Reactions of Allylsilanes with Iminium Salts: Ene Reactions with Inverse Electron Demand

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The *N*,*N*-dialkylmethyleneammonium hexachloroantimonates **1**-$SbCl_6^-$ react with allyltrimethylsilane (**2a**) in dichloromethane to give the alkylideneammonium ions **3** and **3′** via ene reactions with inverse electron demand, where the allyltrimethylsilane (**2a**) behaves as enophile. Under the same conditions (2-methylallyl)trimethylsilane (**2b**) undergoes ordinary ene reactions with iminium ions, with the allylsilane **2b** acting as the ene component. The different course of the ene reactions is explained by the varied steric strain in the pericyclic transition states **14**−**18**. S_E2' products, which are the main products under more nucleophilic reaction conditions, have only been detected in trace amounts.

Introduction

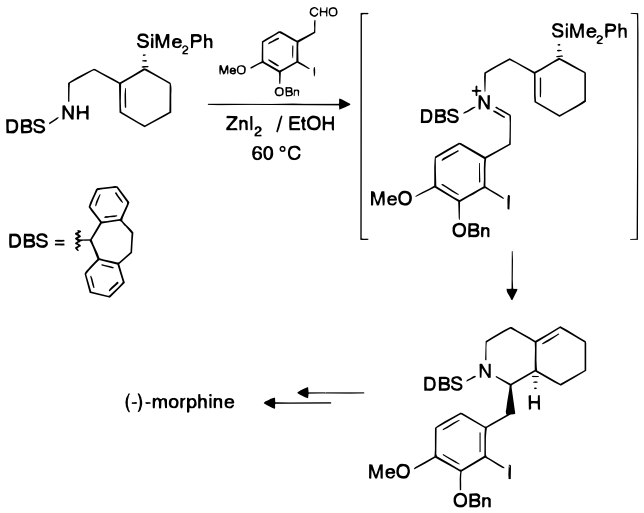
Allylsilanes have frequently been applied as nucleophilic components for the formation of carbon−carbon bonds.[1] In natural product syntheses allylsilane-terminated intramolecular reactions of *N*-acyl and *N*-tosyl iminium ions have been used for the construction of heterocycles.[2] Sometimes the less reactive *N*-alkyl iminium ions have also been employed in this way as shown by the iminium ion allylsilane cyclization in Overman's approach to (−)-morphine (Scheme 1).[3] As demonstrated by this example, the reactions of iminium ions with allylsilanes usually proceed with allyl inversion and loss of the silyl group in analogy to the reactions of allylsilanes with other electrophiles.[1,4]

Further intramolecular "aminomethano-desilylation" reactions have been described by Grieco to yield six-, seven-, and eight-membered nitrogen-containing rings.[5]

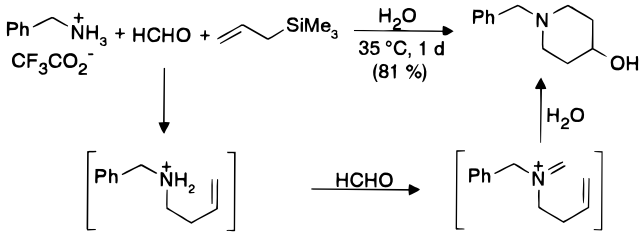
Intermolecular reactions of iminium ions with allylsilanes[6] have been observed when primary amines, formaldehyde, and allylsilanes were combined to give 4-hydroxypiperidines (Scheme 2).[6a]

Under analogous conditions tertiary homoallylamines were produced from allylsilanes and *N*-benzyl-*N*-methylmethyleneammonium ions[6a] *in situ* generated from the

Scheme 1



Scheme 2



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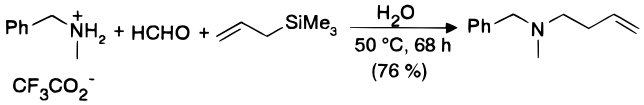

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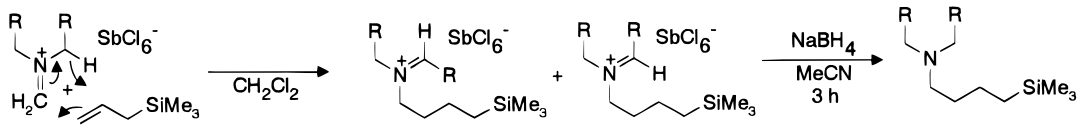
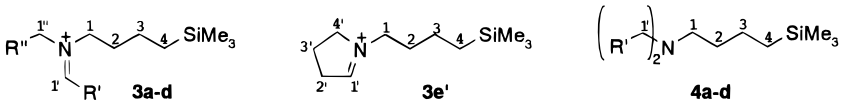
Scheme 4



R =		time / h	% yield				% yield	
Me	**1a**	3	99	**3a**	(70 : 30)	**3a'**	75	**4a**
Et	**1b**	0.75	96	**3b**	(85 : 15)	**3b'**	74	**4b**
Pr	**1c**	1	91	**3c**	(85 : 15)	**3c'**	83	**4c**
i-Pr	**1d**	3	88	**3d**	(95 : 5)	**3d'**	74	**4d**
-(CH_2)-[a]	**1e**	2	81	--	(0 : 100)	**3e'**		

[a] *N*-Methylenepyrrolidinium.

Table 1. ^{13}C Chemical Shifts of Compounds (3a−3d,3e′)-$SbCl_6^-$ (75.5 MHz, CD_3CN)[a] and 1-(Dialkylamino)-4-(trimethylsilyl)butanes 4a−d (75.5 MHz, $CDCl_3$)



	C-1′	C-1″	C-1	C-2	C-3	C-4	$SiMe_3$	R′ and R″
multiplicity	d	t	t	t	t	t	q	
3a	178.87	56.85	53.06	31.09	21.54	16.53	−1.81	18.80, 13.27 (2 q, C-2′ and C-2″)
3b	183.50	62.82	53.37	31.26	21.60	16.38	−1.83	25.84, 21.42 (2 t, C-2′ and C-2″), 10.49, 9.70 (2 q, C-3′ and C-3″)
3c	182.94	61.55	53.62	31.53	21.66	16.64	−1.78	33.91, 30.37 (2 t, C-2′ and C-2″), 19.92, 19.48 (2 t, C-3′ and C-3″), 13.91, 13.68 (2 q, C-4′ and C-4″)
3d	186.12	68.19	53.74	32.27	21.61	16.59	−1.76	31.74, 27.19 (2 d, C-2′ and C-2″), 19.24[b], 18.89[b] (2 q, C-3′ and C-3″)
3e′	181.30[c]	59.95[d]	54.65	30.82	21.27	16.39	−1.80	36.56 (t, C-2′), 20.08 (t, C-3′)
multiplicity	t		t	t	t	t	q	
4a	46.91[b]		52.74	30.82	22.10	16.72	−1.68	11.66[b] (q, C-2′)
4b	56.30[b]		53.96	30.88	21.94	16.68	−1.69	20.18[b] (t, C-2′), 11.98[b] (q, C-3′)
4c	54.03[e]		54.03[e]	31.02	21.98	16.72	−1.67	29.36[b] (t, C-2′), 20.78[b] (t, C-3′), 14.06[b] (q, C-4′)
4d	64.25[b]		55.06	31.31	21.82	16.77	−1.62	26.76[b] (d, C-2′), 20.98[f] (q, C-3′)

[a] For ^{13}C NMR data of the minor isomers **3a′**−**3d′**, see Experimental Section. [b] Doubled intensity. [c] dt, $J_{^{13}C,^{14}N} = 11.7$ Hz. [d] Resonance of C-4′. [e] Only one signal with tripled intensity was detected for C-1 and C-1′. [f] Quadrupled intensity.

corresponding secondary amine, trifluoroacetic acid, and formaldehyde in aqueous solution (Scheme 3).

Benzylideneammonium ions only react with allylsilanes upon irradiation.[7] The formation of products with allyl retention has been interpreted by electron transfer processes.

During the course of our studies on the reactivities of cationic electrophiles,[8] iminium salts with complex, nonnucleophilic counterions were required. Though methyleneammonium salts with complex counterions as ClO_4^-, $AlCl_4^-$, $SbCl_4^-$, or $SbCl_6^-$ were reported in the early 1970s,[9] they have only scarcely been used in synthesis.[9a,10] We now report that unprecedented reactions are observed when preformed Mannich salts are combined with allylsilanes under anhydrous conditions.

Results

Addition of 2 equiv of allyltrimethylsilane (**2a**) to suspensions of the iminium hexachloroantimonates (**1a**−**1e**)-$SbCl_6^-$ in dichloromethane at ambient temperature resulted in dissolution of these salts due to formation of the readily soluble alkylideneammonium hexachloroantimonates. Evaporation of the solvent and other volatile components *in vacuo* caused the precipitation of analytically pure mixtures of the (*E*,*Z*)-isomeric compounds (**3a**−**3d**)-$SbCl_6^-$ and (**3a′**−**3d′**)-$SbCl_6^-$ (Scheme 4). The *N*-methylenepyrrolidinium hexachloroantimonate (**1e**-$SbCl_6^-$) gave **3e′**-$SbCl_6^-$ as the only product. Dissolution of these salts in acetonitrile and treatment with sodium borohydride gave the 1-(dialkylamino)-4-(trimethylsilyl)butanes **4a**−**4d** in 74−83% yield.

Because the closely similar ^{1}H NMR spectra did not allow one to distinguish between **3** and **3′**, the ratios of the (*E*,*Z*)-isomeric iminium ions **3a**−**3d/3a′**−**3d′** had to be determined from the corresponding ^{13}C NMR spectra of the product mixtures (Table 1 and Experimental Section). In order to assign the configuration of the individual stereoisomers, the 70/30 mixture of (**3a/3a′**)-

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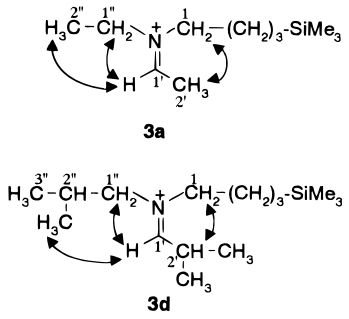
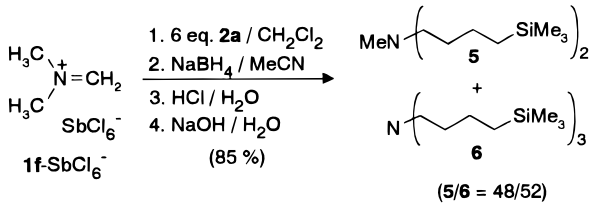


Figure 1. Structural assignment of **3a** and **3d** by nuclear Overhauser effects (indicated by arrows).

Scheme 5



$SbCl_6^-$ was recrystallized from acetonitrile to enrich the major component (**3a**/**3a′** = 90/10). One- and two-dimensional NOE experiments with this sample showed intensity enhancements between 2′-H and 1-H as well as between 1′-H and the *N*-ethyl protons (1″-H and 2″-H, Figure 1). From these results the (*Z*)-configuration of the major isomer **3a** was derived. Similarly, NOE experiments with the **3d**/**3d′** mixture indicated configuration **3d** for the major stereoisomer (Figure 1). For the iminium ions **3b**/**3b′** and **3c**/**3c′** with medium size of R, the (*Z*)-configuration of the major isomer was assumed by analogy, but could not be assigned spectroscopically.

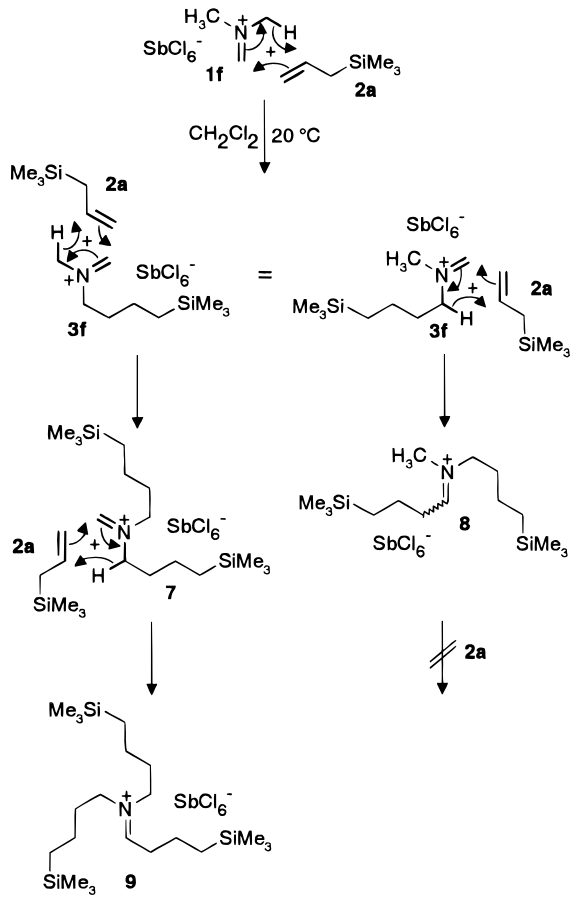
The ^1H and ^{13}C NMR spectra of the reaction product obtained from the *N*,*N*-dimethylmethyleneammonium salt **1f**-$SbCl_6^-$ and allyltrimethylsilane (**2a**) did not show the signals expected for **3f**-$SbCl_6^-$. After treatment with sodium borohydride a mixture of tertiary amines was obtained. NMR spectroscopy and GC-MS indicated the formation of approximately equimolar amounts of **5** and **6** (Scheme 5).

As shown in Scheme 6 the formation of **5** and **6** can be rationalized by the same mechanism that accounts for the generation of the products **3a**−**3d**/**3a′**−**3e′** (Scheme 4). While the reactions described in Scheme 4 yield the weakly electrophilic *alkylidene*ammonium ions **3a**−**3d**/**3a′**−**3e′**, the initial product in the reaction of **1f** with **2a** is the *methylene*ammonium ion **3f** which possesses a similar reactivity as its precursor **1f**. Because **3f**-$SbCl_6^-$ is more soluble in dichloromethane than **1f**-$SbCl_6^-$, its consecutive reaction with **2a** cannot even be prevented by using less than equimolar amounts of the allylsilane.

The reaction of **3f** with **2a** can follow two different pathways to yield either the methyleneammonium ion **7** or the alkylideneammonium ion **8**, both [2:1] products (Scheme 6). Because the reactivity of the latter is very low it does not give a [3:1] product even in the presence of a large excess of **2a**. The methyleneammonium ion **7**, on the other hand, possesses a reactive site similar to that of **1f** or **3f** and undergoes a further reaction with **2a** to give **9**. As a consequence, mixtures of **5** (from **7** and **8**) and **6** (from **9**) are obtained upon successive treatment with sodium borohydride.

The reactions of *N*-benzyl-*N*-methylmethyleneammonium hexachloroantimonate and of the corresponding

Scheme 6



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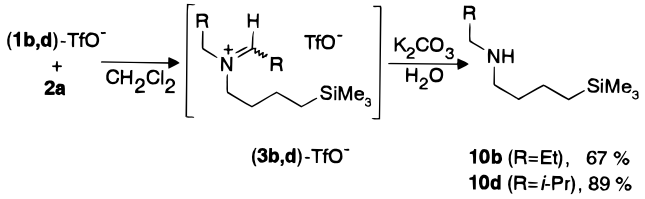


N-methylenemorpholinium salt with **2a** under analogous conditions gave complex product mixtures which have not been identified. *N*,*N*-Diisopropylmethyleneammonium hexachloroantimonate reacted very slowly with **2a**. Since only 15% conversion was observed within 3 days at 20 °C, this reaction has not been investigated further. Trimethylprenylsilane [= trimethyl(3-methyl-2-butenyl)-silane] did not react with the iminium salt **1a**-$SbCl_6^-$ within 12 days at room temperature.

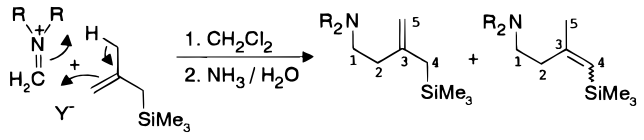
Two of the iminium ions (**1b** and **1d**) described in Scheme 4 have also been employed as triflate salts. Their reaction with allyltrimethylsilane (**2a**) and aqueous workup yielded the secondary amines **10b** and **10d** as major products. The formation of **10b** and **10d** can be explained as above by the intermediate generation of the iminium salts **3b**-TfO^- and **3d**-TfO^-, the isolation of which has not been attempted (Scheme 7).

In the NMR spectra of the compounds **10b** and **10d**, contaminations by minor components were detectable. Approximately 7% of a compound, tentatively assigned to 3-butenyldipropylamine which may be formed by S_E2' reaction of **1b** with **2a**, was accompanying compound **10b**. The secondary amine **10d** was contaminated by 13% of a side product, probably isobutyl(2-methylpropenyl)(4-

Table 2. ^{13}C NMR Chemical Shifts (75.5 MHz, $CDCl_3$) of Compounds 11 and 12

R		C-1	C-2	C-3	C-4	C-5	$SiMe_3$	R
mulitiplicity		t	t	s	t	t	q	
Me	**11f**	58.42	36.25	145.59	26.80	107.74	−1.26	45.43 (q, NCH_3)
Et	**11a**	51.78	35.33	146.18	27.19	107.55	−1.38	46.93 (t, NCH_2), 11.79 (q, CH_3)
Pr	**11b**	52.97	35.24	146.29	27.20	107.47	−1.37	56.20 (t, NCH_2), 20.28 (t, CH_2), 11.96 (q, CH_3)
i-Pr	**11g**	44.85	40.90	146.59	27.35	107.15	−1.35	48.91 (d, NCH), 20.74 (q, CH_3)
mulitplicity		t	t	s	d	q	q	
Me	**12f**	58.73	35.62	153.25	126.09	26.57	0.23	45.43 (q, NCH_3)
Et	**12a**	51.89	34.82	153.74	125.90	26.89	0.28	46.84 (t, NCH_2), 11.89 (q, CH_3)
Pr	**12b**	53.11	34.72	153.98	125.71	26.96	0.30	56.08 (t, NCH_2), 20.36 (t, CH_2), 11.96 (q, CH_3)

Scheme 8

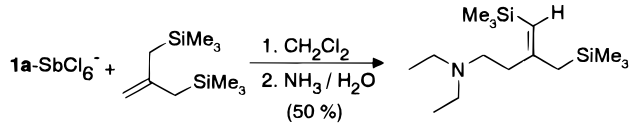


1 **2b** **11** **12**

R =		Y^-	% yield			
Me	**1f**	$AlCl_4^-$	53	**11f**	(89 : 11)	**12f**
Me	**1f**	$SbCl_6^-$	--[a]	**11f**	(92 : 8)	**12f**
Et	**1a**	TfO^-	58	**11a**	(87 : 13)	**12a**
Pr	**1b**	TfO^-	77	**11b**	(91 : 9)	**12b**
i-Pr	**1g**	TfO^-	64	**11g**	(98 : 2)	**12g**

[a] The reaction mixture was not worked up, and the ratio **11f**/**12f** was derived from the ratio of the initially produced ammonium hexachloroantimonates.

Scheme 9



2c **13**

(trimethylsilyl)butyl)amine generated during the workup by deprotonation of **3d**.

In contrast to allyltrimethylsilane (**2a**) which reacts with (**1a**−**1e**)-$SbCl_6^-$ to give the iminium ions **3a**−**3d**/**3a′**−**3e′**, the reaction of (2-methylallyl)trimethylsilane (**2b**) with **1a,b** and **1f,g** produced the unsaturated trimethylsilyl-substituted tertiary amines **11** and **12** (Scheme 8).

According to their ^{13}C NMR spectra (Table 2), only one of the two possible stereoisomers of **12** was formed. Additional resonances detected in the ^1H and ^{13}C NMR spectra of the products obtained from **2b** and **1a** or **1b** may be due to small concentrations of 4-(dialkylamino)-2-methyl-1-butene generated by S_E2' reactions.

The reaction of (2-((trimethylsilyl)methyl)allyl)trimethylsilane (**2c**) with **1a**-$SbCl_6^-$ follows the same course as the corresponding reaction of **2b**. Aqueous workup gave a mixture of **13** with some compounds containing terminal double bonds, from which **13** was isolated in 50% yield by distillation (Scheme 9). NOE experiments on **13** showed an intensity enhancement of the vinylic resonance when the CH_2 group adjacent to the trimethylsilyl group was saturated, and vice versa, in accord with the (*E*)-configuration of **13**. Because the ^{13}C NMR spectrum of the crude product showed only one set of signals, the highly stereoselective formation of the (*E*)-isomer **13** is indicated.

Discussion

Allylsilanes usually react with electrophiles to give S_E2' substitution products. This behavior has also been observed previously in intra- and intermolecular reactions of allylsilanes with iminium ions (see Introduction). However, apart from traces (see Results) such "aminomethano-desilylation" products have not been observed with the preformed methyleneammonium salts studied in this work. Ene reactions were dominating in all cases investigated.

In ordinary ene reactions the electron-rich species acts as the ene while the electron-deficient partner corresponds to the enophile.[11] This behavior seems to be realized in the reactions of the *N*,*N*-dialkylmethyleneammonium ions **1a,b** and **1f,g** with (2-methylallyl)trimethylsilane (**2b**). In a concerted, but nonsynchronous pericyclic reaction the transition state **14** can be assumed to be preferred over the transition states **15a** and **15b** (Figure 2) because only in **14** can the partial positive charge developed at C-2 of the allylsilane moiety be stabilized by Si−C hyperconjugation (β-silyl effect).[12] As a consequence the formation of **11** (from **14**) is favored over the formation of **12** (from **15a** or **15b**). Probably minimization of steric strain is responsible for the selective formation of the (*E*)-isomer **13** (from **16a**, Figure 3) rather than the (*Z*)-isomer (from **16b**, Figure 3) described in Scheme 9.

The sterically least hindered pericyclic transition state **17a** of the corresponding reaction with allyltrimethylsilane (**2a**) is depicted in Figure 4. In the transition states **17a** and **17b**, the (trimethylsilyl)methyl substituent is directed away from the iminium ion. Thus, nitrogen does not get into the proximity of an allylic hydrogen being necessary for the regular ene reaction. Instead, the transfer of hydrogen from the iminium ion to the 2-position of the allylsilane fragment with formation of the alkylideneammonium ions **3** or **3′** takes place. With increasing size of R the steric interaction between the two CH_2R groups at the nitrogen grows, and **17a** (→ **3**) becomes more and more favored over **17b** (→ **3′**) as observed in the **3**/**3′** ratios of Scheme 4. As discussed for the transition states **15a**/**15b**, the transition states **18a**/**18b** which might give rise to the regular ene reaction suffer from destabilizing steric interactions and the lack of hyperconjugative β-silyl stabilization of the partial positive charge at C-2.

In a recent review on imino ene reactions,[13] only few examples with inverse electron demand have been reported.[14,15] Though allylsilanes are well documented to

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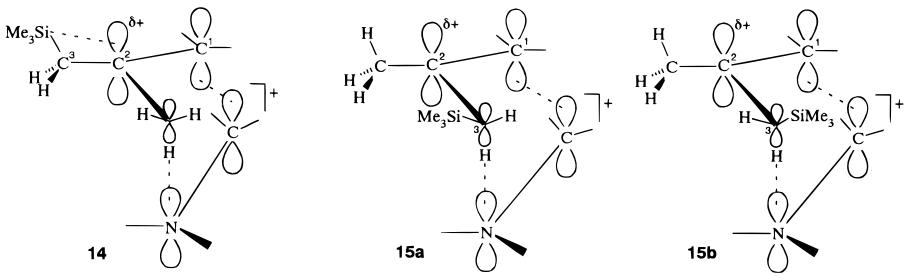

Figure 2. Transition states of the reactions of **1** with **2b**.

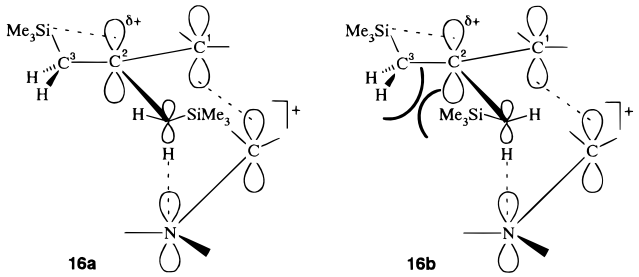

Figure 3. Transition states of the reaction of **1** with **2c**.

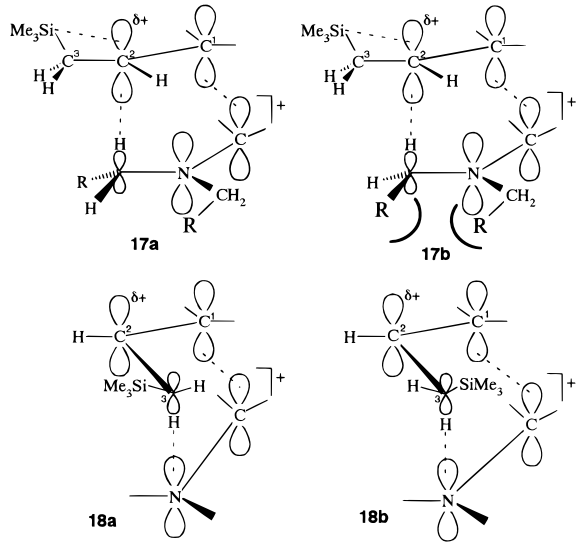

Figure 4. Transition states of the reactions of **1** with **2a**.

act as electron-rich ene components in ene reactions,[16] the role of allyltrimethylsilane (**2a**) as an enophile seems to be without precedent.

The different behavior of allylsilanes with monosubstituted (**2a**) and 1,1-disubstituted double bonds (**2b**/**2c**) is analogous to previous observations on iminium ion olefin reactions. While 1,1-dialkyl- or 1-alkyl-1-aryl-substituted ethylenes react with methyleneammonium ions under preferential formation of tertiary amines via transition states analogous to **14** (ene reaction with normal electron demand[17−20]), monosubstituted ethylenes also give ene reactions with inverse electron demand.[17] In the latter case it can be assumed that in analogy to the transition states **17a**/**17b** allylic hydrogens do not get into the proximity of nitrogen. Hence, hydrogen transfer from the iminium ion to the alkene takes place, and secondary amines are obtained after aqueous workup.

We, therefore, conclude that the factors that control the type of ene reaction of iminium ions with alkenes also influence their reactions with allylsilanes. In addition, the hyperconjugative β-silyl stabilization which is possible in the transition states **17a**/**17b**, but not in **18a**/**18b**, favors the ene reaction with inverse electron demand over the regular ene reaction.

Experimental Section

All reactions with moisture-sensitive reagents were run under an atmosphere of dry nitrogen at room temperature. ^{1}H NMR spectra (300 MHz) refer to *d*-chloroform (δ_H = 7.24 ppm) or d_3-acetonitrile (δ_H = 1.93 ppm). ^{13}C NMR spectra (75.5 MHz) were calibrated to *d*-chloroform (δ_C = 77.00 ppm) or d_3-acetonitrile (δ_C = 1.30 ppm). DEPT experiments were used to obtain information about the multiplicity of ^{13}C resonances. Dichloromethane was freshly distilled from CaH_2 prior to use. Acetonitrile was distilled from P_2O_5. Diethyl ether was dried over and distilled from sodium/benzophenone. *O*,*N*-Acetals were prepared by the method of Duboudin et al.[21] from corresponding secondary amines, paraformaldehyde, and methanol or ethanol. Salts of *N*,*N*-dimethylmethyleneammonium (**1f**-$AlCl_4^-$ and **1f**-$SbCl_6^-$) were prepared from commercially available **1f**-Cl^- (Merck-Schuchardt) by the procedure of Knoll and Krumm.[9b] Other *N*,*N*-dialkylmethyleneammonium hexachloroantimonates were obtained from the corresponding *O*,*N*-acetals, chlorotrimethylsilane, and $SbCl_5$.[22] Allyltrimethylsilane (**2a**) was purchased from Merck, Darmstadt, and trimethylsilyl triflate from Fluka, Steinheim. (2-Methylallyl)trimethylsilane (**2b**)[4m] and bissilane **2c**[23] were synthesized according to methods from the literature.

General Procedure for the Generation of 3/3′-$SbCl_6^-$ from *N*,*N*-Dialkylmethyleneammonium Hexachloroantimonates (1-$SbCl_6^-$) and Allyltrimethylsilane (2a). Two equivalents of allyltrimethylsilane (**2a**) were added by syringe to a stirred suspension of iminium salt **1**-$SbCl_6^-$ in dried dichloromethane (5 mL of CH_2Cl_2 per mmol of **1**-$SbCl_6^-$). The mixture was stirred until the dissolution of **1**-$SbCl_6^-$ was complete. After another 30 min of stirring all volatile components were evaporated in vacuo without heating. The solid residue consisted of analytically pure mixtures of isomers **3**-$SbCl_6^-$ and **3′**-$SbCl_6^-$. The **3**/**3′** ratios (±3%) were determined from characteristic resonances in the ^{13}C NMR spectra of the mixtures.

(*E*/*Z*)-*N*-Ethyl-*N*-(4-(trimethylsilyl)butyl)ethylideneammonium Hexachloroantimonate (3a/3a′-$SbCl_6^-$). Re-

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action of **1a**-$SbCl_6^-$ (2.25 g, 5.35 mmol) with **2a** (1.71 mL, 10.8 mmol) yielded a 70/30 mixture of **3a**-$SbCl_6^-$ and **3a′**-$SbCl_6^-$ (2.83 g, 99%) after 3 h. A NOESY spectrum of a sample with the enriched major isomer (**3a**/**3a′** = 90/10) was recorded for structural assignments: pale yellow powder; ^{1}H NMR (300 MHz, CD_3CN) δ 8.22 (1 H, q, J = 5.8 Hz, 1′-H), 3.89−3.79 (2 H, m, 1″-H), 3.75 (2 H, t, J = 8.0 Hz, 1-H), 2.38 (3 H, d, J = 5.8 Hz, 2′-H), 1.82−1.67 (2 H, m, 2-H), 1.43−1.28 (2 H, m, 3-H), 1.37 (3 H, t, J = 7.3 Hz, 2″-H), 0.56−0.49 (2 H, m, 4-H), −0.03 (9 H, s, $SiMe_3$); ^{13}C NMR data (75.5 MHz, CD_3CN) of **3a**-$SbCl_6^-$ are listed in Table 1, additional resonances (minor isomer **3a′**-$SbCl_6^-$) δ 179.36 (d, C-1′), 61.00, 48.74 (2 t, C-1 and C-1″), 31.75 (t, C-2), 21.10 (t, C-3), 18.69 (q, C-2′), 16.43 (t, C-4), 12.36 (q, C-2″). Anal. Calcd for $C_{11}H_{26}Cl_6NSbSi$ (534.9): C, 24.70; H, 4.90; N, 2.62. Found: C, 24.86; H, 5.00; N, 2.60.

(*E*/*Z*)-*N*-Propyl-*N*-(4-(trimethylsilyl)butyl)propylideneammonium Hexachloroantimonate (3b/3b′-$SbCl_6^-$). Reaction of **1b**-$SbCl_6^-$ (1.15 g, 2.56 mmol) with **2a** (0.820 mL, 5.17 mmol) resulted in a 85/15 mixture of **3b**-$SbCl_6^-$ and **3b′**-$SbCl_6^-$ (1.38 g, 96%) after 45 min: colorless powder; ^{1}H NMR (300 MHz, CD_3CN) δ 8.12 (1 H, t, J = 6.0 Hz, 1′-H), 3.82−3.69 (4 H, m, 1-H and 1″-H), 2.76−2.67 (2 H, m, 2′-H), 1.87−1.67 (4 H, m, 2-H and 2″-H), 1.42−1.31 (2 H, m, 3-H), 1.25 (3 H, t, J = 7.4 Hz, 3′-H), 0.93 (3 H, t, J = 7.3 Hz, 3″-H), 0.56−0.50 (2 H, m, 4-H), −0.04 (9 H, s, $SiMe_3$); ^{13}C NMR data (75.5 MHz, CD_3CN) of **3b**-$SbCl_6^-$ are listed in Table 1, additional resonances (minor isomer **3b′**-$SbCl_6^-$) δ 61.19 (t), 54.85 (t), 31.75 (t), 21.21 (t), 20.93 (t), 16.25 (t), 10.93 (q). Anal. Calcd for $C_{13}H_{30}Cl_6NSbSi$ (562.9): C, 27.74; H, 5.37; N, 2.49. Found: C, 28.04; H, 5.29; N, 2.55.

(*E*/*Z*)-*N*-Butyl-*N*-(4-(trimethylsilyl)butyl)butylideneammonium Hexachloroantimonate (3c/3c′-$SbCl_6^-$). Reaction of **1c**-$SbCl_6^-$ (1.68 g, 3.52 mmol) with **2a** (1.20 mL, 7.56 mmol) gave an 85/15 mixture of **3c**-$SbCl_6^-$ and **3c′**-$SbCl_6^-$ (1.90 g, 91%) after 1 h: colorless powder; ^{1}H NMR (300 MHz, CD_3CN) δ 8.12 (1 H, t, J = 5.9 Hz, 1′-H), 3.81−3.71 (4 H, m, 1-H and 1″-H), 2.65 (2 H, q, J = 6.9 Hz, 2′-H), 1.83−1.65 (6 H, m, 2-H, 2″-H, and 3′-H), 1.43−1.28 (4 H, m, 3-H and 3″-H), 1.01 (3 H, t, J = 7.4 Hz, 4′-H), 0.94 (3 H, t, J = 7.3 Hz, 4″-H), 0.56−0.51 (2 H, m, 4-H), −0.02 (9 H, s, $SiMe_3$); ^{13}C NMR data (75.5 MHz, CD_3CN) of **3c**-$SbCl_6^-$ are listed in Table 1, additional resonances (minor isomer **3c′**-$SbCl_6^-$) δ 32.03 (t), 29.81 (t), 21.20 (t), 20.37 (t), 16.50 (t). Anal. Calcd for $C_{15}H_{34}Cl_6NSbSi$ (591.0): C, 30.48; H, 5.80; N, 2.37. Found: C, 30.68; H, 5.89; N, 2.34.

(*E*/*Z*)-*N*-Isobutyl-*N*-(4-(trimethylsilyl)butyl)isobutylideneammonium Hexachloroantimonate (3d/3d′-$SbCl_6^-$). Reaction of **1d**-$SbCl_6^-$ (1.04 g, 2.18 mmol) with **2a** (0.700 mL, 4.41 mmol) gave a 95/5 mixture of **3d**-$SbCl_6^-$ and **3d′**-$SbCl_6^-$ (1.14 g, 88%) after 3 h. Structural assignments were based on NOESY experiments: pale yellow powder; ^{1}H NMR (300 MHz, CD_3CN) δ 7.95 (1 H, d, J = 9.9 Hz, 1′-H), 3.77−3.72 (2 H, m, 1-H), 3.61 (2 H, d, J = 7.7 Hz, 1″-H), 3.08 (1 H, d sept, J = 9.9 Hz, 6.6 Hz, 2′-H), 2.23−2.09 (1 H, m, 2″-H), 1.82−1.69 (2 H, m, 2-H), 1.46−1.33 (2 H, m, 3-H), 1.24 (6 H, d, J = 6.6 Hz, 3′-H), 0.93 (6 H, d, J = 6.7 Hz, 3″-H), 0.57−0.51 (2 H, m, 4-H), −0.02 (9 H, s, $SiMe_3$); ^{13}C NMR data (75.5 MHz, CD_3CN) of **3d**-$SbCl_6^-$ are listed in Table 1, additional resonances (minor isomer **3d′**-$SbCl_6^-$) δ 61.47 (t), 59.88 (t), 32.07 (t), 27.83 (d), 21.04 (t), 20.06 (q), 19.56 (q). Anal. Calcd for $C_{15}H_{34}Cl_6NSbSi$ (591.0): C, 30.48; H, 5.80; N, 2.37. Found: C, 30.35; H, 5.83; N, 2.44.

***N*-(4-(Trimethylsilyl)butyl)-1-pyrrolinium Hexachloroantimonate (3e′-$SbCl_6^-$).** Reaction of **1e**-$SbCl_6^-$ (1.19 g, 2.84 mmol) with **2a** (0.910 mL, 5.73 mmol) gave **3e′**-$SbCl_6^-$ (1.22 g, 81%) after 2 h: greenish needles (from acetonitrile/acetone), dec 140−141 °C; ^{1}H NMR (300 MHz, CD_3CN) δ 8.42 (1 H, br s, 1′-H), 4.12−4.06 (2 H, m, 4′-H), 3.81 (2 H, t, J = 7.5 Hz, 1-H), 3.13 (2 H, br s, 2′-H), 2.28 (2 H, quint, J = 8.0 Hz, 3′-H), 1.78 (2 H, quint, J = 7.5 Hz, 2-H), 1.40−1.29 (2 H, m, 3-H), 0.55−0.49 (2 H, m, 4-H), −0.03 (9 H, s, $SiMe_3$); ^{13}C NMR data of **3e′**-$SbCl_6^-$ are listed in Table 1, signal assignments were based on ^{1}H,^{13}C and ^{1}H,^{1}H COSY experiments. Anal. Calcd for $C_{11}H_{24}Cl_6NSbSi$ (532.9): C, 24.79; H, 4.54; N, 2.63. Found: C, 25.05; H, 4.39; N, 2.66.

General Procedure for the Reduction of the Iminium Salts 3/3′-$SbCl_6^-$ with $NaBH_4$. Under an atmosphere of dry nitrogen $NaBH_4$ was suspended in acetonitrile (10 mL). After the addition of the iminium salt **3**/**3′**-$SbCl_6^-$ the mixture was stirred for 3 h at room temperature. A black suspension was obtained. The excess of hydride was carefully hydrolyzed with 2 M HCl (15 mL). The solution was basified with concd NH_3/water (10 mL, 1/1), subsequently filtered through Celite, and extracted with dichloromethane (4 × 15 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated in vacuo. Pure tertiary amines **4** were obtained after bulb-to-bulb distillation.

Diethyl(4-(trimethylsilyl)butyl)amine (4a). Reduction of **3a**/**3a′**-$SbCl_6^-$ (2.44 g, 4.56 mmol) with $NaBH_4$ (723 mg, 19.1 mmol) yielded **4a** (689 mg, 75%): colorless liquid, bp 110 °C/0.10 mbar (lit.[24] bp 60 °C/2 Torr); IR (film) 2975, 2955, 2930, 2902, 2878, 2800, 1465, 1383, 1370, 1294, 1260, 1250, 1204, 1096, 1085, 1071, 863, 835, 756, 691 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.48 (4 H, q, J = 7.2 Hz, 1′-H), 2.40−2.34 (2 H, m, 1-H), 1.48−1.38 (2 H, m, 2-H), 1.31−1.19 (2 H, m, 3-H), 0.99 (6 H, t, J = 7.2 Hz, 2′-H), 0.51−0.44 (2 H, m, 4-H), −0.06 (9 H, s, $SiMe_3$); ^{13}C NMR data of **4a** are listed in Table 1; MS (70 eV, EI) *m*/*z* (rel intensity) 201 (M^+, 4), 186 (6), 86 (100), 73 (10), 72 (10). Anal. Calcd for $C_{11}H_{27}NSi$ (201.4): C, 65.59; H, 13.51; N, 6.95. Found: C, 65.33; H, 13.65; N, 6.60.

Dipropyl(4-(trimethylsilyl)butyl)amine (4b). Reduction of **3b**/**3b′**-$SbCl_6^-$ (1.37 g, 2.43 mmol) with $NaBH_4$ (320 mg, 8.46 mmol) yielded **4b** (412 mg, 74%): colorless liquid, bp 130 °C/0.07 mbar; IR (film) 2968, 2941, 2881, 2805, 1468, 1460, 1388, 1380, 1263, 1250, 1196, 1082, 866, 838, 692 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.38−2.29 (6 H, m, 1-H and 1′-H), 1.47−1.34 (6 H, m, 2-H and 2′-H), 1.30−1.18 (2 H, m, 3-H), 0.83 (6 H, t, J = 7.4 Hz, 3′-H), 0.49−0.41 (2 H, m, 4-H), −0.07 (9 H, s, $SiMe_3$); ^{13}C NMR data of **4b** are listed in Table 1; MS (70 eV, EI) *m*/*z* (rel intensity) 229 (M^+, 5), 214 (8), 200 (24), 114 (100), 86 (95), 73 (25). Anal. Calcd for $C_{13}H_{31}NSi$ (229.5): C, 68.04; H, 13.62; N, 6.10. Found: C, 67.82; H, 13.62; N, 6.07.

Dibutyl(4-(trimethylsilyl)butyl)amine (4c). Reduction of **3c**/**3c′**-$SbCl_6^-$ (1.73 g, 2.93 mmol) with $NaBH_4$ (774 mg, 20.5 mmol) yielded **4c** (626 mg, 83%): colorless liquid, bp 165 °C/0.15 mbar; IR (film) 2955, 2935, 2875, 2862, 2799, 2770, 2738, 1467, 1458, 1377, 1259, 1249, 1085, 863, 834, 690 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.37−2.32 (6 H, m, 1-H and 1′-H), 1.46−1.20 (12 H, m, 2-H, 2′-H, 3-H, and 3′-H), 0.87 (6 H, t, J = 7.2 Hz, 4′-H), 0.49−0.44 (2 H, m, 4-H), −0.06 (9 H, s, $SiMe_3$); ^{13}C NMR data of **4c** are listed in Table 1; MS (70 eV, EI) *m*/*z* (rel intensity) 257 (M^+, 7), 242 (11), 214 (52), 143 (10), 142 (100), 100 (71), 98 (12), 73 (33). Anal. Calcd for $C_{15}H_{35}NSi$ (257.5): C, 69.96; H, 13.70; N, 5.44. Found: C, 69.70; H, 13.90; N, 5.37.

Diisobutyl(4-(trimethylsilyl)butyl)amine (4d). Reduction of **3d**/**3d′**-$SbCl_6^-$ (1.43 g, 2.42 mmol) with $NaBH_4$ (390 mg, 10.3 mmol) yielded **4d** (463 mg, 74%): colorless liquid, bp 150 °C/0.15 mbar; IR (film) 2961, 2935, 2910, 2878, 2801, 1471, 1461, 1386, 1365, 1262, 1251, 1085, 865, 837, 692 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.28 (2 H, br t, J = 6.9 Hz, 1-H), 2.03 (4 H, d, J = 7.2 Hz, 1′-H), 1.66 (2 H, nonet, J = 6.7 Hz, 2′-H), 1.43−1.26 (4 H, m, 2-H and 3-H), 0.86 (12 H, d, J = 6.5 Hz, 3′-H), 0.50−0.45 (2 H, m, 4-H), −0.04 (9 H, s, $SiMe_3$); ^{13}C NMR data of **4d** are listed in Table 1; MS (70 eV, EI) *m*/*z* 257 (M^+, 4), 242 (11), 215 (15), 214 (84), 142 (22), 100 (100), 98 (11), 73 (33). Anal. Calcd for $C_{15}H_{35}NSi$ (257.5): C, 69.96; H, 13.70; N, 5.44. Found: C, 69.72; H, 14.06; N, 5.42.

Generation of the Tertiary Amines 5 and 6 from *N*,*N*-Dimethylmethyleneammonium Hexachloroantimonate (1f-$SbCl_6^-$) and Allyltrimethylsilane (2a). Six equivalents of **2a** (4.80 mL, 30.2 mmol) were added to a stirred suspension of **1f**-$SbCl_6^-$ (1.94 g, 4.94 mmol) in dry dichloromethane (14 mL). The salt **1f**-$SbCl_6^-$ dissolved completely after stirring for 45 min at room temperature. After another 3 h of stirring all volatile components were evaporated in vacuo without heating to yield 3.20 g of a colorless, solid residue. Reduction of this

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residue with $NaBH_4$ (612 mg, 16.2 mmol) in acetonitrile (20 mL) and workup as described above yielded a 48/52 mixture of methylbis(4-(trimethylsilyl)butyl)amine (**5**) and tris(4-(trimethylsilyl)butyl)amine (**6**) as a colorless liquid (1.45 g, 85%, product ratio determined by ^{1}H NMR): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.44−2.39 (6 H, m, 1-H of **6**), 2.30−2.25 (4 H, m, 1-H of **5**), 2.16 (3 H, s, NCH_3 of **5**), 1.49−1.32 (4 H, m, 2-H of **5**; 6 H, m, 2-H of **6**), 1.26−1.15 (4 H, m, 3-H of **5**; 6 H, m, 3-H of **6**), 0.44−0.38 (4 H, m, 4-H of **5**; 6 H, m, 4-H of **6**), −0.12 (18 H, s, $SiMe_3$ of **5**; 27 H, s, $SiMe_3$ of **6**); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 57.35 (t, C-1 of **5**), 53.47 (t, C-1 of **6**), 42.07 (q, NCH_3 of **5**), 30.66 (t, C-2 of **6**), 29.87 (t, C-2 of **5**), 21.82 (t, C-3 of **5**), 21.75 (t, C-3 of **6**), 16.57 (t, C-4 of **5**), 16.49 (t, C-4 of **6**), −1.80 (q, $SiMe_3$ of **5** and **6**); GC-MS (column, DB 5 30 m, helium; temperature range, 40−300 °C) MS **5** (t_R = 6.90 min, EI) *m/z* (rel intensity) 288 (3), 287 (M^+, 13), 273 (11), 272 ($M^+ - CH_3$, 42), 173 (33), 172 (100), 98 (11), 73 (89), 58 (100); **6** (t_R = 8.83 min, EI) *m/z* (rel intensity) 401 (M^+, 4), 387 (9), 386 (25), 288 (10), 287 (28), 286 (100), 172 (40), 98 (6), 73 (27), 58 (51).

Propyl(4-(trimethylsilyl)butyl)amine (10b). The iminium salt **1b**-TfO^- was generated by addition of trimethylsilyl triflate (0.500 mL, 2.77 mmol) to a solution of (dipropylamino)-methoxymethane (356 mg, 2.45 mmol) in dichloromethane (10 mL). After 30 min of stirring, **2a** (0.480 mL, 3.02 mmol) was added with a syringe. The reaction mixture was stirred for 14 h at room temperature, before a saturated, aqueous solution of K_2CO_3 (15 mL) was added. The mixture was transferred to a separatory funnel and shaked vigorously. After separation of the organic layer and extraction of the aqueous phase with dichloromethane (4 × 20 mL), the combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. Bulb-to-bulb distillation yielded **10b** (306 mg, 67%, purity 93%): colorless liquid, bp 90 °C/0.10 mbar; IR (film) 3270 (br, N−H), 2945, 2918, 2863, 2795, 1452, 1405, 1372, 1255, 1243, 1123, 851, 828, 740, 686 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.57−2.50 (4 H, m, 1-H and 1′-H), 1.53−1.35 (4 H, m, 2-H and 2′-H), 1.33−1.23 (3 H, m, 3-H and NH), 0.87 (3 H, t, J = 7.4 Hz, 3′-H), 0.50−0.42 (2 H, m, 4-H), −0.07 (9 H, s, $SiMe_3$); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 51.99, 49.77 (2t, C-1 and C-1′), 34.05 (t, C-2), 23.18 (t, C-2′), 21.76 (t, C-3), 16.64 (t, C-4), 11.77 (q, C-3′), −1.72 (q, $SiMe_3$); MS (70 eV, EI) *m/z* (rel intensity) 187 (M^+, 4) 172 (6), 158 (6), 114 (7), 73 (27), 72 (100), 59 (11), 44 (89). Anal. Calcd for $C_{10}H_{25}NSi$ (187.4): C, 64.09; H, 13.45; N, 7.47. Found: C, 63.91; H, 13.33; N, 7.08.

Contamination by 7% of 3-butenyldipropylamine was indicated by the following NMR signals: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.80−5.71 (1 H, m, 3-H), 5.03−4.91 (2 H, m, 4-H), 2.37−2.30 (4 H, m, 1′-H), 2.19−2.11 (2 H, m, 1-H), 0.83 (6 H, t, J = 7.3 Hz, 3′-H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 137.15 (d, C-3), 115.17 (t, C-4), 56.29 (t, C-1), 56.09 (2 C, t, C-1′), 31.44 (t, C-2), 20.21 (2 C, t, C-2′), 11.93 (2 C, q, C-3′).

Isobutyl(4-(trimethylsilyl)butyl)amine (10d). As described above for **10b**, diisobutylmethoxymethane (384 mg, 2.22 mmol), trimethylsilyl triflate (0.460 mL, 2.55 mmol), and **2a** (0.450 mL, 2.84 mmol) reacted in dichloromethane (14 mL) to give **10d** (411 mg, 89%): colorless liquid, bp 160 °C/21 mbar; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.55 (2 H, t, J = 7.2 Hz, 1-H), 2.36 (2 H, d, J = 6.8 Hz, 1′-H), 1.71 (1 H, nonet, J = 6.7 Hz, 2′-H), 1.52−1.42 (2 H, m, 2-H), 1.41−1.20 (2 H, m, 3-H), 1.06 (1 H, br s, NH), 0.87 (6 H, d, J = 6.6 Hz, 3′-H), 0.51−0.41 (2 H, m, 4-H), −0.06 (9 H, s, $SiMe_3$); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 58.22 (t, C-1′), 49.90 (t, C-1), 34.05 (t, C-2), 28.27 (d, C-2′), 21.73 (t, C-3), 20.66 (2 C, q, C-3′), 16.65 (t, C-4), −1.71 (q, $SiMe_3$).

The NMR spectra show a contamination (of about 13%) probably by isobutyl(2′-methylpropenyl)(4-(trimethylsilyl)-butyl)amine: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.07 (1 H, sept, J = 1 Hz, 1′-H), 2.45−2.40 (2 H, m, 1-H), 2.19 (2 H, d, J = 7.2 Hz, 1″-H), 1.63, 1.57 (each 3 H, 2d, J = 1 Hz, 2′-$(CH_3)_2$), 0.83 (6 H, d, J = 6.6 Hz, 3″-H), −0.07 (9 H, s, $SiMe_3$); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 136.06 (d, C-1′), 123.42 (s, C-2′), 64.55, 56.34 (2 t, C-1 and C-1″), 31.95 (t, C-2), 27.41 (d, C-2″), 22.16 (q, 2′-CH_3), 21.60 (t, C-3), 20.72 (2 C, q, C-3″), 17.61 (q, 2′-CH_3), resonances of C-4 and $SiMe_3$ seem to be identical with those of **10d**.

Reaction of *N,N*-Dimethylmethyleneammonium Tetrachloroaluminate (1f-$AlCl_4^-$) with (2-Methylallyl)trimethylsilane (2b). The silane **2b** (0.557 mL, 3.20 mmol) was injected at ambient temperature into a suspension of iminium salt **1f**-$AlCl_4^-$ (762 mg, 3.36 mmol) in dichloromethane (23 mL). After 21 h of stirring, the reaction was quenched by addition of a mixture of concd NH_3/water (15 mL, 1/1). The resulting heterogeneous mixture was stirred vigorously and filtered by suction through Celite. The filtrate was extracted with dichloromethane (3 × 20 mL), and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. Bulb-to-bulb distillation gave a 89/11 mixture of isomeric compounds **11f** and **12f** (313 mg, 53%, product ratio determined by ^{1}H NMR): colorless liquid, bp 70 °C/0.10 mbar. All analytical data were obtained from the mixture of isomers. **11f**/**12f**: IR (film) 3075, 2955, 2860, 2815, 2765, 1633, 1461, 1260, 1250, 1160, 1042, 853, 694 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) **11f** δ 4.55−4.53 (1 H, m, 5-H), 4.49 (1 H, br s, 5-H), 2.35−2.30 (2 H, m, 1-H), 2.17 (6 H, s, NMe_2), 2.09−2.04 (2 H, m, 2-H), 1.48 (2 H, d, J = 0.8 Hz, 4-H), −0.04 (9 H, s, $SiMe_3$); **12f** δ 5.20 (1 H, q, J = 1.3 Hz, 4-H), 2.29−2.24 (4 H, m, covered in part by signals of **11f**, 1-H and 2-H), 2.19 (6 H, s, NMe_2), 1.78 (3 H, d, J = 1.3 Hz, 5-H), 0.04 (9 H, s, $SiMe_3$); ^{13}C NMR data of **11f** and **12f** are listed in Table 2; MS (70 eV, EI) *m/z* (rel intensity) 185 (M^+, <1), 73 (9), 58 (100). Anal. Calcd for $C_{10}H_{23}NSi$ (185.4): C, 64.79; H, 12.51; N, 7.56. Found: C, 64.48; H, 12.48; N, 7.57.

Reaction of *N,N*-Diethylmethyleneammonium Triflate (1a-TfO^-) with (2-Methylallyl)trimethylsilane (2b). Following the procedure described for the formation of **10b** (see above), (diethylamino)methoxymethane (204 mg, 1.74 mmol), trimethylsilyl triflate (0.317 mL, 1.75 mmol), and **2b** (293 mg, 2.28 mmol) were combined in dichloromethane (7 mL) for 15 h. Bulb-to-bulb distillation of the crude product (80 °C/0.02 mbar) gave a 78/12/10 mixture (207 mg, 58%, product ratio determined by ^{1}H NMR) of three components, **11a**, **12a**, and probably 4-(diethylamino)-2-methyl-1-butene. Further distillations yielded a fraction of a mixture containing only **11a** and **12a** (86/14): colorless liquid, bp 70 °C/0.05 mbar. All analytical data were obtained from the mixture of isomers. **11a**/**12a**: ^{1}H NMR (300 MHz, $CDCl_3$) **11a** δ 4.58−4.56, (1 H, m, 5-H), 4.51 (1 H, s, 5-H), 2.58−2.46 (6 H, m, 1-H and 1′-H), 2.11−2.06 (2 H, m, 2-H), 1.52 (2 H, d, J = 0.9 Hz, 4-H), 1.01 (6 H, t, J = 7.2 Hz, 2′-H), 0.00 (9 H, s, $SiMe_3$); **12a** δ 5.23 (1 H, q, J = 1.3 Hz, 4-H), 2.58−2.46 (6 H, covered by signals of **11a**, 1-H and 1′-H), 2.28−2.22 (2 H, m, 2-H), 1.82 (3 H, d, J = 1.3 Hz, 5-H), 1.02 (6 H, t, J = 7.2 Hz, 2′-H), 0.07 (9 H, s, $SiMe_3$); ^{13}C NMR data of **11a** and **12a** are listed in Table 2; MS (70 eV, EI) *m/z* (rel intensity) 213 (M^+, <1), 87 (42), 86 (100), 73 (25), 58 (32). Anal. Calcd for $C_{12}H_{27}NSi$ (213.4): C, 67.53; H, 12.75; N, 6.56. Found: C, 67.51; H, 12.80; N, 6.57.

The assignment of 4-(diethylamino)-2-methyl-1-butene as one of the components in the mixture after the first distillation was based on the following ^{1}H and ^{13}C resonances: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.67, 4.64 (each 1 H, 2 br s, 1-H), 2.13−2.06 (2 H, m, covered in part by 2-H of **11a**, 3-H), 1.69 (3 H, s, 2-CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 144.46 (s, C-2), 110.53 (t, C-1), 51.36 (t, C-4), 35.02 (t, C-3), 22.60 (q, 2-CH_3), resonances of C-1′ and C-2′ seem to be identical with either **11a** or **12a**.

Reaction of *N,N*-Dipropylmethyleneammonium Triflate (1b-TfO^-) with (2-methylallyl)trimethylsilane (2b). As described for the formation of **10b** (see above), (dipropylamino)methoxymethane (410 mg, 2.82 mmol), trimethylsilyl triflate (0.544 mL, 3.01 mmol), and **2b** (403 mg, 3.14 mmol) reacted in dichloromethane (20 mL) for 19 h. Bulb-to-bulb distillation of the crude product (110 °C/0.04 mbar) gave a 77/8/15 mixture (502 mg, 77%, product ratio determined by ^{1}H NMR) of three components, **11b**, **12b**, and probably 4-(dipropylamino)-2-methyl-1-butene. Further distillations yielded a fraction of a mixture containing only **11b** and **12b** (90/10): colorless liquid, bp 100 °C/0.04 mbar. All analytical data were obtained from the mixture of isomers. **11b**/**12b**: IR (film)

3075, 2960, 2875, 2800, 1633, 1462, 1380, 1249, 1192, 1165, 1075, 850, 692 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) **11b** δ 4.56−4.55 (1 H, m, 5-H), 4.50 (1 H, br s, 5-H), 2.57−2.52 (2 H, m, 1-H), 2.39−2.34 (4 H, m, 1′-H), 2.10−2.04 (2 H, m, 2-H), 1.51 (2 H, d, J = 0.6 Hz, 4-H), 1.50−1.37 (4 H, m, 2′-H), 0.85 (6 H, t, J = 7.3 Hz, 3′-H), 0.00 (9 H, s, $SiMe_3$); **12b** δ 5.21 (1 H, q, J = 1.3 Hz, 4-H), 2.27−2.21 (2 H, m, 2-H), 1.81 (3 H, d, J = 1.3 Hz, 5-H), 0.07 (9 H, s, $SiMe_3$), all other signals are covered by **11b**; ^{13}C NMR data of **11b** and **12b** are listed in Table 2; MS (70 eV, EI) *m/z* (rel intensity) 241 (M^+, <1), 115 (10), 114 (100), 86 (10), 73 (18), 72 (12); MS (FI) *m/z* (rel intensity) 243 (7), 242 (27), 241 (M^+, 100). Anal. Calcd for $C_{14}H_{31}NSi$ (241.5): C, 69.63; H, 12.94; N, 5.80. Found: C, 69.60; H, 12.98; N, 5.77.

The assignment of 4-(dipropylamino)-2-methyl-1-butene as one of the components in the mixture after the first distillation was based on the following ^1H and ^{13}C resonances: ^1H NMR (300 MHz, $CDCl_3$) δ 4.67, 4.63 (each 1 H, 2 br s, 1-H), 2.14−2.05 (2 H, m, covered in part by 2-H of **11b**, 3-H), 1.69 (3 H, s, 2-CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 144.55 (s, C-2), 110.45 (t, C-1), 56.09 (t, C-1′), 52.60 (t, C-4), 34.95 (t, C-3), 22.69 (q, 2-CH_3), resonances of C-2′ and C-3′ seem to be identical with either **11b** or **12b**.

Reaction of *N,N*-Diisopropylmethyleneammonium Triflate (1g-TfO^-) with (2-Methylallyl)trimethylsilane (2b). Following the procedure described for the formation of **10b** (see above), (diisopropylamino)ethoxymethane (260 mg, 1.63 mmol), trimethylsilyl triflate (0.300 mL, 1.66 mmol), and **2b** (269 mg, 2.10 mmol) were combined in dichloromethane (5 mL) for 15 h to give **11g** (251 mg, 64%): colorless liquid, bp 120 °C/0.03 mbar; IR (film) 3065, 2950, 2860, 2800, 1628, 1460, 1379, 1357, 1244, 1200, 1158, 1104, 1040, 843, 689 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.56−4.55 (1 H, m, 5-H), 4.49 (1 H, br s, 5-H), 2.99 (2 H, sept, J = 6.6 Hz, 1′-H), 2.52−2.47 (2 H, m, 1-H), 2.07−2.01 (2 H, m, 2-H), 1.51 (2 H, s, 4-H), 0.99 (12 H, d, J = 6.6 Hz, 2′-H), 0.00 (9 H, s, $SiMe_3$); ^{13}C NMR data of **11g** are listed in Table 2; MS (70 eV, EI) *m/z* (rel intensity) 241 (M^+, <1), 115 (61), 114 (100), 73 (30), 72 (77). Anal. Calcd for $C_{14}H_{31}NSi$ (241.5): C, 69.63; H, 12.94; N, 5.80. Found: C, 69.78; H, 13.10; N, 5.90.

(*E*)-4-(Diethylamino)-1-(trimethylsilyl)-2-((trimethylsilyl)methyl)-1-butene (13). (2-((Trimethylsilyl)methyl)allyl)trimethylsilane (**2c**) (1.89 g, 9.43 mmol) was injected at ambient temperature into a suspension of iminium salt **1a**-$SbCl_6^-$ (2.05 g, 4.87 mmol) in dichloromethane (18 mL). After 30 min of stirring, all volatile components were evaporated in vacuo without heating. The viscous residue was hydrolyzed by addition of a mixture of concd NH_3/water (15 mL, 1/1). The resulting heterogeneous mixture was stirred vigorously and filtered by suction through Celite. The filtrate was extracted with dichloromethane (2 × 20 mL), and the combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. After bulb-to-bulb distillation (125 °C/0.08 mbar) of the residue, 1.09 g of a mixture of at least three components was obtained. Further bulb-to-bulb distillations yielded a fraction of pure (*E*)-4-(diethylamino)-1-(trimethylsilyl)-2-((trimethylsilyl)methyl)-1-butene (**13**, 700 mg, 50%): colorless liquid, bp 110 °C/0.08 mbar; IR (film) 2958, 2936, 2899, 2875, 2800, 1600, 1455, 1383, 1370, 1258, 1247, 1200, 1171, 1145, 1065, 845, 689 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.98 (1 H, s, 1-H), 2.57−2.50 (2 H, m, 4-H), 2.53 (4 H, q, J = 7.2 Hz, 1′-H), 2.22−2.16 (2 H, m, 3-H), 1.63 (2 H, d, J = 0.5 Hz, 2-CH_2), 1.04 (6 H, t, J = 7.1 Hz, 2′-H), 0.08 (9 H, s, 1-$SiMe_3$), 0.00 (9 H, s, 2-$CH_2Si(CH_3)_3$), structural assignments were based on NOE experiments; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 155.76 (s, C-2), 122.43 (d, C-1), 52.45 (t, C-4), 46.83 (2 C, t, C-1′), 35.17 (t, C-3), 31.03 (t, 2-CH_2), 11.90 (2 C, q, C-2′), 0.54 (q, 1-$SiMe_3$), −1.35 (q, 2-$CH_2Si(CH_3)_3$); MS (70 eV, EI) *m/z* (rel intensity) 285 (M^+, <1), 270 (2), 86 (100), 73 (15). Anal. Calcd for $C_{15}H_{35}NSi_2$ (285.6): C, 63.08; H, 12.35; N, 4.90. Found: C, 62.97; H, 12.61; N, 4.67.

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