# Aluminum Chloride Catalyzed Intramolecular Cyclization and Allylsilylation of Diallylsilanes

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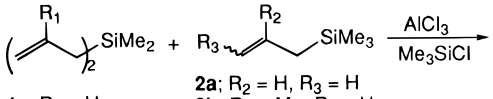
*Received February 3, 1997*⊗

*Summary: Reactions of diallylsilanes with allyltrimethylsilane in the presence of aluminum chloride as a catalyst resulted in intramolecularly cyclized allylsilylation products of trans- and cis-3-allyl-1,1-dimethyl-5-((trialkylsilyl)methyl)-1-silacyclohexanes in good yields. The reaction proceeded faster and gave better yields with the incorporation of chlorotrimethylsilane in the aluminum chloride catalyst.*



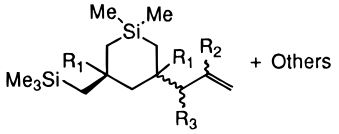
Recently, we reported a novel aluminum chloride catalyzed addition reaction of allyltrimethylsilane to simple unactivated alkenes[1] and alkynes.[2] In the allylsilylation, the silyl group regiospecifically and stereospecifically adds to the terminal carbon and the allyl group to the inner carbon of multiple bonds. The allylsilylation of carbon−carbon multiply bonded compounds proceeded at room temperature in the presence of a catalytic amount (5−10 mol %) of aluminum chloride, in contrast to the requirement for more than stoichiometric quantities (1.2 equiv) of Lewis acid catalyst in the allylation of carbonyl compounds.[3−7] Yamamoto and his co-workers reinvestigated allylsilylations of alkynes in the presence of $AlCl_3$ or $EtAlCl_2$ catalyst.[8] The allylsilylation proceeded at temperatures as low as −47 °C, and yields were higher in the presence of Lewis acid catalysts in combination with chlorotrimethylsilane as an activator. They confirmed that the allylsilylations gave the regio- and stereoselective allylsilylation products.

Subsequently we applied this new carbon−carbon bond formation reaction to diallylsilanes and found unusual aluminum chloride catalyzed intramolecular cyclization of diallylsilanes, followed by allylations of the cyclic carbocation. In this communication, we wish to report the results obtained from the allylsilylation of diallyldialkylsilanes **1** with allylsilanes **2** in the presence of aluminum chloride catalyst. The reaction gives the intramolecularly cyclized allylsilylation products of *trans*- and *cis*-3-allyl-1,1-dimethyl-5-((trialkylsilyl)methyl)-1-silacyclohexanes in yields from 45 to 76% (eq 1). The results of allylsilylations are summarized in Table 1.




**1a**: $R_1$ = H
**1b**: $R_1$ = Me

**2a**; $R_2$ = H, $R_3$ = H
**2b**; $R_2$ = Me, $R_3$ = H
**2c**; $R_2$ = H, $R_3$ = Me




(1)

**3a**; $R_1 = R_2 = R_3$ = H
**3b**; $R_1 = R_3$ = Me, $R_2$ = H
**3c**; $R_1 = R_2$ = H, $R_3$ = Me
**3d**; $R_1 = R_2$ = Me, $R_3$ = H
**3e**; $R_1$ = Me, $R_2 = R_3$ = H

As a typical example of the allylsilylation, diallyldimethylsilane **1a** (0.48 g, 3.4 mmol) was added dropwise to a suspended solution of allyltrimethylsilane **2a** (1.17 g, 10.2 mmol), chlorotrimethylsilane (1.85 g, 17.0 mmol), and aluminum chloride (0.23 g, 1.7 mmol) in *n*-hexane (10 mL) with vigorous stirring in a −10 °C salt bath. The solution was stirred for 1 h and then quenched with 5 mL of water. Usual workup and distillation gave *trans*- and *cis*-3-allyl-1,1-dimethyl-5-((trimethylsilyl)-methyl)-1-silacyclohexane (**3a**,[9] 2.2 g) and dicyclic products **4a**[10] in 70% and 14% yields, respectively, based on **1a** used. Other byproducts were hexamethyldisiloxane (10%) and unidentified polymeric materials (5%). The samples for characterization were purified by preparative GLC. The structural isomers of the cyclic allylsilylated products **3** were fully characterized by $^1$H, proton

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⊗ Abstract published in *Advance ACS Abstracts,* July 15, 1997.

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(9) The product mixture was separated and purified by preparative GLC. Spectroscopic data for *trans*- and *cis*-**3a** are as follows. $^1$H NMR for *trans* (*cis*)-**3a**: $\delta$ −0.01 (0.01) (s, 9H, Si($CH_3$)$_3$), −0.02, 0.01 (0.02, 0.06) (s, 3H, Si($CH_3$)$_2$), 0.07 (0.36) (t (dd), 1H, $J$ = 14 (14.3, 9.4) Hz), 0.73 (0.69) (m (dd), 1H ($J$ = 4.5, 14.3 Hz)) (ring Si$CH_2$), 0.16 (0.45) (t (dd), 1H, $J$ = 14 (7.3, 14.4) Hz), 0.76 (0.70) (m (dd), 1H ($J$ = 4.3, 14.4 Hz)) (ring Si$CH_2$), 0.56 (0.62) (dd (d), 1H, $J$ = 7, 15 (7.2) Hz), 0.64 (0.62) (m (d), 1H ($J$ = 7.2 Hz)) (Si$CH_2$), 0.64, 1.64 (1.30, 1.37) (m, 1H) (ring $CH_2$), 1.51 (1.89) (m, 1H, CH), 1.60 (2.11) (m, 1H, $CHCH_2SiMe_3$), 1.98 (2.04) (m, 2H, $CH_2$), 4.96, 4.97 (4.96, 4.97) (m, 1H) (=$CH_2$), 5.78 (5.78) (ddt, 1H, $J$ = 7, 10, 7 (7.1, 9.6, 17.9) Hz, =$CH$). $^{13}$C NMR for *trans* (*cis*)-**3a**: $\delta$ −3.72, −1.64 (−0.82, −0.20) (ring Si($CH_3$)$_2$), −0.40 (-0.57) (Si($CH_3$)$_3$), 20.30, 24.77 (19.21, 22.70) (ring Si$CH_2$), 30.54 (31.10) (Si$CH_2$), 32.71, 36.09 (26.55, 28.47) ($CH$), 46.01 (43.64) (allylic $CH_2$), 46.80 (43.38) (ring $CH_2$), 115.47 (115.39) (=$CH_2$), 137.77 (137.59) (=$CH$). HRMS ($m/z$): calcd for $Si_2C_{13}H_{27}$, $(M - CH_3)^+$, 239.1651; found, 239.1654.

S0276-7333(97)00075-7 CCC: $14.00 

**Table 1. Allylsilylation of Diallylsilanes with Allylsilanes[a]**

| entry no. | reactants 1 | reactants 2 | products yield,[b] % | products 3 | products *trans*:*cis* |
|---|---|---|---|---|---|
| 1 | **1a** | **2a** | 70 | **3a** | 92:8 |
| 2 | **1a** | **2b** | 76 | **3b** | 86:14 |
| 3 | **1b** | **2a** | 45 | **3c** | 76:34 |
| 4 | **1b** | **2b** | 59 | **3d** | 76:34 |
| 5 | **1a** | **2c** | 56 | **3e** | 88:12 |

[a] Reaction was carried out at −10 °C for 1 h in the persence of aluminum chloride. [b] Isolated yield.

**Table 2. Effects of $Me_3SiCl$/Lewis Acid in the Allylsilylation of 1a with 2a[a]**

| entry no. | amt of **1a**,[b] % | catalyst | $Me_3SiCl$/ catalyst | product **3a** yield,[c] % | product **3a** *trans*:*cis* |
|---|---|---|---|---|---|
| 6 | 92 (5)[d] | $AlCl_3$ | 0 | 6 (61)[d] | 93:7 |
| 7 | 81 | $EtAlCl_2$ | 0 | 13 | 93:7 |
| 8 | 7 | $AlBr_3$ | 0 | 63 | 91:9 |
| 9 | 69 | $AlCl_3$ | 0.5 | 21 | 94:6 |
| 10 | 37 | $AlCl_3$ | 1 | 44 | 94:6 |
| 11 | 19 | $AlCl_3$ | 2 | 57 | 93:7 |
| 12 | 6 | $AlCl_3$ | 5 | 66 | 92:8 |

[a] Reaction was carried out at −10 °C for 30 min. [b] Recovered **1a**. [c] Isolated yield. [d] Data in parentheses were obtained from 2.5 h reaction.



decoupling, NOE, $^{13}C$, and 2D (proton−proton or proton−carbon correlation) NMR techniques.

Chlorotrimethylsilane has been known as an activator for Lewis acid catalysts in cationic polymerization[11] and allylsilylation.[8] Yamamoto has proposed a mechanism for the allylsilylation of phenylacetylene in which chlorotrimethylsilane replaces the aluminum of the alkenyl−aluminum-bond-containing complex derived from the addition of $EtAlCl_2$ to phenylacetylene and subsquently to allyltrimethylsilane.[8] To study the effect of chlorotrimethylsilane addition to aluminum chloride catalyst for the allylsilylation of **1a** with **2a**, the reaction was carried out using various amounts of chlorotrimethylsilane activator. The results are summarized in Table 2.

As shown in Table 2, the allylsilylation of **1a** with **2a** in the presence of 50 mol % $AlCl_3$ catalyst without chlorotrimethylsilane for 30 min gave the product **3a** in only 6% yield (entry 6), but the yield increased to 61% after 2.5 h. The allylsilylation using $AlBr_3$ as a catalyst proceeded faster and gave 63% yield (entry 8). These results, showing that chlorotrimethylsilane is not essential for the allylsilylations, are consistent with our previous reports[1,2] but are in contrast with Yamamoto's report.[8] As shown in entry 7, $EtAlCl_2$ also catalyzes the reaction and shows slightly higher activity than $AlCl_3$, probably due to higher solubility in the reaction mixture.[12]

When chlorotrimethylsilane was added as an activator to aluminum chloride catalyst, the rate of allylsilylation drastically increased. As the mole ratio of chlorotrimethylsilane to $AlCl_3$ increased from 0.5 to 5, the yields of **3a** also increased from 21% to 66%. The results show that chlorotrimethylsilane promotes the aluminum chloride catalyzed reaction. However, no better results were obtained when more than a 5-fold amount of chlorotrimethylsilane with respect to $AlCl_3$ was used. This result is in contrast with the report for the allylsilylation of alkynes, where 20 equiv of chlorotrimethylsilane was required.[8]

The protodesilylation of allyltrimethylsilane by acids is well-known,[2,13−15] and we also detected propylene in the off-gas from the allylsilylation of alkenes catalyzed by aluminum chloride without chlorotrimethylsilane activator.[1] However, the complex, $Me_3Si^+AlCl_4^-$, was postulated from the direct addition of aluminum chloride with trimethylsilyl chloride in the Friedel-Crafts type silylation reaction of ferrocene by Olah and his coworkers.[16,17] To check if a trialkylsilyl cation was generated and involved in the allylsilylation, we ran the allylsilylation of **1a** using chlorodimethylethylsilane[18] as an activator instead of chlorotrimethylsilane. The product **5a**, containing a dimethylethylsilyl group, was obtained in predominance at the beginning stage, and then the **5a**/**3a** ratio decreased as the reaction proceeded further. This suggests strongly that the dimethylethylsilyl cation might be generated as aluminum chloride was mixed with dimethylethylsilyl chloride and the silyl cation could initiate the allylsilylation reaction. Although it is not clear at this moment whether the direct complexation of aluminum chloride with trialkylsilyl chloride or the protodesilylation of allyltrimethylsilane is the major source of silylenium ions, the results are suggestive of a trialkylsilylenium ion intermediate in the allylsilylation. The addition of such a silylenium ion to the terminal carbon of the multiple bond to give a more stable secondary carbocation and the $\sigma-\pi$ interaction[19−24] between the silyl group and a carboca-

(10) Four peaks (6%, 49%, 36%, and 9% in the order of GLC retention time) were detected by a analytical GLC, and their GC/MS fragmentation patterns were similar, indicating a mixture of isomeric products. Mass spectra for four isomers: *m*/*z* (relative intensity) 379 (1, M − $CH_3$)$^+$, 353 (10, M − $CH_2$=$CHCH_2$)$^+$, 213 (100), 167 (10), 139 (14), 125 (18), 99 (91), 73 (60), 59 (30). Spectroscopic data for two major products among the eight isomers are as follows. NMR data for two major diastereomers are given without the assignment for both compounds. $^1H$ NMR ($CDCl_3$): $\delta$ −0.01 (s, 18H, Si($CH_3$)$_3$), −0.04, −0.02, 0.00 (s, 3H, Si($CH_3$)$_2$), −0.10 (dd, 1H, $J$ = 12.8, 13.1 Hz), −0.02 (overlapped with Si($CH_3$)$_3$, 1H), 0.09 (t, 1H, $J$ = 14 Hz), 0.16 (t, 1H, $J$ = 13 Hz), 0.50−0.76 (m, 4H) (ring Si$CH_2$), 0.55 (dd, 1H, $J$ = 7.3, 14.7 Hz), 0.62 (dd, 1H, $J$ = 7.3, 14.7 Hz) (Si$CH_2$), 0.52−0.65 (m, 4H), 1.48−1.64 (m, 4H) (ring C$H_2$), 1.02 (quin, 1H, $J$ = 6.7 Hz), 1.05−1.13 (m, 2H), 1.18 (quin, 1H, $J$ = 6.7 Hz) (bridged C$H_2$), 1.48−1.64 (m, 8H, C*H*), 1.95, 2.02 (m, 2H, allylic C$H_2$), 4.96, 4.97, 5.77 (m, 2H) (vinyl protons). $^{13}C$ NMR ($CDCl_3$): $\delta$ −3.66, −1.52, −0.36 (Si$CH_3$), 20.06, 20.50, 20.95, 25.33, 30.66, 32.45, 32.55, 32.69, 35.91, 46.02 (Si$CH_2$, *C*H), 43.06, 43.67, 46.75, 47.83 (ring $CH_2$), 53.32, 53.81 (bridged $CH_2$), 115.47 (=$CH_2$), 137.81 (=CH). HRMS (*m*/*z*): calcd for $Si_3C_{21}H_{43}$, (M − $CH_3$)$^+$, 379.2673; found, 379.2674. Full characterizations of other minor isomeric products are in progress.

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(12) Surprisingly, $AlCl_3$ was obtained quantitatively when $EtAlCl_2$ was stirred with an equivalent amount of chlorotrimethylsilane overnight at room temperature. Several organosilanes such as ethyltrimethylsilane (25%), tetramethylsilane (27%), ethyldimethylchlorosilane (18%), diethyltetramethyldisiloxane (11%), and diethyldimethylsilane (14%) were also obtained, due to the coupling of chlorotrimethylsilane with $EtAlCl_2$ and disproportionation of the organosilanes in the presence of Lewis acid catalyst. These results suggest that $EtAlCl_2$ is not the catalyst, but $AlCl_3$ is, in the allylsilylation using chlorotrimethylsilane as an activator.[8]

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(18) Reaction was carried out in the same manner as the reaction of **1a** with **2a,** except that chlorodimethylethylsilane instead of chlorotrimethylsilane was used as an activator. The ratio of products, **5a**/**3a**, decreased from 2.5 at 15 min to 1.5 at 25 min of reaction time.

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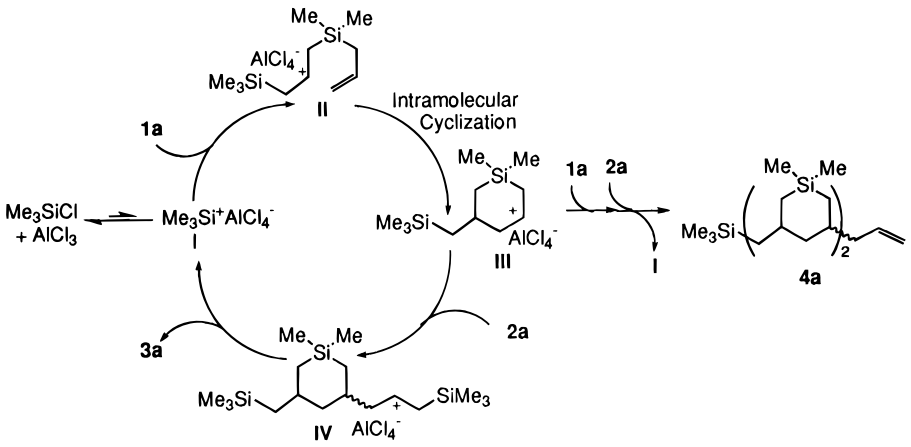
**Scheme 1**




tion were thought to be responsible for the regio- and stereoselectivity observed in the allylsilylation of alkenes[1] and alkynes.[2] In contrast to the previously reported regio- and stereoselectivity, two stereoisomers of *trans*- and *cis*-**3a** were obtained from the allylsilylation of diallylsilane in a 93:7 ratio. This result suggests that the $\sigma-\pi$ interactions in the allylsilylation of diallylsilane are less important than in that of monoallylsilane.[1,2]

On the basis of the analogy to the allylsilylation of alkenes[1] and alkynes,[2] we propose a possible mechanism for the allylsilylation of diallyldimethylsilane as illustrated in Scheme 1. When the silylenium ion intermediate **I** formed at the beginning stage of the reaction as explained above interacts with **1a**, the trimethylsilyl cation would be transferred to the terminal carbon of one of the allyl groups of **1a** to generate the new intermediate **II**. The formation of the more stable secondary carbocation and the $\beta$ stabilization effect[19−24] in the intermediate **II** would be responsible for the regiochemistry of the products. When the intermediate **II** interacts intramolecularly with the double bond of the other allyl group to form a new carbon−carbon bond, the cyclic carbenium ion center at the carbon $\beta$ to the dimethylsilyl silicon, **III**, would be generated. Since the silyl group is located in the ring frame after the cyclization, the $\beta$ stabilization effect in the intermediate **III** would be relatively small. This might be a reason for the formation of *trans* and *cis* isomeric products **3a**. As the intermediate **III** interacts intramolecularly with the double bond of **2a**, the intermediate **IV** would be generated. When the intermediate **IV** interacts with **1a**, *trans*- and *cis*-allylsilylated products **3a** would be obtained by transferring the trimethylsilyl cation to $AlCl_4^-$ to regenerate the intermediate **I** or directly to **1a** to regenerate the intermediate **II**.

If the intermediates **III** interact with **2a** before coupling with **1a**, a dicyclic carbonium ion will be generated to afford the dicyclic products **4a**. In the same manner, polycyclic intermediates can be generated to give high boiling species. The stereochemistry of the allylsilylation of diallyldimethylsilane could be explained by the approach of **2a** to the intermediate **III** type carbocation predominantly from the other side of (trimethylsilyl)methyl group, which is less hindered. The steric interactions between the trimethylsilylmethyl group and incoming **2a** would be much less compared with those in the allylsilylation of alkenes because of the two methylene spacer groups. This may be the reason that both stereoisomers of *trans*- and *cis*-allylsilylation products were obtained, while stereoselectivity was observed in the allylsilylation of alkenes[1] and alkynes.[2] The ratio of about 9:1 of *trans* to *cis* stereoisomers may be attributed to the steric hindrance difference between the upper and lower sides of the carbocation intermediates **III**. As a methyl group is introduced at the carbocation center, the isomeric ratio decreases to 76:34 (entries 3 and 4) due to the smaller difference in bulkiness between two sides of the carbocation center. When crotylsilane was used instead of allylsilane, the same allylic inversion reported in other systems[1,2,8] was also obtained and could be best explained by forming a new double bond between the carbons $\alpha$ and $\beta$ to silicon of the incoming allylsilane **2c** and the eliminating trimethylsilyl cation as illustrated in Scheme 1.

The results of this work show a possibility for the generation of a trialkylsilylenium ion which initiated intramolecular cyclization of diallylsilanes, followed by the allylation reaction of the cyclic carbocation to give 3-allyl-1,1-dimethyl-5-((trimethylsilyl)methyl)-1-silacyclohexanes. Although Yamamoto and his co-workers proposed another mechanism of aluminum-carbon bond formation for the allylsilylation of alkynes,[8] all the allylsilylation reactions of alkenes,[1] alkynes,[2,8] diallylsilanes, and conjugated dienes[25] can be explained best by our mechanism. The possibility that trimethylsilylenium ions as true catalytic species are involved in Lewis acids catalyzed allylation of aldehydes and acetals with allyltrimethylsilane has recently been reported.[26] Further studies for the cationic intramolecular cyclization and polymerization of diallylsilanes are in progress and will be reported in due time.

**Acknowledgment.** This research was supported financially by the Ministry of Science and Technology of Korea (Project 2N13771). We thank Prof. D. Seyferth of MIT and Prof. H. G. Woo of Chonnam National University for many valuable suggestions and discussions on this work.

**Supporting Information Available:** Figures giving NMR spectra for *cis*, *trans*-**3a**−**e** (13 pages). Ordering information is given on any current masthead page.

OM970075K

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