45 (d, aroma-CH), 118.85 (t, C-4), 57.43 (d, C-1), 41.73 (t, C-2). IR (KBr): 3270 (NH), 1643 (C=C). MS (CI, 70 eV): 288 (M^++1, 100), 246 (M^+−allyl, 33.8), 131 (M^+−$PhSO_2NH$, 11.6). HRMS (CI, 70 eV): calculated ($C_{16}H_{18}O_2NS$) 288.0980 (M^++1); found 288.1060.

Elemental analysis: $C_{16}H_{17}O_2NS$ (287.37); calculated C 66.87, H 5.96, N 4.87; found C 66.79, H 5.95, N 4.85.

4.2.2. 4-Methyl-*N*-(1-pentyl-but-3-enyl)-benzenesulfonamide (4c). Prepared by the typical procedure from *N*-hexylidene-4-methyl-benzenesulfonamide (3 mmol) and allyltrimethylsilane (6 mmol) under $InCl_3$ (0.3 mmol) in dry CH_3NO_2 (6 mL). A colorless liquid **4c** (0.63 g, 79%) was obtained, after chromatography (hexane/EtOAc, 8:2) and distillation. Bp 150°C/1.1×10^{-1} mm Hg. ^{1}H NMR (270 MHz, $CDCl_3$): δ=7.77 (d, J=8.31 Hz, 2H, aroma), 7.29 (d, J=8.31 Hz, 2H, aroma), 5.66–5.51 (m, 1H, 3-H), 5.02–4.92 (m, 2H, 4-H_2), 4.83 (d, J=8.30 Hz, 1H, NH), 3.32–3.12 (m, 1H, 1-H). 2.42 (s, 3H, CH_3), 2.12 (t, J=6.35 Hz, 2H, 2-H_2), 1.45–1.12 (m, 8H, alkyl-H_2), 0.81 (t, J=6.83 Hz, 3H, terminal-H_3). ^{13}C NMR (67.9 MHz, $CDCl_3$): 143.06 (s, 4-Ph), 138.18 (s, 1-Ph), 133.38 (d, C-3), 129.44 (d, aroma-CH), 127.03 (d, aroma-CH), 118.47 (t, C-4), 53.26 (d, C-1), 39.12 (t, C-3′), 34.28 (t, C-1′), 31.33 (t, C-3′), 24.90 (t, C-2′ or C-4′), 22.36 (t, C-2′ or C-4′), 21.40 (q, CH_3), 13.83 (q, C-5′). IR (neat): ν=3278 (NH), 1643 (C=C). MS (EI, 70 eV): 295 (M^++1, 0.2), 254 (M^+−allyl, 100), 155 (Ts^+, 55.9), 91 ($PhCH_3^+$, 50.2). HRMS (CI, 70 eV): calculated ($C_{16}H_{26}O_2NS$) 296.1606 (M^++1); found 296.1675. Elemental analysis: $C_{16}H_{25}O_2NS$ (295.44); calculated C 65.05, H 8.53, N 4.74; found C 65.07, H 8.67, N 4.64.

4.2.3. 4,5-Bis(trimethylsiloxy)-3-phenyl-hexene (7). Prepared by the typical procedure from 2-hydroxy-1-phenyl-propan-1-one (2 mmol) and allyltrimethylsilane (6 mmol) under $InCl_3$ (0.2 mmol) and chlorotrimethylsilane (0.4 mmol) in dry nitromethane (4 mL). A colorless liquid **7** (0.12 g, 36%) was obtained after chromatography (hexane) and distillation. Bp 115°C/1.1×10^{-1} mm Hg. ^{1}H NMR (270 MHz, $CDCl_3$): 7.33–7.14 (m, 5H, aroma), 5.57–5.42 (m, 1H, 2-H), 4.92–4.85 (m, 2H, 1-H), 3.94 (q, J=6.35 Hz, 1H, 5-H), 2.99 (dd, J=15.13, 6.35 Hz, 1H, 3-H_a), 2.45 (dd, J=15.13, 7.32 Hz, 1H, 3-H_b), 0.78 (d, J=6.35 Hz, 3H, 6-H), 0.23 (s, 9H, $OSiMe_3$), 0.18 (s, 9H, $OSiMe_3$). ^{13}C NMR (67.9 MHz, $CDCl_3$): 145.09 (s, 1-Ph), 134.71 (d, C-2), 127.70 (d, aroma-CH), 126.11 (d, 4-Ph), 125.90 (d, aroma-CH), 116.91 (t, C-1), 83.42 (s, C-4), 74.88 (d, C-5), 42.96 (t, C-3), 17.70 (q, C-6), 2.88 (q, $OSiMe_3$), 0.39 (q, $OSiMe_3$). IR (neat): 1643 (C=C). MS (CI, 70 eV): 337 (M^++1, 2.9), 295 (M^+−allyl, 52.1), 247 (M^+−$OSiMe_3$, 100). HRMS (CI, 70 eV): calculated ($C1_8H_{33}O_2Si_2$) 337.1941 (M^++1); found 337.2001. Elemental analysis: $C_{18}H_{32}O_2Si_2$ (336.62); calculated C 64.23, H 9.58; found C 64.08, H 9.44.

4.2.4. 5,5-Diphenyl-octa-1,7-diene-4-ol (8). Prepared by typical procedure from benzoin (2 mmol) and allyltrimethylsilane (6 mmol) under $InCl_3$ (0.1 mmol) in dry CH_3NO_2 (4 mL). A pale yellow liquid **8** (0.17 g, 30%) was obtained, after chromatography (hexane/EtOAc, 19:1) and distillation. Bp 120°C/1.1×10^{-1} mm Hg. ^{1}H NMR (270 MHz, $CDCl_3$): δ=7.34–7.16 (m, aroma, 10H), 5.87 (dddd, J=6.43, 7.33, 10.49, 16.80 Hz, 1H, 2-H), 5.41 (dddd, J=6.92, 6.93, 9.89, 16.81 Hz, 1H, 7-H), 5.01 (dd, J=0.98, 16.81 Hz, 1H, 8-H_{cis}), 5.01 (dd, J=0.99, 16.80 Hz, 1H, 1-H_{cis}), 4.94 (dd, J=0.99, 10.49 Hz, 1H, 1-H_{trans}), 4.94 (dd, J=0.98, 9.89 Hz, 1H, 8-H_{trans}), 4.43 (ddd, J=1.49, 6.43, 10.25 Hz, 1H, 4-H), 3.07 (dd, J=6.93, 13.85 Hz, 1H, 6-H_a), 2.87 (dd, J=6.92, 13.85 Hz, 1H, 6-H_b), 2.47 (ddd, J=1.49, 6.43, 14.84 Hz, 1H, 3-H_a), 1.54 (ddd, J=7.33, 10.25, 14.84 Hz, 1H, 3-H_b), 1.52 (d, J=6.43 Hz, 1H, OH; D_2O exchange). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ=144.19 (s, 1-Ph), 135.90 (d, 2-C), 134.61 (d, 7-C), 127.65–127.61 (d, 2-Ph, 3-Ph), 126.23 (d, 4-Ph), 117.74 (t, 1-C), 117.35 (t, 8-C), 72.84 (d, 4-C), 55.21 (s, 5-C), 42.74 (t, 6-C), 37.69 (t, 3-C). IR (neat): ν=3563 (OH), 1639 (C=C). MS (EI, 70 eV): 278 (M^++1, 0.13), 237 (M^+−allyl, 6.29), 208 (M^+−C_4H_7O, 55.9), 91 ($PhCH_3^+$, 50.2), 77 (Ph^+, 8.65). HRMS (CI, 70 eV): calculated ($C_{20}H_{23}O$) 279.1749 (M^++1); found 279.1722.

4.2.5. 4-Methyl-4-phenylhepta-1,6-diene (12d). Prepared by the typical procedure from acetophenone (3 mmol) and allyltrimethylsilane (9 mmol) under $InCl_3$ (0.15 mmol) and $(CH_3)_2ClSiOSiCl(CH_3)_2$ (0.2 mmol) in dry CH_3NO_2 (3 mL). A colorless liquid **12d** (0.21 g, 38%) was obtained, after chromatography (hexane) and distillation. Bp 40°C/1.1×10^{-1} mm Hg. ^{1}H NMR (270 MHz, $CDCl_3$): 7.33–7.26 (m, 4H, aroma), 7.21–7.14 (m, 1H, aroma), 5.60–5.45 (m, 2H, 2,6-H), 5.01–4.92 (m, 4H, 1,7-H_2), 2.51 (dd, J=13.67, 6.35 Hz, 1H, 3,5-H_a), 2.29 (dd, J=13.67, 7.81 Hz, 1H, 3,5-H_b), 1.27 (s, 3H, CH_3). ^{13}C NMR (67.9 MHz, $CDCl_3$): 147.06 (s, 1-Ph), 135.05 (d, C-2,6), 127.99 (d, aroma-CH), 126.39 (d, aroma-CH), 125.59 (s, 4-Ph), 117.14 (t, C-1.7), 46.93 (t, C-3,5), 40.59 (s, C-4), 24.12 (q, CH_3). IR (neat): 1639 (C=C). MS (CI, 70 eV): 187 (M^++1, 12.1), 145 (M^+−allyl, 100), 109 (M^+−Ph, 23). HRMS (CI, 70 eV): calculated ($C_{14}H_{19}$) 187.1409 (M^++1); found 187.1472, 187.1487, 187.1481. Elemental analysis: $C_{14}H_{18}$ (186.29); calculated C 90.26, H 9.74; found C 78.63, H 9.08.

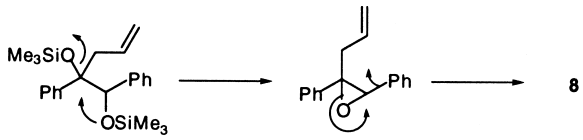
4.2.6. 4-Methyl-4-(4-chlorophenyl)hepta-1,6-diene (12f). Prepared by the typical procedure from *p*-chloroacetophenone (6 mmol) and allyltrimethylsilane (9 mmol) under $InCl_3$ (0.3 mmol) and chlorotrimethylsilane (0.3 mmol) in dry $ClCH_2CH_2Cl$ (12 mL). A colorless liquid **12f** (0.22 g, 22%) was obtained, after chromatography (hexane) and distillation. Bp 73°C/1.1×10^{-1} mm Hg. ^{1}H NMR (270 MHz, $CDCl_3$): 7.29–7.21 (m, 4H, aroma), 5.58–5.43 (m, 2H, 2,6-H), 5.00–4.94 (m, 4H, 1,7-H_2), 2.47 (dd, J=13.67, 6.34 Hz, 1H, 3,5-H_a), 2.28 (dd, J=13.67, 7.81 Hz, 1H, 3,5-H_b), 1.26 (s, 3H, CH_3). ^{13}C NMR (67.9 MHz, $CDCl_3$): 145.56 (1-Ph), 134.58 (C-2,6), 131.37 (4-Ph), 128.08 (aroma-CH), 127.93 (aroma-CH), 117.52 (C-1,7), 46.88 (C-3,5), 40.48 (C-4), 24.07 (CH_3). IR (neat): 1639 (C=C). MS (EI, 70 eV): 220 (M^+, 0.4), 179 (M^+−allyl, 100). HRMS (EI, 70 eV): calculated ($C_8H_{17}Cl$) 220.1019 (M^+); found 220.1030. Elemental analysis: $C_{14}H_{17}Cl$ (220.74); calculated C 76.18, H 7.76; found C 75.97, H 7.87.

Acknowledgements

This work was supported by a Grant-in Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of the Japanese Government and this research has been carried out at the strategic research base 'Handai Frontier Research Center' supported by the Japanese Government's Special Coordination Fund for Promoting Science and Technology.

References

1. (a) Ishihara, K. *Lewis Acids in Organic Synthesis*; Yamamoto, H., Ed.; Wiley-VCH: Weinheim, 2000; Vol. 1. Part 4. (b) Ooi, T.; Maruoka, K. *Lewis Acids in Organic Synthesis*, Yamamoto, H., Ed.; Wiley-VCH: Weinheim, 2000; Vol. 1. (c) Scheiber, S. L. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Part 1. (d) Heathcock, C. H. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Part 2. (e) Paquette, L. A. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Part 5 and references are cited therein.
2. Olah, G. A.; Kobayashi, S.; Tashiro, M. *J. Am. Chem. Soc.* **1972**, *94*, 7448–7761.
3. (a) Marshall, J. A.; Hinkle, K. W. *J. Org. Chem.* **1995**, *60*, 1920–1921. (b) Yasuda, M.; Miyai, T.; Shibata, I.; Baba, A. *Tetrahedron Lett.* **1995**, *36*, 9497–9500.
4. (a) Loh, T. P.; Pei, J.; Lin, M. *Chem. Commun.* **1996**, 2315–2316. (b) Babu, G.; Perumal, P. T. *Tetrahedron Lett.* **1997**, *38*, 5025–5026. (c) Kobayashi, S.; Busujima, T.; Nagayama, S. *Tetrahedron Lett.* **1998**, *39*, 1579–1582. (d) Loh, T. P.; Wei, L. L. *Tetrahedron Lett.* **1998**, *39*, 323–326.
5. (a) Babu, G.; Perumal, P. T. *Aldrichim. Acta* **2000**, *33*, 16–22. (b) Chauhan, K. K.; Frost, C. G. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3015–3019, and references cited therein.
6. For the recent reports on using indium compounds as a catalyst. See: (a) Muthusamy, S.; Babu, S. A.; Gunanathan, C. *Tetrahedron Lett.* **2002**, *43*, 3133–3136. (b) Yadav, J. S.; Subba Reddy, B. V.; Sadashiv, K.; Harikishan, K. *Tetrahedron Lett.* **2002**, *43*, 2099–2101. (c) Yadav, J. S.; Reddy, B. V. S.; Raman, J. V.; Niranjan, N.; Kiran Kumar, S.; Kunwar, A. C. *Tetrahedron Lett.* **2002**, *43*, 2095–2098. (d) Viswanathan, G. S.; Li, C. J. *Tetrahedron Lett.* **2002**, *43*, 1613–1615. (e) Choudhary, V. R.; Jana, S. K.; Patil, N. S. *Tetrahedron Lett.* **2002**, *43*, 1105–1107. (f) Kelly, B. G.; Gilheany, D. G. *Tetrahedron Lett.* **2002**, *43*, 887–890. (g) Inoue, K.; Sawada, A.; Shibata, I.; Baba, A. *J. Am. Chem. Soc.* **2002**, *124*, 960–961. (h) Friestad, G. K.; Ding, H. *Angew. Chem. Int. Ed.* **2001**, *40*, 4491–4493.
7. (a) Miyai, T.; Onishi, Y.; Baba, A. *Tetrahedron Lett.* **1998**, *39*, 6291–6294. (b) Miyai, T.; Onishi, Y.; Baba, A. *Tetrahedron* **1999**, *55*, 1017–1026.
8. Yasuda, M.; Onishi, Y.; Ito, T.; Baba, A. *Tetrahedron Lett.* **2000**, *41*, 2425–2428.
9. Miyai, T.; Ueba, M.; Baba, A. *Synlett* **2000**, 182–183.
10. Yasuda, M.; Onishi, Y.; Ueba, M.; Baba, A. *J. Org. Chem.* **2001**, *66*, 7741–7744.
11. (a) Mukaiyama, T.; Ohno, T.; Han, J. S.; Kobayashi, S. *Chem. Lett.* **1991**, 941–952. (b) Mukaiyama, T.; Ohno, T.; Han, J. S.; Kobayashi, S. *Chem. Lett.* **1991**, 949–952. (c) Mukaiyama, T.; Ohno, T.; Nishimura, T.; Han, J. S.; Kobayashi, S. *Bull. Chem. Soc. Jpn* **1991**, *64*, 2524–2527.
12. (a) Hosomi, A.; Sakurai, H. *Tetrahedron Lett.* **1976**, 1295–1296. (b) Hosomi, A. *Acc. Chem. Res.* **1988**, *21*, 200–206.
13. (a) Hosomi, A.; Shirahata, A.; Sakurai, H. *Tetrahedron Lett.* **1978**, 3043–3046. (b) Davis, A. P.; Jaspars, M. *J. Chem. Soc., Perkin Trans. 1* **1992**, 2111–2118. (c) Kaur, G.; Manju, K.; Trehan, S. *Chem. Commun.* **1996**, 581–582. (d) Gauthier, Jr. D. R.; Carreira, E. M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2363–2365. (e) Aggarwal, V. K.; Vennall, G. P. *Synthesis* **1998**, 1823–1826. (f) Marx, A.; Yamamoto, H. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 178–181. (g) Ishihara, K.; Mouri, M.; Gao, Q.; Maruyama, T.; Furuta, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1993**, *115*, 11490–11495. (h) Komatsu, N.; Uda, M.; Suzuki, H.; Takahashi, T.; Domae, T.; Wada, M. *Tetrahedron Lett.* **1997**, *38*, 7215–7218. (i) Fang, X.; Watkin, J. G.; Warner, B. P. *Tetrahedron Lett.* **2000**, *41*, 447–449. (j) Wang, M. W.; Chen, Y. J.; Wang, D. *Synlett* **2000**, 385–387.
14. Onishi, Y.; Ito, T.; Yasuda, M.; Baba, A.; Eur, *J. Org. Chem.* **2002**, 1578–1581.
15. Quite recently, Sakurai–Hosomi type allylation of enones promoted by catalytic amounts of $InCl_3$ and stoichiometric amounts of Me_3SiCl was reported; Lee, P. H.; Lee, K.; Sung, S.; Chang, S. *J. Org. Chem.* **2001**, *66*, 8646–8649.
16. We confirmed that the Sakurai–Hosomi reaction also proceeded in $CHCl_3$ solvent.
17. The smaller amounts of the combined catalyst were effective for the allylation (see Ref. 14). Decompositon of allyltrimethylsilane and numerous side reactions (cf. Prins-type cyclization) tend to occur under large amounts of the combined catalyst.
18. The corresponding signals to allyltrimethylsilane, hexamethyldisiloxane and *t*-$BuMe_2SiCl$ were detected by ^{29}Si NMR.
19. Allylation proceeded in the presence of 1 equiv. of Me_3SiCl. See Ref. 7b.
20. There are a few reports of catalytic allylation of imines using allyltrimethylsilane. See Ref. 6h.
21. Rearrangement plausibly proceeded via epoxide **17** shown in Scheme 4.



17

Scheme 4. Plausible mechanism of rearrangement.

22. $InCl_3$-promoted rearrangement of epoxides to aldehydes was reported in; Ranu, B. C.; Jana, U. *J. Org. Chem.* **1998**, *63*, 8212–8216.
23. In the case of the allylation of α-hydroxyketones, TBAF is not a suitable quenching reagent. The fluoride anion derived from TBAF was probably coordinated not to the silicon atom on the silylether, because a considerable amount of the silicon reagent or residue was found in the solution.
24. We presume that **11a** is the intermediate in the allylation of **5**. The silylether formation from alcohols and allylsilanes under similar conditions has been reported in Ref. 13.
25. The coordination ability of the oxygen atom of the –OMe group to the combined catalyst is thought to be stronger than that of the $-OSiMe_3$ group, because the non-bonded electron pair of the $-OSiMe_3$ group is used for stabilization through the pπ–dπ interaction.
26. Diallylation products were obtained when *para*-methoxybenzaldehyde was used. See Refs. 13e and 14. In this case, the stabilized carbocation formed after the first allylation tends to be further allylated.
27. (a) Rumin, R. *J. Organomet. Chem.* **1983**, *247*, 351–356. (b) Keinan, E.; Perez, D. *J. Org. Chem.* **1987**, *52*, 2576–2580.
28. Akiyama, T.; Iwai, J.; Sugano, M. *Tetrahedron* **1999**, *55*, 7499–7508.

29. Bortalotti, B.; Leardini, R.; Nanni, D.; Zanardi, G. *Tetrahedron* **1993**, *49*, 10157–10174.
30. Yasuda, M.; Fujibayashi, T.; Baba, A. *J. Org. Chem.* **1998**, *63*, 6401–6404.
31. Iwama, T.; Ogawa, M.; Kataoka, T.; Muraoka, O.; Tanabe, G. *Tetrahedron* **1998**, *54*, 8941–8974.
32. Kataoka, Y.; Makihara, I.; Akiyama, H.; Tani, K. *Tetrahedron* **1997**, *53*, 9525–9540.
33. Duboudin, J. G.; Jousseaume, B.; Pinet-Vallier, M. *J. Organomet. Chem.* **1979**, *172*, 1–10.
34. Moriuchi-Kawakami, T.; Matsuda, H.; Shibata, I.; Miyatake, M.; Suwa, T.; Baba, A. *Bull. Chem. Soc. Jpn* **1999**, *72*, 465–470.