Silver Iodide Mediated Amination Reaction of Allylic Chlorides with Lithium Bis(trimethylsilyl)amide: A New Synthetic Method of *N,N*-Disilylallylamines via Lithium Amide Argentates

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The nucleophilic substitution reaction of allylic chlorides with lithium bis(trimethylsilyl)amide (1) in the presence of silver halides has been studied in detail. Silver iodide (AgI) was found to be most effective for facilitation of the amination reaction. The reaction of alkyl-substituted allylic chlorides proceeded smoothly in S_N2 fashion to give *N,N*-disilylallylamines in high yields when 0.1 or 0.5 equiv of AgI was used as an additive, whereas a stoichiometric amount of AgI was indispensable in the reaction of allylic chlorides having a phenyl group. The reaction of geranyl or neryl chloride proceeded with retention of configuration of the C=C bond to give only one isomer **4** or **5**, respectively. The oxygen-containing functional groups and chlorine remained intact during the reaction. The reaction of α-silylmetallyl chloride **17** proceeded in an S_N2' manner to afford (*Z*)-allylamine **18**. So as to disclose the active species in the AgI-mediated reaction, the variable low-temperature ^{13}C NMR experiments using the mixture of AgI and **1** in THF have been performed. It has been suggested that lithium amide argentates such as $(Me_3Si)_2NAg(I)Li$ (**20**) and $[(Me_3Si)_2N]_2Ag(I)Li_2$ (**21**) are formed in the reaction mixture, and the nucleophilicity and basicity of **1** are controlled by forming these species.

Introduction

Nucleophilic substitution reaction of allylic halides are of great importance in organic synthesis.[1] Numerous reactions using organocopper reagents[1a,2] and those catalyzed by transition metals such as copper[3] and palladium[4] have been devised to establish new methods for the formation of C–C bonds. The conversion of allylic halides to primary allylamines as a protected form of using nitrogen nucleophiles[5-8] has also been intensively studied because of the growing importance of the allylamines.[9] However, the regioselectivities of these reactions have been low compared with those in the reaction with carbon nucleophiles. For example, the reaction of sodium azide with allylic iodides prepared in situ gives the regioisomeric mixtures.[5e] The regioselectivity cannot be improved by the amination reaction of allylic substrates via π-allylmetal complexes.[7] In the course of our study on the synthesis of *N,N*-disilylamino compounds,[10] the reaction of lithium bis(trimethylsilyl)amide (**1**) with allylic chlorides was carried out. However, the desired reaction did not proceed so well. The use of allylic bromides allowed for the formation of *N,N*-disilylallylamines in good to excellent yields.[8] Nevertheless, proton abstraction of the substrates occurred predominantly rather than the nucleophilic substitution reaction in many cases. This is mainly because

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Table I. Reaction of Crotyl Chloride with $LiN(SiMe_3)_2$ in the Presence of Additives[a]

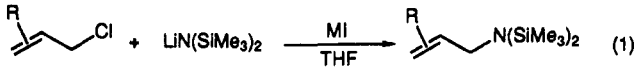
entry	MX	equiv of MX	time, h	$CH_3CH{=}CHCH_2N(SiMe_3)_2$ (2)[b] % yield[c]
1			20	34
2	CuI	0.1	1.5	79
3	CuI	0.5	1.5	49
4	AgI	0.02	4.5	85
5	AgI	0.1	1.5	99
6	AgI	0.5	1.5	100
7	AgI	1.0	20	51
8	AgCl	0.1	0.1	81
9	AgBr	0.1	20	77
10	AgCN	0.1	20	38

[a] The reactions were carried out at 67 °C under nitrogen using 2 mmol of crotyl chloride (*E*/*Z* = 84/16) and 2.4 mmol of 1 in the presence of copper or silver halide. [b] *E*/*Z* ratio of 2 was 84/16 regardless of the reaction conditions. [c] GLC yields.

of low nucleophilicity and strong basicity of 1.[11,12] So as to attain the substitution reaction selectively, a variety of metal salts have been examined as an additive. As a result, silver iodide (AgI) was found to effectively facilitate the reaction of allylic chlorides with 1 to afford *N,N*-disilylallylamines[13] in high yields.[10c,d] To the best of our knowledge, this represents the first example of the high catalytic activity of AgI.[14] In this paper we report the full details of the amination reaction and ^{13}C NMR studies of the mixture of lithium amide 1 and AgI in order to clarify the nature of active species of the reaction.

Results and Discussion

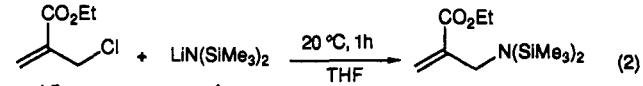
Reaction of Allylic Chlorides with 1 in the Presence of Silver Iodide. The results of the reaction of crotyl chloride with 1 in the presence of copper and silver halides (eq 1) have been shown in Table I. The substitution



1 (1)

reaction completely took place at the α-carbon of chlorine. AgI was most effective among copper and silver halides. The amount of AgI added was crucial. For example, the reaction was facilitated even with 0.02 equiv of AgI to give 2 in high yield, although the longer reaction time was necessary (entry 4). On the other hand, 1.0 equiv of AgI exerted little effect (entry 7). The highly insoluble silver halides completely dissolved in the THF solution containing 1 and gave light yellow solutions, whereas the reaction mixture using AgCN as an additive instantly turned deep green gray, and no effect was observed (entry 10).

The reaction of allylic chlorides substituted with a variety of functional groups at various positions with 1 has been examined (eq 1). As shown in Table II, *N,N*-disilylallylamines **3**–**14** were obtained when AgI was employed as an additive, although the temperature and the amounts of AgI were dependent on the substrates. In all cases the substitution reaction has occurred at the allylic carbon substituted with chlorine. These results are in marked contrast to those of the amination reaction of allylic substrates using sodium azide or via π-allyl palladium complexes.[5,6,9] For the reaction of allylic chlorides having alkyl groups, the addition of 0.1 or 0.5 equiv of AgI was effective to afford products **3**–**6** (entries 2, 5, 7, and 9). The reaction of geranyl and neryl chlorides proceeded stereospecifically to give *N,N*-disilylallylamines **4** and **5**, respectively (entries 5 and 7). On the other hand, 1.0 equiv of AgI was indispensable in the reaction of phenyl-substituted allylic chlorides (entries 12 and 15). In the reaction of cinnamyl chloride with 1 using 0.1 equiv of AgI or 1.0 equiv of AgCl or CuI, 1,6-diphenylhexa-1,3,5-triene was detected in ca. 20% yield. In these cases the proton abstraction of cinnamyl chloride at the α-position of chlorine may predominantly take place to give allyl anion, which attacks another cinnamyl chloride, followed by elimination of hydrogen chloride to give the triene. Functional groups such as chlorine, siloxy, benzoyl, and methoxymethyl groups have survived under the reaction conditions (entries 17, 23, 26, 29, and 32). The amination reactions of allylic chlorides having these functional groups were also attained by the use of 1.0 equiv of AgI. Accordingly, the nucleophilic substitution predominated over the proton abstraction in the system of 1.0 equiv of AgI and 1, and the latter process was highly suppressed. The substituent effect of the carbethoxy group was observed for the reaction of allylic chloride **15** (eq 2). The



15 **1** **16** (2)

Michael-assisted S_N2' reaction of **15** with 1 took place smoothly at room temperature even in the absence of AgI to afford a 94% yield of *N,N*-disilylallylamine **16**. No product derived from proton abstraction was obtained.

The reaction of α-silylmethallyl chloride **17** with 1 in the presence of 1 equiv of AgI proceeded regio- and stereoselectively in an S_N2' manner to give (*Z*)-*N,N*-disilylallylamine **18** in 54% yield.[17] This selectivity of the

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(12) The replacement of the trimethylsilyl group of 1 with a benzyl group enhanced the nucleophilicity of lithium amide: Asao, N.; Uyehara, T.; Yamamoto, Y. *Tetrahedron* **1988**, *44*, 4173.

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(14) In organic synthesis the thermodynamic stability of silver halides[15] has been utilized as a driving force to construct carbon–carbon and –oxygen bonds from allylic halides and silver salts such as AgOTf and $AgBF_4$.[16]

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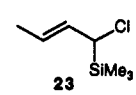
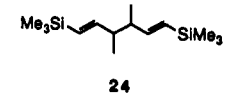
(17) Attempts to attain the similar S_N2' reaction of allylic chloride **23** have failed and resulted in the recovery of **23**. Instead of lithium amide 1, $LiN(SiMe_3H)_2$ was used with 0.1 equiv of AgI. However, the reaction gave mainly the homocoupling products involving **24**.

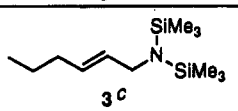
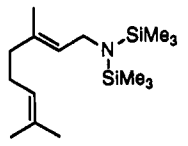
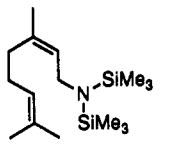
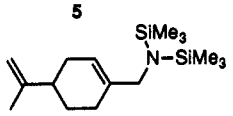
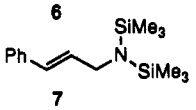
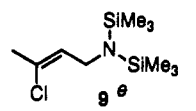
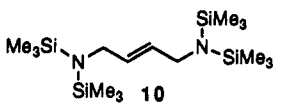
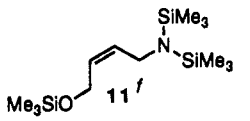
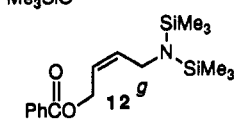
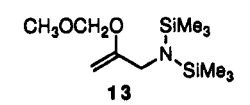
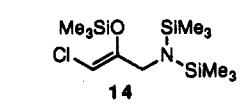


23



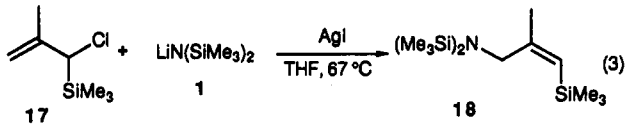
24

Table II. Reaction of Allylic Chloride with $LiN(SiMe_3)_2$ in the Presence of AgI[a]

entry	product	equiv of AgI	yield[b] (%)
1		0	21
2		0.1	89
3	3[c]	1.0	85
4		0	1[d]
5	4	0.1	82[d]
6		0	trace[d]
7	5	0.1	100[d]
8		0	10
9	6	0.5	76
10		0	trace
11		0.1	trace
12	7	1.0	(59)
13		0	3
14		0.1	19
15	8	1.0	(46)
16		0	6
17	9[e]	0.1	60
18		0	0
19		0.5	trace
20	10	1.0	(30)
21		0	2
22		0.1	14
23	11[f]	1.0	(69)
24		0	trace
25		0.1	4
26	12[g]	1.0	(42)
27		0	1
28		0.5	13
29	13	1.0	48
30		0	0
31		0.1	8
32	14	1.0	40

[a] The reactions were carried out at 67 °C for 20 h under nitrogen using 2 mmol allylic chloride and 2.4 mmol of 1 in THF (5 mL) in the presence of AgI unless otherwise noted. [b] GLC yield. Isolated yields are in parentheses. [c] The ratio of *E*/*Z* of both the corresponding allylic chloride and 3 was 85/15. [d] At 20 °C. [e] The ratio of *E*/*Z* was 25/75 in both the corresponding allylic chloride and 9. [f] (*Z*)-Allylic chloride was used as a starting material. The ratio of *E*/*Z* of 11 was 20/80. [g] (*Z*)-Allylic chloride was used as a starting material. The stereochemistry of 12 was tentatively assigned as the *Z*-isomer.

present reaction can be understood by considering the stable conformation of 17. When 17 is observed based on



(3)

the Felkin–Ahn model, it may be represented as two conformational isomers 17-I and 17-II described in Scheme I. In each case the chlorine as a leaving group orients itself perpendicular to the plane of the carbon–carbon double bond. The nitrogen nucleophile seems to attack 17 on the side antiperiplaner to the leaving group to give the *Z*-isomer from 17-I and to give the *E*-isomer from 17-II.[18] The unfavorable gauche interaction depicted in conformer 17-II should lead to preferential reaction via conformer 17-I, resulting in the observed stereoselectivity.

Mechanistic Survey. The following three possibilities shown in Scheme II can be considered as facilitating effect of AgI: (1) Iodination of allylic chlorides with AgI, followed by amination with lithium amide 1. (2) As in the case of $CuN(SiMe_3)_2$,[19] $AgN(SiMe_3)_2$ (19)[20,21] initially formed by transmetalation of the Ag–I bond to the Ag–N bond reacts with allylic chlorides. (3) Lithium amide argentate is formed by mixing AgI with lithium amide 1 in THF and then reacts with allylic chlorides.

The first two possibilities seem to be less plausible because of the following reasons: (1) If they are true, 1.0 equiv of AgI should always exhibit the high efficiency. (2) The reaction of allyl iodide with 1 in the presence of 0.1 equiv of AgI proceeded twice as fast as that in the absence of AgI. (3) During the reaction course, AgI gradually precipitated and ca. 60% of AgI, which showed the same efficiency as fresh AgI toward the amination reaction, was recovered from the reaction mixture. (4) The formation of AgCl and allylic iodide or of 19 and LiI from more stable AgI and allylic chloride or 1 is thermodynamically unfavorable. Accordingly, the third one can be proposed as the most plausible process at the present time. In order to obtain some evidences to support it, ^{13}C-NMR studies on the mixture of lithium amide 1 and AgI were carried out.

In the ^{13}C-NMR spectra shown in Figure 1, the signal due to the methyl carbon attached to the silicon of 1 was observed at δ 5.8 as a sharp singlet in THF. Lithium amide 1 has been reported to be a monomer–cyclic dimer mixture in THF.[22] However, these two species were not distinguished in ^{13}C NMR. When 1.0 equiv of AgI was added to a THF solution of 1, the signal at δ 5.8 was shifted to lower field by 1.8 ppm. Interestingly, AgI was recovered nearly quantitatively from this NMR sample.[23] Accordingly, the addition of 1.0 equiv of AgI to a THF solution of 1 may give rise to lithium amide argentate which can

(18) Alternatively, the syn-S_N2' displacement is possible: the nucleophile attacks on the side syn-periplaner to the leaving group by forming six-membered ring transition state with 17-I. As another reason, the reviewer has suggested that the formation of *Z*-isomer is due to internal coordination of nitrogen to silicon atom attached to vinylic carbon.

(19) The formation of $CuN(SiMe_3)_2$ from 1 and CuI has been suggested: King, F. D.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1974**, 256.

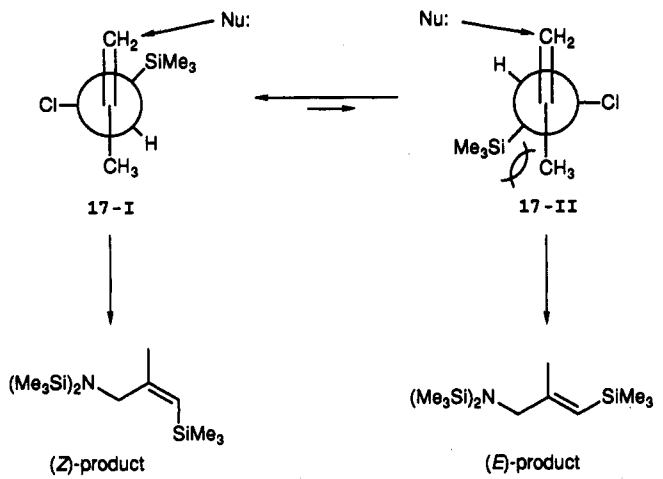
(20) Silver amide 19 has been noted to be explosive: Bürger, H.; Seyffert, H. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 646.

(21) The tetramer of 19 was also reported: Burns, C. L.; Smith, W. H.; Huffman, J. C.; Sattelberger, A. P. *J. Am. Chem. Soc.* **1990**, *112*, 3237.

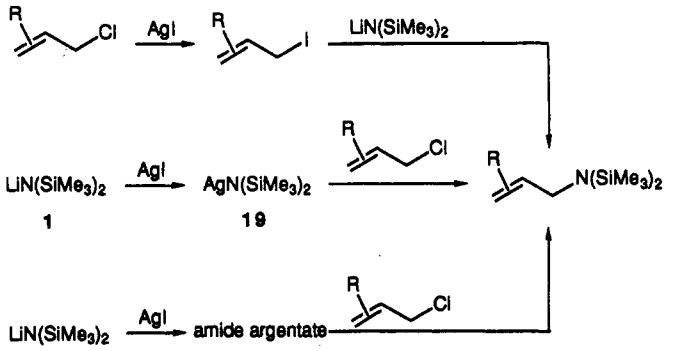
(22) Romesberg, F. E.; Bernstein, M. P.; Gilchrist, J. H.; Harrison, A. T.; Fuller, D. J.; Collum, D. B. *J. Am. Chem. Soc.* **1993**, *115*, 3475.

(23) Attempts to dissolve AgI in other solvent such as toluene, dioxane, and ether containing 1 have failed. The solvation of 1 in THF or the existence of 1 as a monomer may play an important role to form lithium amide argentate.

Scheme I



Scheme II



be formulated as **20** analogously to the mixed organocuprates,[24] although the actual structure of **20** cannot be estimated at the present stage. On the other hand, the ^{13}C-NMR spectrum of the mixture of 1 and 0.5 equiv of AgI exhibited the broad signal at δ 6.7, and this implies there exists rapid equilibrium among several species in THF solution of 1 and 0.5 equiv of AgI.

$(Me_3Si)_2NAg(I)Li$ **20** $[(Me_3Si)_2N]_2Ag(I)Li_2$ **21**

$[(Me_3Si)_2N]_3Ag_2(I)_2Li_3$ **22**

Variable low-temperature NMR studies on the mixture of 1 and 0.5 equiv of AgI in THF by using C_6D_6 as an internal standard have further supported the existence of these new species (Figure 2). The three sharp singlets (**A**–**C**) were observed at −50 °C, and two of them, i.e., **A** and **C**, are consistent with those of the methyl carbon of 1 and the complex to be considered as lithium amide argentate **20**, respectively. The other signal is probably due to the methyl signal of a 1:2 complex of AgI and 1. Similarly to the case of **20** and higher order organocuprates,[24,25] this new complex may be formulated as the higher order amide argentate **21**.[26] The peaks **B** and **C** gradually became broad while the temperature was raised

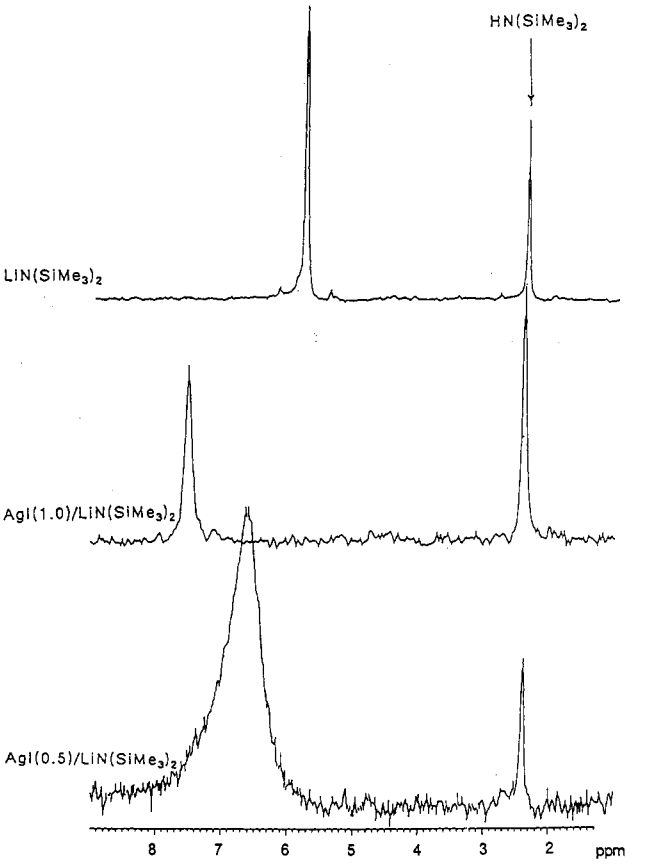


Figure 1. ^{13}C NMR spectra of 1 and the mixture of AgI and 1 in THF.

to −20 °C, and new peaks (**D**, **E**) have appeared in the lower fields. When the temperature was raised to 0 °C, all the peaks became broad, and reaching room temperature gave rise to only one broad singlet. Thus, in the solution of the mixture of 1 and 0.5 equiv of AgI three discrete species, i.e., **1**, **20**, and **21**, which are distinguishable in the NMR time scale at −50 °C, came to equilibrium with one another as it was raised to room temperature. Furthermore, some other higher order complexes such as **22** may also be in equilibrium since the new peaks **D** and **E** were observed at −20 °C. Accordingly, it is possible that lithium amide argentates **20**–**22** are in equilibrium when not more than 0.5 equiv of AgI was added to the THF solution of **1**, the same system which facilitates the amination reaction of crotyl chloride most effectively (Table I). The nucleophilicity of lithium amide argentates **21** and **22** seems to be stronger than that of 1 and the lower order complex **20** since the reaction of the latter two systems gave the product in poorer yields (Table I, entries 1 and 7). As for cinnamyl chloride, lithium amide 1 is still present in the mixture of 0.1 equiv of AgI and 1, and it predominantly abstracts the proton at the carbon substituted with chlorine to result in the formation of the triene (entries 11 and 14 in Table II). When the mixture of 1 and 1.0 equiv of AgI was used, nucleophilic attack proceeded preferentially to proton abstraction probably

(24) (a) Lipshutz, B. H.; Kozlowski, J. A.; Wilhelm, R. S. *J. Org. Chem.* **1984**, *49*, 3943. (b) Bertz, S. H.; Dabbagh, G. *J. Am. Chem. Soc.* **1988**, *110*, 3668. (c) Bertz, S. H. *J. Am. Chem. Soc.* **1990**, *112*, 4031.

(25) The synthetic reactions using higher order organocuprates have been widely developed: (a) Lipshutz, B. H.; Wilhelm, R. S.; Kozlowski, J. A. *Tetrahedron* **1984**, *40*, 5005. (b) Lipshutz, B. H. *Synthesis* **1987**, 325. (c) Lipshutz, B. H. *Synlett* **1990**, 119.

(26) The formation of amide cuprates from 2 equiv of LiNBn(SiMe$_3$) and 1 equiv of CuI in THF was reported.[27] In this case CuI is considered to initially form copper amide and then to form amide cuprate. On the contrary, AgI does not form **19** in the present system since AgI can be recovered. Thus, an Ag–I bond should exist in lithium amide argentates **20**–**22**.

(27) Shida, N.; Uyahara, T.; Yamamoto, Y. *J. Org. Chem.* **1992**, *57*, 5049.

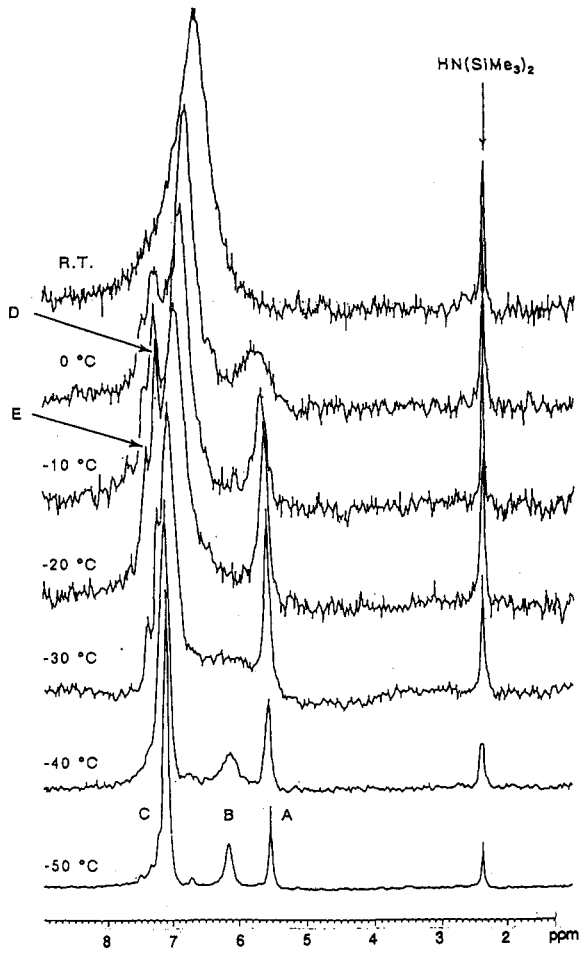


Figure 2. Variable low-temperature ^{13}C NMR spectra of 1 and the mixture of AgI (0.5 equiv) and 1 in THF.

because the basicity of the complex 20 was weaker than that of 1 and/or the complexes 21 and 22.

In summary, the nucleophilic substitution of allylic chlorides using the system of AgI and 1 gave *N,N*-disilylallylamines in high yields. The reaction of alkyl-substituted allylic chlorides proceeded highly regio- and stereoselectively by mixing 1 with not more than 0.5 equiv of silver iodide. As for α-silylmethallyl chloride 17, the amination reaction selectively took place in an S_N2' manner to give (*Z*)-allylamine 18. The amination reaction of cinnamyl chlorides and oxygen-containing functional groups was attained only by using 1.0 equiv of AgI. The existence of unprecedented lithium amide argentates[28] was suggested on the basis of ^{13}C NMR studies. The bacisity and nucleophilicity of 1 may be finely tuned by forming lithium amide argentates.

Experimental Section

General. ^1H and ^{13}C NMR were recorded at 270 MHz and 67.5 MHz, respectively. Elemental analyses were performed by the Elemental Analysis Center of Kyoto University. Analytical gas chromatography (GLC) was carried out with a flame ionization detector, using a 3-m × 3-mm stainless steel column packed with 1% silicone SE-30 supported on 60–80-mesh Chromosorb G(AW). Preparative GLC was performed using a 2-m × 10-mm stainless steel column packed with 5% silicone OV-1 supported on 60–80-mesh Uniport HP. Bulb to bulb distillation was carried out with a Kugelrohr apparatus.

Material. Tetrahydrofuran (THF) was distilled from sodium metal prior to use. Hexamethyldisilazane and tetramethyldisilazane distilled from CaH_2 were stored under a nitrogen atmosphere. Crotyl chloride purchased from Nacalai tesque was distilled from CaH_2. Cinnamyl chloride and *trans*-1,4-dichloro-2-butene were purchased from Nacalai tesque or Tokyo Kasei and purified by vacuum distillation. Allyl iodide purchased from Tokyo Kasei was used without further purification. 2-Hexenyl chloride,[29] geranyl chloride,[29] neryl chloride,[29] perillyl chloride,[29] 2-(methoxymethoxy)allyl chloride,[30] 3-chloro-2-(trimethylsiloxy)-allyl chloride,[16b] 2-carbethoxyallyl chloride,[31] α-(trimethylsilyl)-methallyl chloride,[32] and α-(trimethylsilyl)crotyl chloride[32] were prepared according to literature procedures. *n*-Butyllithium/*n*-hexane solution was commercially available from Nacalai tesque.

General Procedure for the Reaction of Allylic Chloride with Lithium Bis(trimethylsilyl)amide (1) in the Presence of Silver Iodide. In a 10-mL two-necked flask, fitted with a reflux condenser, was placed 1 prepared from hexamethyldisilazane (0.56 mL, 2.4 mmol) and a 1.6 M *n*-hexane solution of *n*-butyllithium (1.5 mL, 2.4 mmol) in THF (5 mL). To this solution was added appropriate amounts of silver iodide and the mixture stirred for 1 h at room temperature. To the resulting homogeneous solution was added allylic chloride (2.0 mmol) and the mixture stirred under reflux in THF. The reaction mixture obtained above was filtered and concentrated. The resulting crude oil was distilled by Kugelrohr to afford an analytically pure product as a colorless oil. The structure of the known *N,N*-disilylallylamines was confirmed by comparison of their spectroscopic data in the literature.

***N,N*-Bis(trimethylsilyl)-2-hexen-1-amine (3):** bp 120 °C, 5 mmHg; IR (neat) 2950, 1460, 1350, 1245, 1095, 1025, 965, 925, 870, 830, 755, 675, 610 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 0.08 (s, 18H, $SiMe_3$), 0.88 (t, J = 7.3 Hz, 3H, CH_3), 1.36 (sextet, J = 7.3 Hz, 2H, CH_2), 1.95 (q, J = 7.3 Hz, 2H, $=CCH_2$), 3.37 (dd, J^1 = 4.8 Hz, J^2 = 1.3 Hz, 1.7H, CH_2N of (*E*)-**3**), 3.92 (dd, J^1 = 6.2 Hz, J^2 = 0.9 Hz, 0.3H, CH_2N of (*Z*)-**3**), 5.31 (dt, J^1 = 15.2 Hz, J^2 = 4.9 Hz, 0.85H, =CH of (*E*)-**3**), 5.44 (dt, J^1 = 15.2 Hz, J^2 = 6.2 Hz, 0.85H, =CH of (*E*)-**3**), 5.47–5.73 (m, 0.3H, =CH of (*E*)-**3**); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 2.1 ($SiMe_3$), 13.8 (CH_3), 22.7 (CH_2), 34.5 (CH_2N), 46.6 (CH_2), 129.4, 132.9 (C=C); HRMS calcd for $C_{12}H_{29}NSi_2$ 243.1837, found 243.1841.

***N,N*-Bis(trimethylsilyl)nerylamine (5):** bp 160 °C, 2 mmHg; IR (neat) 2950, 1655, 1440, 1370, 1245, 1080, 1030, 875, 830, 750, 675, 610 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 0.07 (s, 18H, $SiMe_3$), 1.60 (s, 3H, CH_3), 1.65 (q, J = 1.5, 3H, CH_3), 1.68 (s, 3H, CH_3), 1.93–2.09 (m, 4H, CH_2CH_2), 3.42 (dq, J^1 = 5.6 Hz, J^2 = 1.5 Hz, 2H, CH_2N), 4.95–5.13 (m, 2H, =CH) [the stereochemistry was supported by the NOE measurement as follows: irradiation of =CH at δ 5.11 enhanced the intensity of CH_3 by 14%]; ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 2.1 ($SiMe_3$), 17.7, 23.3 (CH_2), 25.8, 26.4, 32.4 (CH_3), 42.6 (CH_2N), 124.3, 130.4, 131.7, 133.0 (C=C); HRMS calcd for $C_{16}H_{35}NSi_2$ 297.2306, found 297.2310.

***N,N*-Bis(trimethylsilyl)perillylamine (6):** bp 160 °C, 2 mmHg; IR (neat) 2950, 1640, 1450, 1240, 1125, 1060, 1010, 910, 880, 830, 750, 670, 610 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 0.06 (s, 18H, $SiMe_3$), 1.35–1.57 (m, 1H, CH), 1.73 (s, 3H, CH_3), 1.75–2.20 (m, 6H, CH_2), 3.25 (br, 2H, CH_2N), 4.70 (s, 2H, $=CH_2$), 5.57 (br, 1H, =CH); ^{13}C-NMR ($CDCl_3$) δ 1.9 ($SiMe_3$), 20.9 (CH_3), 27.1, 27.9, 30.5, 41.7, 50.1 (CH and CH_2), 108.4, 119.8, 138.5, 150.3 (C=C); HRMS calcd for $C_{16}H_{33}NSi_2$ 295.2150, found 295.2163.

***N,N*-Bis(trimethylsilyl)cinnamylamine (7):** bp 170 °C, 5 mmHg; IR (neat) 3050, 3000, 1610, 1500, 1455, 1360, 1255, 1165, 1060, 1030, 940, 880, 835, 760, 730, 690, 610 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 0.20 (s, 18H, $SiMe_3$), 3.70 (dd, J^1 = 4.9 Hz, J^2 = 1.8 Hz, 2H, CH_2N), 6.21 (dt, J^1 = 15.7 Hz, J^2 = 4.9 Hz, 1H, =CH), 6.52 (dt,

(28) For examples of organoargentates: (a) Leusink, A. J.; Koten, G. V.; Marsman, J. W.; Noltes, J. G. *J. Organomet. Chem.* **1973**, *55*, 419. (b) Westmijze, H.; Kleijn, H.; Vermeer, P. *J. Organomet. Chem.* **1979**, *172*, 377. (c) Blenkers, J.; Hofstee, H. K.; Boersma, J.; Van der Kerk, G. J. M. *J. Organomet. Chem.* **1979**, *168*, 251. (d) Westmijze, H.; Kleijn, H.; Vermeer, P. *Tetrahedron Lett.* **1979**, 3327.

(29) Calzada, J. G.; Hooz, J. *Org. Synth.* **1972**, *54*, 63.

(30) Gu, X.-P.; Nishida, H.; Ikeda, I.; Okahara, M. *J. Org. Chem.* **1987**, *52*, 3192.

(31) Villieras, J.; Rambaud, M. *Org. Synth.* **1987**, *66*, 220.

(32) Hosomi, A.; Ando, M.; Sakurai, H. *Chem. Lett.* **1984**, 1385.

J^1 = 15.7 Hz, J^2 = 1.8 Hz, 1H, =CH), 7.27–7.43 (m, 5H, Ar); ^{13}C-NMR ($CDCl_3$) δ 2.0 ($SiMe_3$), 46.9 (CH_2N), 126.2, 127.0, 128.5, 128.8, 133.3, 137.7 (Ar and C=C); mass spectrum (EI) *m/z* 277 (M^+). Anal. Calcd for $C_{15}H_{27}NSi_2$: C, 64.91; H, 9.81. Found: C, 64.79; H, 9.72.

***N,N*-Bis(trimethylsilyl)-2-methyl-3-phenyl-2-propen-1-amine (8):** bp 180 °C, 5 mmHg; IR (neat) 2995, 1600, 1495, 1445, 1370, 1250, 1085, 1055, 990, 915, 890, 870, 835, 745, 700 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.12 (s, 18H, $SiMe_3$), 1.75 (s, 3H, CH_3), 3.44 (d, *J* = 1.1 Hz, 2H, CH_2N), 6.49 (s, 1H, =CH), 7.20–7.32 (m, 5H, Ar); ^{13}C-NMR ($CDCl_3$) δ 2.3 ($SiMe_3$), 16.8 (CH_3) 52.7 (CH_2N), 123.9, 126.2, 128.5, 129.2, 139.4, 140.5 (Ar and C=C); mass spectrum (CI) *m/z* 292 (M^+ + 1). Anal. Calcd for $C_{16}H_{29}NSi_2$: C, 65.91; H, 10.02. Found: C, 65.74; H, 10.21.

***N,N*-Bis(trimethylsilyl)-3-chloro-2-buten-1-amine (9):** bp 150 °C, 5 mmHg; IR (neat) 2950, 1660, 1440, 1380, 1345, 1250, 1110, 1080, 1030, 1015, 970, 870, 830, 755, 680, 635, 610 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.08 (s, 18H, $SiMe_3$), 2.01 (q, *J* = 1.3 Hz, 0.75H, CH_3 of (*E*)-**9**), 2.05 (q, *J* = 1.5 Hz, 2.25H, CH_3 of (*Z*)-**9**), 3.43 (dq, J^1 = 6.2 Hz, J^2 = 1.1 Hz, 0.5H, CH_2N of (*E*)-**9**), 3.54 (tq, J^1 = 5.5 Hz, J^2 = 1.3 Hz, 1.5H, CH_2N of (*Z*)-**9**), 5.29 (tq, J^1 = 5.5 Hz, J^2 = 1.3 Hz, 0.75H, =CH of (*Z*)-**9**), 5.44 (tq, J^1 = 6.2 Hz, J^2 = 1.3 Hz, 0.25H, =CH of (*E*)-**9**); mass spectrum (EI) *m/z* 214 (M^+ − Cl). Anal. Calcd for $C_{10}H_{24}ClNSi_2$: C, 48.06; H, 9.68. Found: C, 48.04; H, 9.94.

(*E*)-*N,N,N′N′*-Tetrakis(trimethylsilyl)-2-butene-1,4-diamine (10). bp 180 °C, 3 mmHg; IR (neat) 2950, 1250, 1090, 1030, 970, 870, 840, 750, 670, 610 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.07 (s, 36H, $SiMe_3$), 3.40 (d, *J* = 2.9 Hz, 4H, CH_2N), 5.42 (t, *J* = 2.3 Hz, 2H, =CH); ^{13}C-NMR ($CDCl_3$) δ 2.0 ($SiMe_3$), 46.2 (CH_2N), 131.7 (C=C) (the stereochemistry of **10** was tentatively estimated as *trans*-configuration since the ^{13}C-NMR spectrum showing only three signals suggests that the sample contained only one isomer); HRMS calcd for $C_{16}H_{42}N_2Si_4$ 374.2423, found 374.2412.

***N,N*-Bis(trimethylsilyl)-4-(trimethylsiloxy)-2-buten-1-amine (11):** bp 100 °C, 3 mmHg; IR (neat) 2950, 1395, 1250, 1060, 1015, 940, 870, 830, 760, 680 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.08 (s, 18H, $NSiMe_3$), 0.12 (s, 9H, $SiMe_3$), 3.34 (d, *J* = 4.8 Hz, 0.4H, CH_2N of (*E*)-**11**), 3.47 (d, *J* = 5.9 Hz, 1.6H, CH_2N of (*Z*)-**11**), 4.13 (d, *J* = 5.9 Hz, 1.6H, CH_2O of (*Z*)-**11**), 4.17 (d, *J* = 4.4 Hz, 0.4H, CH_2O of (*E*)-**11**), 5.31 (dt, J^1 = 11.3 Hz, J^2 = 4.7 Hz, 0.8H, =CH of (*Z*)-**11**), 5.39 (dt, J^1 = 11.3 Hz, J^2 = 5.1 Hz, 0.8H, =CH of (Z)-**11**), 5.47–5.57 (m, 0.4H, =CH of (*E*)-**11**); ^{13}C-NMR ($CDCl_3$) δ −0.4 ($SiMe_3$), 2.0 ($NSiMe_3$), 42.2 (CH_2N), 58.8 (CH_2O), 127.1, 135.9 (C=C); HRMS calcd for $C_{13}H_{33}NOSi_3$ 303.1868, found 303.1843. Anal. Calcd for $C_{13}H_{33}NOSi_3$: C, 51.42; H, 10.95. Found: C, 51.56; H, 11.14.

(*Z*)-*N,N*-Bis(trimethylsilyl)-4-(benzoyloxy)-2-buten-1-amine (12): bp 150 °C, 1 mmHg; IR (neat) 3000, 1730, 1610, 1460, 1270, 1110, 1070, 1030, 875, 840, 720 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.10 (s, 18H, $SiMe_3$), 3.42 (m, 2H, CH_2N), 4.84 (m, 2H, CH_2O), 5.55 (dd, J^1 = 19.0 Hz, J^2 = 11.6 Hz, 1H, =CH), 5.55 (dd, J^1 = 20.3 Hz, J^2 = 11.6 Hz, 1H, =CH), 7.42–8.06 (m, 5H, Ar); ^{13}C-NMR ($CDCl_3$) δ 2.1 ($SiMe_3$), 42.2 (CH_2N), 60.8 (CH_2O), 121.3, 128.4, 129.6, 130.3, 132.9, 139.8 (Ar and C=C), 166.5 (C=O) (the stereochemistry of **12** was estimated as *cis*-configuration since the ^{13}C-NMR spectrum showing 10 signals suggests that the sample contained only one isomer and in the ^{1}H-NMR spectrum the coupling constant between vinyl protons was nearly 0 Hz); HRMS calcd for $C_{17}H_{29}NO_2Si_2$ 355.1736, found 335.1723; Anal. Calcd for $C_{17}H_{29}NO_2Si_2$: C, 60.84; H, 8.71. Found: C, 60.99; H, 8.96.

***N,N*-Bis(trimethylsilyl)-2-(methoxymethoxy)-2-propen-1-amine (13):** bp 100 °C, 5 mmHg; IR (neat) 2950, 1640, 1450, 1245, 1150, 1030, 924, 870, 760, 680 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 18H, $SiMe_3$), 3.34 (s, 2H, OCH_2), 3.40 (s, 3H, OCH_3), 4.20 (d, *J* = 1.5 Hz, 1H, CH), 4.25 (d, *J* = 1.5 Hz, 1H, CH), 4.93 (s, 2H, $=CH_2$); mass spectrum (CI) 262 (M^+ + 1). Anal. Calcd for $C_{11}H_{27}NO_2Si_2$: C, 50.52; H, 10.41. Found: C, 50.63; H, 10.68.

(*Z*)-*N,N*-Bis(trimethylsilyl)-3-chloro-2-[(trimethylsilyl)-oxy]-2-propen-1-amine (14): bp 100 °C, 5 mmHg; IR (neat) 2950, 1640, 1490, 1250, 1155, 1095, 1020, 960, 870, 835, 760, 680 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 18H, $SiMe_3$), 0.24 (s, 9H, $SiMe_3$), 3.30 (d, *J* = 1.8 Hz, 2H, CH_2N), 5.46 (t, *J* = 1.8 Hz, 1H, CHCl); HRMS calcd for $C_{12}H_{30}NOSi_3Cl$; 323.1322, found 323.1316.

***N,N*-Bis(trimethylsilyl)-2-carbethoxy-2-propen-1-amine (16):** bp 110 °C, 5 mmHg; IR (neat) 2955, 1716, 1639, 1452, 1395, 1380, 1368, 1288, 1254, 1150, 1074, 1034, 948, 877, 830, 756, 681, 648, 610 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.07 (s, 18H, $SiMe_3$), 1.29 (t, *J* = 7.2 Hz, 3H, CH_3), 3.65 (t, *J* = 2.2 Hz, 2H, CH_2N), 4.20 (q, *J* = 7.0 Hz, 2H, CH_2), 5.80 (q, *J* = 2.2 Hz, 1H, CH=), 6.26 (d, *J* = 2.2 Hz, 1H, CH=); ^{13}C NMR ($CDCl_3$) δ 1.7, 14.2, 45.4, 60.5, 124.4, 142.9, 174.4; mass spectrum (CI) *m/z* 274 (M^+ + 1). Anal. Calcd for $C_{12}H_{27}NO_2Si_2$: C, 52.70; H, 9.95. Found: C, 52.52; H, 10.16.

(*Z*)-*N,N*,3-Tris(trimethylsilyl)-2-methyl-2-propen-1-amine (18): bp 150 °C, 2 mmHg; IR (neat) 2950, 1630, 1450, 1400, 1370, 1350, 1250, 1120, 1080, 1055, 985, 970, 890, 830, 770, 760, 680, 610 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.04 (s, 18H, $NSiMe_3$), 0.08 (s, 9H, $SiMe_3$), 1.65 (s, 3H, CH_3), 3.25 (s, 2H, CH_2N), 5.50 (s, 1H, =CH) [the stereochemistry was supported by the NOE measurement as follows: irradiation of CH_3 at δ 1.65 enhanced the intensity of =CH by 43%, and irradiation of $SiMe_3$ at δ 0.08 enhanced the intensity of CH_2N by 31%); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 0.1 ($SiMe_3$), 1.8 ($NSiMe_3$), 40.5 (CH_2N), 53.3 (CH_3), 120.6, 129.0 (C=C); mass spectrum (EI) *m/z* 287 (M^+). Anal. Calcd for $C_{13}H_{33}NSi_3$: C, 54.28; H, 11.56. Found: C, 54.58; H, 11.77.

Preparation of the Sample for ^{13}C-NMR Measurement. In a 10-mL two-necked flask containing a *n*-hexane solution of *n*-butyllithium (0.15 mL, 0.15 mmol) was added hexamethyldisilazane and the mixture stirred for 1 h at room temperature. Then, the solvent was removed under reduced pressure, and to the resulting white solid was added THF (0.3 mL) and silver iodide (47 mg, 0.2 mmol). After the solution was stirred for 1 h, benzene (0.05 mL) and benzene-d_6 (0.15 mL) were added, and this was injected to the NMR tube via syringe.

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Supplementary Material Available: ^{1}H NMR spectra for compounds **3**, **5**, **6**, **10**, and **14** (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.