Formation of Vinylsilanes and Allylsilanes in Thermal Elimination Reactions of Esters of β-Hydroxyalkyltrimethylsilanes

Francis A. Carey* and J. Richard Toler

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901

Received November 21, 1975

Thermolysis of esters of β-hydroxyalkyltrimethylsilanes $R_1R_2C(OH)CH_2SiMe_3$ was investigated as a route to the synthetically useful vinylsilanes $R_1R_2C{=}CHSiMe_3$. A survey of product composition vs. leaving group for esters of 2-trimethylsilylmethyl-2-adamantanol (**1a**) revealed exclusive alkene formation with a good leaving group and exclusive vinylsilane formation with a poor leaving group. Methanesulfonate ester **1f** decomposed under the conditions of its formation to give a 91% yield of methyleneadamantane (**2**). Thermolysis of 2-trimethylsilylmethyl-2-adamantyl *N*-phenylcarbamate (**1b**) at 160 °C produced 2-(trimethylsilylmethylene)adamantane (**3**) in 94% yield. Mixtures of **2** and **3** were obtained with other leaving groups. The vinylsilane 1-trimethylsilyl-3,3-dimethyl-1-butene (**9**) was obtained in 72% yield on thermolysis of 1-trimethylsilyl-3,3-dimethyl-2-butyl *N*-phenylthiocarbamate (**4c**). Mixtures of vinylsilanes and allylsilanes were obtained from esters which could eliminate in two directions. Thermolysis of 1-trimethylsilylmethyl-1-cyclohexyl *N*-phenylcarbamate (**5b**) or *S*-methyl xanthate (**5d**) gave the allylic silane 1-(trimethylsilylmethyl)cyclohexene (**12**) as the major product. Thermolysis of 1-trimethylsilyl-3-phenyl-2-propyl *N*-phenylthiocarbamate (**6c**) at 125 °C produced *trans*-1-trimethylsilyl-3-phenyl-1-propene (**13**) and *trans*-1-phenyl-3-trimethylsilyl-1-propene (**14**) in comparable amounts. Mixtures of the vinylsilane **15** and the allylsilane **16** were produced when 1-trimethysilyl-2-octanol (**7a**) was subjected to the Chugaev elimination sequence. *trans*-β-Styryltrimethylsilane was obtained in 43% yield on thermolysis of 1-phenyl-2-trimethylsilylethyl *N*-phenylcarbamate (**8b**), along with the product of ion-pair return, *N*-(1-phenyl-2-trimethylsilylethyl)aniline (**18**, 33%). The results are discussed in terms of ion-pair intermediates. Stabilization of the developing carbonium ion by carbon–silicon hyperconjugation requires the trimethylsilyl substituent to be anti to the leaving group. Retention of trimethylsilyl in the product is believed to occur because deprotonation of the carbonium ion by the anion of the leaving group is faster than rotation around the C(α)–C(β) bond with poorer (more basic) leaving groups. The ease of decomposition as a function of substrate structure (tertiary > secondary) and formation of ion-pair return products from **8b** and **8c** are consistent with this interpretation.

The readily available β-hydroxyalkyltrimethylsilanes, formed by addition of trimethylsilylmethylmagnesium chloride to aldehydes and ketones,[1] would appear to be useful substrates for the synthesis of vinylsilanes if methods could be developed to control the mode of their decomposition. Elimination reactions of β-functional organosilanes usually proceed with cleavage of the silicon–carbon bond to afford alkenes.[2] The few cases where vinylsilanes are produced are either heterogeneous reactions or are limited in terms of general applicability.[3]

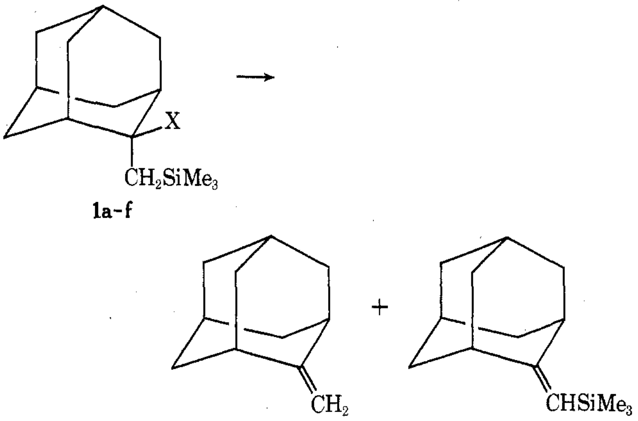
Considerable recent interest has been shown in reactions of vinylsilanes directed toward synthetic applications. Potential utility in the synthesis of alkenes,[4] aldehydes,[5] ketones,[6] vinyl halides,[7] and in the annelation of ketones[8] has been demonstrated. Most of these efforts, as well as many mechanistic studies,[9] have focused on lightly substituted vinylsilanes.

The work reported here describes a study of the thermal decomposition of various esters of some β-hydroxyalkyltrimethylsilanes, performed with a view toward determining the factors which influence the relative proportions of vinylsilane and alkene formed. It was also hoped that such a study would provide a basis for developing a general method for converting β-hydroxyalkyltrimethylsilanes to vinylsilanes.[10]

Results

The β-hydroxyalkylsilanes utilized in this study were all prepared by addition of trimethylsilylmethylmagnesium chloride to the appropriate aldehyde or ketone and are listed in Table I.

The system chosen for most detailed study was 2-trimethylsilylmethyl-2-adamantanol (**1a**). Elimination reactions in this system can lead only to methyleneadamantane (**2**) and 2-(trimethylsilylmethylene)adamantane (**3**), thereby simplifying analysis of the product mixtures and interpretation of the results.



1a–f

2

3

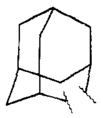
1a, X = OH
b, X = OC(O)NHPh
c, X = OC(S)NHPh
d, X = OC(S)SCH$_3$
e, X = OSO$_2$NHCO$_2$CH$_3$
f, X = OSO$_2$CH$_3$

The elimination reactions of the esters **1b–f** derived from **1a** were strikingly dependent on the nature of the leaving group.

Treatment of the anion of **1a** (generated with *n*-butyllithium) with methanesulfonyl chloride afforded directly on workup a 91% yield of methyleneadamantane (**2**) as the exclusive product.

Conversion of **1a** to its crystalline *N*-phenylcarbamate **1b** was effected by treatment of its alkoxide ion with phenyl isocyanate. Pyrolysis of the *N*-phenylcarbamate at 160 °C and distillation of the resulting liquid, followed by dilute acid extraction of aniline from the distillate, gave a 94% yield of the pure vinylsilane **3**. The vinylsilane was characterized by its NMR, ir, and mass spectra and elemental analysis (see Experimental Section for details).

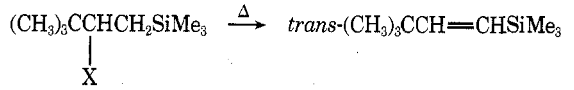
Table I. β-Hydroxyalkyltrimethylsilanes Obtained by Addition of Trimethylsilylmethylmagnesium Chloride to Aldehydes and Ketones

Carbonyl compd	β-Hydroxyalkyl-trimethylsilane, $R_1R_2C(OH)CH_2SiMe_3$	Purified yield, %
2-Adamantanone	1a, $R_1 + R_2 =$ 	89
Pivaldehyde	4a, $R_1 = (CH_3)_3C$; $R_2 = H$	73
Cyclohexanone	5a, $R_1 + R_2 = -(CH_2)_5-$	86
Phenylacetaldehyde	6a, $R_1 = PhCH_2$; $R_2 = H$	35
1-Heptanal	7a, $R_1 = CH_3(CH_2)_5$; $R_2 = H$	84
Benzaldehyde	8a, $R_1 = Ph$; $R_2 = H$	83

Other thermal elimination sequences, Chugaev (xanthate ester),[11] Burgess (N-carbomethoxysulfamate ester),[12] and N-phenylthiocarbamate ester pyrolysis, were also examined and gave results intermediate between the two extremes with mixtures of **2** and **3** being produced. These results are summarized in Table II. Except in the case of the N-phenylcarbamate ester, the esters derived from **1a** could not be isolated but underwent decomposition to **2** and **3** under the conditions of their formation. The ratio **2**:**3** appears to parallel leaving group abilities, with greater proportions of the vinylsilane **3** being produced as the leaving group becomes poorer.

Encouraged by the efficient synthesis of **3** from **1b**, the thermolyses of esters of other β-hydroxyalkyltrimethylsilanes (**4a–8a**) were investigated. With the relationship between vinylsilane and alkene formation established by the study of esters of **1a**, extending the investigation to other systems was done with the objective of broadening the scope of vinylsilane synthesis. The reaction conditions used were those judged to have the best chance of success and no attempt was made to isolate the alkenes formed in competition with the vinylsilanes. Indeed, most of the alkenes are sufficiently volatile to present problems in isolation under the reaction and workup conditions employed.

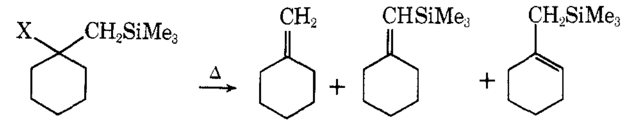
The N-phenylcarbamate (**4b**) of 1-trimethylsilyl-3,3-dimethyl-2-butanol was more stable to thermolysis than **1b** and significant quantities of diphenylurea were produced along with a 28% yield of *trans*-1-trimethylsilyl-3,3-dimethyl-1-butene (**9**) after 30 h at 200 °C. Thermolysis of the more labile N-phenylthiocarbamate **4c** proved more satisfactory. The crystalline N-phenylthiocarbamate was sufficiently stable to be isolated, but underwent smooth decomposition at 140 °C to give the vinylsilane **9** in 72% yield. None of the cis vinylsilane could be detected by NMR analysis.



$$(CH_3)_3C\underset{\displaystyle X}{\underset{|}{C}}HCH_2SiMe_3 \xrightarrow{\Delta} trans\text{-}(CH_3)_3CCH{=}CHSiMe_3$$

4a, X = OH — **9**
b, X = OC(O)NHPh — 28%
c, X = OC(S)NHPh — 72%

The reactions of the corresponding esters of 1-trimethylsilylmethyl-1-cyclohexanol (**5a**) are more complicated in that an allylic silane (1-trimethylsilylmethylcyclohexene, **12**) can be formed as well as the vinylsilane (1-trimethylsilylmethylenecyclohexane, **11**) and the alkene (methylenecyclohexane, **10**).



5a, X = OH — **10** — **11** — **12**
b, X = CO(O)NHPh — 12% — 81%
d, X = OC(S)SCH$_3$ — 8% — 55%
e, X = OSO$_2$NHCO$_2$CH$_3$ — 48%

Table II. Product Composition from Elimination Reactions of 2-Trimethylsilylmethyl-2-adamantyl Esters

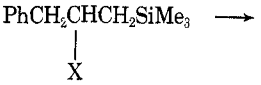
Compd	X	Conditions	Yield of product, %[a] 2	3
1b	OC(O)NHPh	No solvent, 160 °C		94
1c	OC(S)NHPh	THF, 25 °C		73[b]
1d	OC(S)SCH$_3$	THF, 25 °C		44
			(28)[c]	(70)[c]
1e	OSO$_2$NHCO$_2$CH$_3$	Toluene, 110 °C	(51)[c]	(39)[c]
1f	OSO$_2$CH$_3$	THF, 25 °C	91	

[a] Isolated yields of purified product. [b] Determined by GLC to contain 3% of **2**. [c] Analytical yield determined by GLC vs. an internal standard.

As was the case with **1b** and **4c**, high conversion to silicon-containing products was observed in the thermolysis of the N-phenylcarbamate **5b**. The combined yield of the vinylsilane **11** and the allylic silane **12** was 93%. The allylic silane predominated over the vinylsilane by a ratio of 87:13. An identical ratio of **12** to **11** was obtained by the Chugaev route via **5d**, but the isolated yield was reduced to 63%. The two isomeric products **11** and **12** could not be separated by GLC and their ratio was determined by NMR analysis of the areas of the two trimethylsilyl resonances.

The yield of silicon-containing products decreased to 48% (quantitative GLC analysis vs. an internal standard) when the Burgess reagent was used with **5a**. Isolation of this product revealed it to be exclusively the allylic silane **12**, which was characterized by satisfactory analyses for C, H, and Si, and NMR and mass spectra consistent with the proposed structure (see Experimental Section).

The thermal elimination reactions of esters of 1-trimethylsilyl-3-phenyl-2-propanol (**6a**) and 1-trimethylsilyl-2-octanol (**7a**) were similar to those of **5a** in that allylic silanes were formed in addition to the desired vinylsilanes. Thermolysis of N-phenylcarbamate **6c** at 125 °C for 1 h, followed by distillation and preparative GLC separation of the products, gave *trans*-1-trimethylsilyl-3-phenyl-1-propene (**13**) and *trans*-1-phenyl-3-trimethylsilyl-1-propene (**14**). The approximate yields were 45 and 38%, respectively. The GLC analysis indicated that a third component was present in less than 10% yield, but it was not isolated and identified.

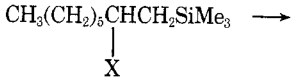


$$PhCH_2\underset{\displaystyle X}{\underset{|}{C}}HCH_2SiMe_3 \longrightarrow$$

6a, X = OH
c, X = OC(S)NHPh

trans-PhCH$_2$CH=CHSiMe$_3$ + *trans*-PhCH=CHCH$_2$SiMe$_3$
13 ~45% — **14** ~38%

The Chugaev process applied to **7a** was effective in the sense that a 72% conversion to silicon-containing products occurred, but the elimination was not highly regioselective. The ratio of vinylsilane to allylsilane was somewhat variable in separate



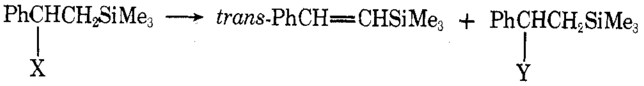
$$CH_3(CH_2)_5\underset{\displaystyle X}{\underset{|}{C}}HCH_2SiMe_3 \longrightarrow$$

7a, X = OH
d, X = OC(S)SCH$_3$

trans-CH$_3$(CH$_2$)$_5$CH=CHSiMe$_3$ + CH$_3$(CH$_2$)$_4$CH=CHCH$_2$SiMe$_3$
15 — **16**

experiments and ranged from 2/1 to 3/1. The vinylsilane was identified as *trans*-1-trimethylsilyl-1-octene (**15**) on the basis of its NMR spectrum and analysis. The allylic silane could not be isolated, but its presence was inferred from the NMR spectrum of the product.

Application of ester thermolyses to the synthesis of β-styryltrimethylsilane was complicated by the formation of side products characteristic of ion-pair return processes. Thus, the *N*-phenylcarbamate **8b** on heating yielded, in addition to a 43% yield of the desired *trans*-1-phenyl-2-trimethylsilylethene (**17**), a 33% yield of *N*-(1-phenyl-2-trimethylsilylethyl)aniline (**18**). The Chugaev procedure via **8d** gave no isolable quantities of **17**. The only product identified was the methyl thioether **19**, isolated in 25% yield.



$$\underset{\displaystyle X}{\mathrm{PhCHCH_2SiMe_3}} \longrightarrow trans\text{-}\mathrm{PhCH{=}CHSiMe_3} + \underset{\displaystyle Y}{\mathrm{PhCHCH_2SiMe_3}}$$

8a, X = OH **17**

b, X = OC(O)NHPh 43% **18**, Y = NHPh, 33%

d, X = OC(S)SCH$_3$ **19**, Y = SCH$_3$, 25%

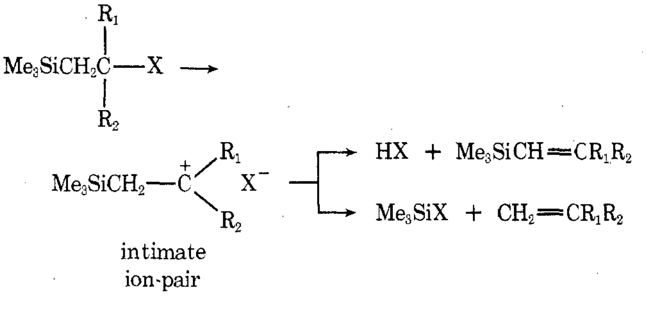
Discussion

The most significant observation in this study is that elimination reactions of esters of β-hydroxyalkyltrimethylsilanes can be controlled to proceed with complete C–SiMe$_3$ cleavage or complete C–H cleavage simply by varying the leaving group. Elimination reactions involving C–SiMe$_3$ cleavage of β-functional organosilanes, both polar and thermal four-center, are common and well documented.[2] Retention of silicon in the elimination product, over the range of substrates reported here, is without precedent. Syntheses of vinylsilanes in preparatively useful amounts can be accomplished by thermolysis of *N*-phenylcarbamates or *N*-phenylthiocarbamates if the elimination reaction can proceed in only one direction. This is best evidenced by the conversion of **1b** to **3** in 94% yield and **4c** to **9** in 72% yield.

Ester thermolysis is not a general route to vinylsilanes, however, because the reactions are not highly regioselective. When elimination can occur in more than one direction, mixtures of vinylsilane and allylic silane are produced. This limitation is most clearly seen in the case of esters of **5a** where the allylic silane **12** was the major product.

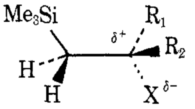
The reactions appear to be highly stereoselective, favoring the formation of trans vinylsilanes. This conclusion is only tentative, however, inasmuch as the analysis was by NMR on purified materials and small amounts of cis vinylsilanes, if formed, may have escaped detection.

In order to rationalize the dependence of vinylsilane vs. alkene formation on the leaving group, as is evident from the data in Table II, we envision as the critical step formation of an ion-pair intermediate. Deprotonation of the carbonium ion yields vinylsilane; desilylation yields alkene. The species acting as the base is either the anion of the leaving group or some species derived from the leaving group. For example, in thermolysis of *N*-phenylcarbamates the base could be either PhNHCO$_2^-$ or PhNH$^-$. Previous work in thermal elimination reactions of esters has established the importance of ion-pair intermediates and has shown that it is the counterion (rather than an external base) which abstracts the proton from the carbonium ion.[13]



$$\mathrm{Me_3SiCH_2}\overset{\displaystyle R_1}{\underset{\displaystyle R_2}{\mathrm{C}}}\mathrm{{-}X} \longrightarrow \mathrm{Me_3SiCH_2{-}\overset{+}{C}R_1R_2\ X^-} \begin{cases} \longrightarrow \mathrm{HX + Me_3SiCH{=}CR_1R_2} \\ \longrightarrow \mathrm{Me_3SiX + CH_2{=}CR_1R_2} \end{cases}$$

Developing cationic character at the carbon β to silicon will be facilitated by hyperconjugative electron release from the C(β)–Si bond in the transition state.[14] Hyperconjugative stabilization of this type is believed to be most effective when the trimethylsilyl group and the leaving group are anti to each other.[2a]



The ion pair generated from such a transition state will have the anion of the leaving group oriented at the opposite face of the R$_1$CR$_2$ plane from the trimethylsilyl group. If the anion is strongly basic, deprotonation will be fast relative to motion within the ion pair and vinylsilane will be formed. If the anion is more weakly basic, deprotonation will be slowed relative to rotation about the C(α)–C(β) bond, the trimethylsilyl group and the anion will be brought into closer proximity, and desilylation can occur. For the case of the methanesulfonate ester **1f**, decomposition under the conditions of its formation may proceed by attack by chloride ion at the trimethylsilyl group during the ionization process.[2b]

The poorer leaving groups examined in this study are also the more basic. The transition state for a poorer leaving group will appear later along the reaction coordinate, cationic character will be more highly developed, and the geometric requirement for carbon–silicon hyperconjugation more pronounced. This factor also favors vinylsilane formation relative to alkene formation.

While the above discussion was presented in the context of vinylsilane formation, exactly the same argument applies to allylsilane formation. Insufficient evidence is available to assess the factors which influence the vinylsilane to allylsilane ratio. The tendency for formation of one or the other is not particularly pronounced. Thermolysis of **6c** produces almost equal amounts of vinylsilane **13** and allylsilane **14**. Vinylsilane **15** predominates over allylsilane **16** by 2–3/1 on thermolysis of **7d**. The vinylsilane/allylsilane ratio from **5b** and **5d** was 1/7, but here the tendency for formation of double bonds endocyclic to six-membered rings seems to be the most important factor.

Support for the ion-pair mechanism can be found among several observations. The pattern of reactivity relative to substrate structure and leaving group ability parallels that observed in reactions which proceed through carbonium ion intermediates. The tertiary and sterically compressed[15] 2-trimethylsilylmethyl-2-adamantyl *N*-phenylthiocarbamate **1c** underwent spontaneous decomposition at 25 °C while the secondary *N*-phenylthiocarbamates **4c** and **6c** were stable enough to be isolated, and required temperatures of 125–140 °C to effect rapid elimination.

The side products **18** and **19** obtained from thermolysis of the benzylic esters **8b** and **8c** are typical nucleophilic substitution products associated with ion-pair return.

In agreement with its postulated involvement in stabilizing the transition state for ionization, the presence of a β-trimethylsilyl substituent exerts an accelerating effect on these ester thermolyses. The *N*-phenylcarbamates **1b**, **4b**, **5b**, and **8b** underwent smooth elimination at temperatures in the range 120–200 °C. Conditions for thermolysis of alkyl carbamate esters to alkenes are usually in the range 325–350 °C for kinetic studies in the gas phase[16] and 230–300 °C for preparative work in condensed phases.[17] Similarly, the *S*-methyl xanthate pyrolyses occurred at lower temperatures than those reported for Chugaev eliminations in the literature.[11]

Experimental Section

Nuclear magnetic resonance (NMR) spectra were recorded on JEOL PS-Fourier transform, Varian HA-100, and Hitachi Perkin-Elmer R-20 spectrometers in $CDCl_3$ or CCl_4 and chemical shifts are reported in parts per million (δ) from internal tetramethylsilane. Infrared spectra (ir) were obtained on a Perkin-Elmer 337 grating spectrophotometer as KBr disks for solids and pressed films for liquids and were calibrated with either the 1601- or the 907-cm^{-1} band of polystyrene. Melting points are corrected and were measured on a Thomas-Hoover apparatus. Boiling points are uncorrected. Mass spectra were obtained using a Hitachi Perkin-Elmer RMU-6E spectrometer at an ionizing potential of 70 eV. Gas chromatography was carried out on a Varian Aerograph 90-P3 with a thermal conductivity detector. Peak areas were determined with a disc integrator.

Elemental microanalyses were performed by Alfred Bernhardt, Engelskirchen, West Germany, and by Atlantic Microlab, Inc., Atlanta, Ga.

All reactions involving air-sensitive compounds were carried out in an atmosphere of dry nitrogen. Tetrahydrofuran was distilled from calcium hydride and stored over molecular sieves 4A under argon or nitrogen. *n*-Butyllithium in *n*-hexane was purchased from Alfa Inorganics.

β-Hydroxyalkyltrimethylsilanes. The addition of trimethylsilylmethylmagnesium chloride to carbonyl compounds in tetrahydrofuran was performed as described by Peterson.[1b]

2-Trimethylsilylmethyl-2-adamantanol (1a) was obtained in 89% yield, mp 48–55 °C, and purified by recrystallization from absolute ethanol (mp 58.5–59.5 °C): ir (KBr) 3520, 3455, 1245, 855, and 837 cm^{-1}; NMR (CCl_4) δ 0.08 (s, 9, $SiMe_3$), 1.1 (s, 2, CH_2Si), and 1.5–2.2 (m, 14, ring H); mass spectrum *m/e* (rel intensity) 223 (13), 220 (10), 205 (35), 151 (15), 148 (63), 75 (100), and 73 (53).

Anal. Calcd for $C_{14}H_{26}OSi$: C, 70.52; H, 10.99; Si, 11.78. Found: C, 70.61; H, 10.94; Si, 11.53.

1-Trimethylsilyl-3,3-dimethyl-2-butanol (4a) was prepared by addition of the Grignard reagent prepared from 10.5 g (85 mmol) of chloromethyltrimethylsilane to 7.9 g (92 mmol) of pivaldehyde. After distilling at 26 °C (1 Torr), 10.34 g (73%) of **4a** was obtained: ir (thin film) 3505 (OH), 2955, 2900, 2870, 1248, 862, and 838 cm^{-1}; NMR (CCl_4) δ 0.07 (s, 9, $SiMe_3$), 0.68 and 0.73 (m, 2, CH_2SiMe_3, ABM system), 0.88 (s, 9, *t*-Bu), 1.3 (s, 1, OH), and 3.4 (d, d, J = 4, 10 Hz, 1, CHOH); mass spectrum *m/e* (rel intensity) 117 (44), 75 (60), 73 (100), 57 (26), and 41 (38).

Anal. Calcd for $C_9H_{22}OSi$: C, 62.00; H, 12.72; Si, 16.11. Found: C, 61.90; H, 12.63; Si, 15.92.

1-Trimethylsilylmethylcyclohexanol (5a). The addition of trimethylsilylmethylmagnesium chloride to cyclohexanone has been reported without details.[1b] We obtained **5a** in 86% yield after sublimation (mp 35–36.5 °C): ir (KBr) 3300, 1246, 864, and 838 cm^{-1}; NMR (CCl_4) δ 0.08 (s, 9, $SiMe_3$), 0.88 (s, 2, CH_2Si), 1.04 (s, 1, OH), and 1.4 [br s, $(CH_2)_5$]; mass spectrum *m/e* (rel intensity) 186 (5), 171 (3), 168 (3), 153 (3), 96 (10), 91 (27), 81 (26), 75 (90), 73 (100), and 54 (58).

1-Trimethylsilyl-3-phenyl-2-propanol (6a) was isolated in 35% yield after distillation: bp 62 °C (0.17 Torr); ir (neat) 3445 (m, OH), 1246 (s), 853 and 838 (s, $SiMe_3$), 743 (m), and 698 cm^{-1} (s); NMR ($CDCl_3$) δ 7.28 (s, 5, aromatic), 4.0 (m, 1, CHO), 2.8 (m, 2, AB part of ABM system, PhCH_2), 1.63 (s, 1, OH), 0.98 (d, 2, J = 14 Hz, CH_2Si), and 0.17 (s, 9, $SiMe_3$); mass spectrum *m/e* (rel intensity) 208 (<1), 190 (1), 189 (1), 175 (1), 119 (5), 118 (13), 117 (56), 92 (19), 91 (20), 75 (54), 74 (12), and 73 (100).

Anal. Calcd for $C_{12}H_{20}OSi$: C, 69.17; H, 9.67; Si, 13.48. Found: C, 69.41; H, 9.78; Si, 13.49.

1-Trimethylsilyl-2-octanol (7a) was isolated in 80% yield after distillation at atmospheric pressure (bp 156–168 °C): ir (neat) 3360, 2960, 2930, 2860, 1248, 858, and 836 cm^{-1}; NMR (CCl_4) δ 0.0 (s, 9, Me_3Si), 0.5–1 (m, 5, CH_3 and CH_2Si), 1–1.5 (m, 10, CH_2), 1.6 (s, 1, OH), and 3.4–3.7 (m, 1, CHOH); mass spectrum *m/e* (rel intensity) 189 (4), 169 (4), 147 (4), 118 (8), 117 (73), 75 (97), and 73 (100).

Anal. Calcd for $C_{11}H_{26}OSi$: C, 65.27; H, 12.95; Si, 13.88. Found: C, 65.20; H, 12.72; Si, 13.85.

1-Phenyl-2-trimethylsilylethanol (8a) has been described by Hauser and Hance[1b] (bp 103–104 °C, 3 Torr). The material we obtained crystallized on standing, mp 27.5–29.5 °C.

Reaction of 2-Trimethylsilylmethyl-2-adamantanol (1a) with Methanesulfonyl Chloride. A solution containing 2.0 g (8.4 mmol) of **1a** in 30 ml of purified tetrahydrofuran was cooled to −30 °C and 8.4 mmol (4.2 ml of a 2.0 M solution in *n*-hexane) of *n*-butyllithium was added. After 10 min, 0.97 g (8.4 mmol) of methanesulfonyl chloride was added via syringe and the solution stirred at 25 °C for 12 h. The reaction mixture was diluted with 60 ml of ether, washed with three 50-ml portions of saturated ammonium chloride solution, and dried over magnesium sulfate. Evaporation of the solvent left 1.44 g of crude product which was examined by NMR. No vinylsilane was present. The product was taken up in 5 ml of pentane, passed through a short column of neutral alumina, and the column washed with 50 ml of pentane. The pentane was evaporated to leave 1.14 g (91%) of methyleneadamantane (**2**), mp 134–136 °C (lit. 135.8–136.5 °C),[18] identified further by comparing its NMR spectrum with that reported.

Isolation of 2-(Trimethylsilylmethylene)adamantane (3) from Chugaev Reaction of 1a. A solution of 7.25 g (0.03 mol) of **1a** in 50 ml of tetrahydrofuran was cooled to −5 °C and treated successively with 13.2 ml (0.03 mol) of *n*-butyllithium in *n*-hexane and 11.55 g (0.15 mol) of carbon disulfide. After stirring at 25 °C for 4 h, the solution was cooled to −5 °C and 8.6 g (0.06 mol) of iodomethane added. The solution was then stirred at 25 °C for 1.5 h. The solvent was evaporated and the residue partitioned between 100 ml of ether and 100 ml of saturated ammonium chloride solution. The aqueous layer was extracted with 100 ml of ether and the combined ether solutions dried ($MgSO_4$) and evaporated. The residue was chromatographed on 88 g of silica gel (column prepared in *n*-pentane) and eluted with 240 ml of *n*-pentane to afford 5.39 g of product identified by NMR as a 3:1 mixture of 2-(trimethylsilylmethylene)adamantane (**3**) and methyleneadamantane (**2**). The composition was determined by integration of the respective vinyl proton signals of **3** (δ 4.96) and **2** (δ 4.48).

A portion (2.93 g) of the mixture was purified by chromatography on a column prepared from 50 g of silica gel, 12 g of silver nitrate, and 2.5 g of Celite.[19] Elution with dichloromethane gave 1.57 g (44%) of **3** as a colorless liquid: ir (neat) 3040 (w, vinyl C–H), 2955 (sh), 2910, 2855, 1620, 1245, 895, 861, and 841 cm^{-1}; NMR (CCl_4) δ 0.13 (s, 9, Me_3Si), 1.9 (br s, 12, ring H), 2.2–2.8 (m, 2, allylic H), and 4.96 (s, 1, vinyl H); mass spectrum *m/e* (rel intensity) 221 (6), 220 (17), 206 (23), 205 (100), 73 (17), and 59 (24).

Anal. Calcd for $C_{14}H_{24}Si$: C, 76.28; H, 10.97; Si, 12.74. Found: C, 76.34; H, 10.86; Si, 12.54.

Reaction of 1a with Phenyl Isothiocyanate. 2-Trimethysilylmethyl-2-adamantanol (**1a**, 3.1 g, 13 mmol) dissolved in 80 ml of dry tetrahydrofuran was cooled to −30 °C under an atmosphere of nitrogen. Then 7.2 ml (13 mmol) of a 1.8 M solution of *n*-butyllithium in *n*-hexane was added slowly keeping the temperature at or below −30 °C. The solution was stirred for 40 min before phenyl isothiocyanate (1.7 g, 13 mmol) was added slowly. The reaction mixture stood for 22 h at room temperature. Workup was carried out by adding 100 ml of dichloromethane and then extracting the dichloromethane solution twice with 100-ml portions of saturated ammonium chloride. After drying ($MgSO_4$) the solvent was removed on a rotary evaporator to leave 4.1 g of crude product. This was subjected to dry column chromatography on silica gel using a mixture of hexanes as solvent. There was obtained from the highest R_f band (0.6–1.0) 2.1 g (73%) of vinylsilane **3** which was analyzed by GLC to be 95% pure. The only impurity apparent in the GC analysis and by NMR was methyleneadamantane (**2**).

Preparation of 2-Trimethylsilylmethyl-2-adamantyl *N*-Phenylcarbamate (1b). In the same manner, 10.0 g (42 mmol) of **1a** was converted to its alkoxide with *n*-butyllithium and allowed to react with 5.0 g (42 mmol) of phenyl isocyanate. The crude product, a solid (15.6 g), was recrystallized from a dichloromethane-n-hexane (1:5) solution to give 11.7 g (78%) of **1b**, mp 140.5–142 °C dec. The analytical sample was obtained by recrystallization from ether: mp 154.5–155 °C dec; ir (KBr) 3330 (s, NH), 1695 (s, C=O) and 859 cm^{-1} (m, $SiMe_3$); NMR ($CDCl_3$) δ 7.03–7.39 (m, 5, aromatic), 6.49 (br, 1, NH), 1.58–2.56 (br m, 14, adamantyl), 1.75 (s, 2, $-CH_2SiMe_3$), and 0.09 (s, 9, $SiMe_3$).

Anal. Calcd for $C_{21}H_{31}NO_2Si$: C, 70.54; H, 8.74; N, 3.92; Si, 7.85. Found: C, 70.47; H, 8.67; N, 4.04; Si, 7.92.

Thermolysis of 1b. A 100-ml round-bottom flask fitted with a short-path distillation head and containing 7.1 g (19.9 mmol) of **1b** was placed in an oil bath preheated to 165 °C. Gas was evolved as the ester melted. The resulting liquid was distilled (0.1 Torr) to give 6.1 g of a clear, colorless mixture of two liquids. The distillate was taken up in *n*-pentane (50 ml), extracted with three 50-ml portions of 2 N HCl, washed with 50 ml of water, and dried ($MgSO_4$). The pentane was evaporated to leave 4.1 g (94%) of vinylsilane **3**, the NMR of which was identical with that of the analytical sample described above, except for the presence of a trace of pentane as the only impurity.

Reaction of 1a with Burgess' Reagent. Analysis by Gas Chromatography. To a solution containing 200 mg (0.84 mmol) of (carboxysulfamoyl)triethylammonium hydroxide inner salt methyl ester[12] in 20 ml of toluene at reflux was added 153 mg (0.64 mmol) of **1a** in 3 ml of toluene. After 16 h at reflux, the reaction mixture was cooled and extracted with two 10-ml portions of saturated ammonium chloride. Analysis of the product was carried out using a 10 ft × 0.25 in. 20% SE-30 on Chromosorb W column at 178 °C at a helium flow rate of 40 ml/min. Cyclododecene was added as an internal standard and the areas of the peaks corrected by calibration with known mixtures. The analytical yields determined by three separate experiments were vinylsilane **3**, 39% and methyleneadamantane **2**, 51%.

Analysis of Chugaev Reaction of 1a by Gas Chromatography. The reaction was carried out as described previously but on a smaller scale (0.64 mmol) and analyzed as in the preceding experiment. The analytical yields were vinylsilane **3**, 70%, and methyleneadamantane **2**, 28%.

Preparation of 1-Trimethylsilyl-3,3-dimethyl-2-butyl *N*-Phenylcarbamate (4b). Conversion of 9.1 g (52 mmol) of **4a** to its *N*-phenylcarbamate was carried out as described previously for the synthesis of **1b** from **1a**. The crude product (15.5 g) was recrystallized from ether–pentane (1:5) to give 11.6 g (76%) of **4b**: mp 75.5–77.5 °C; ir (KBr) 3410 (NH), 1720 (C=O), 1535, 1450, 1370, 1320, 1250, 1230, 1220, 1069, 950, 858, 840, 750, and 690 cm^{-1}; NMR ($CDCl_3$) δ 0.07 (s, 9, $SiMe_3$), 0.84 (d, 2, J = 6 Hz, CH_2SiMe_3), 0.94 (s, 9, *t*-Bu), 4.88 (d, d, 1, CH), 6.54 (br, 1, NH), and 6.96–7.52 (m, 5, aromatic).

Anal. Calcd for $C_{16}H_{27}NO_2Si$: C, 65.48; H, 9.27; N, 4.77; Si, 9.57. Found: C, 65.50; H, 9.18; N, 4.82; Si, 9.83.

1-Trimethylsilyl-3,3-dimethyl-2-butyl *N*-phenylthiocarbamate (4c) was prepared in a similar manner from **4a** using phenyl isothiocyanate. The purified material, mp 117–118 °C, was obtained in 79% yield after recrystallization from *n*-pentane: ir (KBr) 3180 (NH), 2970, 1530, 1390, 1246, 1224, 1204, 1172, 1151, 1061, 1016, 863, 836, 740, and 693 cm^{-1}; NMR ($CDCl_3$) δ 0.13 (s, 9, $SiMe_3$), 1.0 (s, 9, *t*-Bu), 0.9–1.12 (m, 2, CH_2SiMe_3), 5.71 (d, d, 1, CHO), 7.04–7.47 (br, 5, arom), 8.35–8.9 (br, 1, NH). The analytical sample was obtained by further recrystallization from *n*-pentane, mp 118.5–119.5 °C dec.

Anal. Calcd for $C_{16}H_{27}NOSSi$: C, 62.08; H, 8.79; N, 4.52; S, 10.36; Si, 9.07. Found: C, 62.31; H, 8.94; N, 4.51; S, 10.53; Si, 9.24.

Thermolysis of 4c. A 25-ml round-bottom flask fitted with a short path distillation head and containing 6.42 g (20.7 mmol) of **4c** was heated (oil bath) while cooling the distillation receiver in an ice–salt bath. Decomposition occurred on melting (bath temperature 120 °C). The temperature was maintained at 120 °C for 20 min, then the temperature increased to 140 °C and vacuum applied to the system resulting in the distillation of a clear, colorless liquid containing two phases. The distillate was taken up in 100 ml of pentane and extracted with two 25-ml portions of 2 N hydrochloric acid followed by 25 ml of water. The pentane was removed by distilling through a Vigreux column and the product purified by distillation at atmospheric pressure. The yield of *trans*-1-trimethylsilyl-3,3-dimethyl-1-butene (**9**) was 2.32 g (72%), bp 132–134 °C (reported bp 128–130 °C). The ir, NMR, and mass spectra corresponded to those reported.[10f,20]

Thermolysis of 4b was slow even at 200 °C. After 30 h 11.61 g (40 mmol) of **4b** gave 1.73 g (28%) of **9** along with 15% of *N,N'*-diphenylurea (1.32 g).

Preparation and Thermolysis of 1-Trimethylsilylmethyl-1-cyclohexyl *N*-Phenylcarbamate (5b). The *N*-phenylcarbamate was prepared from 6.6 g (35 mmol) of **5a** and phenyl isocyanate exactly as described previously for the preparation of **1b**. The crude product (11.4 g) was recrystallized from pentane to give 5.3 g (49%) of **5b**: mp 81–82 °C; ir (KBr) 3305 (s, NH), 1690 (s, C=O), 1234 (s, C–O), and 842 cm^{-1} (m, $SiMe_3$); NMR ($CDCl_3$) δ 7.12–7.59 (m, 5, aromatic), 6.62 (br, 1, NH), 1.32–2.60 (br, 12, cyclohexyl and $-CH_2Si$), and 0.16 (s, 9, $SiMe_3$).

Anal. Calcd for $C_{17}H_{27}NO_2Si$: C, 66.84; H, 8.91; N, 4.58; Si, 9.19. Found: C, 66.82; H, 8.97; N, 4.73; Si, 9.35.

Thermal decomposition of 5.02 g (16.4 mmol) of **5b** was carried out as described for **1b**. The bath temperature was 113–125 °C. After distillation at 0.05 Torr and extraction with ether and 2 N HCl, 2.58 g (93%) of a mixture of **11** and **12** was obtained. Analysis of the mixture by NMR was performed by integration of their respective trimethylsilyl signals. The NMR spectrum of **11** has been reported.[10d] Characterization of **12** is described below. The ratio **11**/**12** was 13/87.

Characterization of 1-Trimethylsilylmethylcyclohexene (12). Methyl(carboxylsulfamoyl)triethylammonium hydroxide inner salt[12] (3.57 g, 15 mmol) was dissolved in 60 ml of dichloromethane and added to an ice-cooled solution of 2.64 g (14.1 mmol) of **5a** in 30 ml of dichloromethane. The solution was allowed to warm to room temperature for 5 min, extracted with two 100-ml portions of water, and dried over magnesium sulfate. Evaporation of the solvent left 4.57 g of a mixture containing a liquid and a solid. The liquid (1.28 g) was removed by pipet and determined to be a 3:2 mixture of **12** and methylenecyclohexane (**10**) by NMR. Preparative GLC separation on a 10-ft 20% Silicone Fluoro QF-1 column at 166 °C afforded a pure sample of **12**: ir (neat) 2940, 2860, 2845, 1245, 1170, 920, 860, 845, and 695 cm^{-1}; NMR (CCl_4) δ 0.05 (s, 9, $SiMe_3$), 1.38 (br s, 2, $SiCH_2$), 1.4–2.1 (m, 8, ring protons), 5.15 (br s, 1, vinyl H); mass spectrum *m/e* 168, 73 (base peak).

Anal. Calcd for $C_{10}H_{20}Si$: C, 71.34; H, 11.97; Si, 16.68. Found: C, 71.31; H, 11.94; Si, 16.90.

Chugaev Reaction of 1-Trimethylsilylmethyl-1-cyclohexanol (5a). The procedure followed was similar to that used for **1a**. The experiment was carried out on 7.2 g (38.5 mmol) of **5a**. The crude product was heated at 160 °C (oil bath) for 30 min and separated by dry column chromatography on 350 g of silica gel. There was obtained 4.08 g (63%) of material (R_f 0.6–1.0) analyzed by NMR to be a mixture of **11** (13%) and **12** (87%).

The vinylsilane **11** was isolated from the mixture by the following procedure which is based on its much slower rate of epoxidation than the allylsilane **12**. A sample (0.314 g, 1.87 mmol) of the product was treated with 0.378 g (1.87 mmol) of 85% *m*-chloroperoxybenzoic acid in 12 ml of dichloromethane at −14 to −24 °C for 12 h. The solution was extracted with four 10-ml portions of saturated sodium bicarbonate, then with 10 ml of brine and dried ($MgSO_4$). The crude product (0.289 g) was subjected to preparative GLC on a 10-ft 20% SE-30 column at 158 °C. Three peaks were collected having retention times of 5.5, 7.7, and 9.2 min. The product with the longest retention time was identified as **11** by comparing its NMR and ir spectra with those reported.[10d] The products with retention times of 5.5 and 7.7 min are 2-methylenecyclohexanol and its corresponding trimethylsilyl ether formed by epoxidation and cleavage of **12**.

Preparation and Thermolysis of 1-Trimethylsilyl-3-phenyl-2-propyl *N*-Phenylthiocarbamate (6c). The preparation of ester **6c** from 5.0 g (24 mmol) of **6a** and phenyl isothiocyanate was similar to those described previously. The crude product (9.9 g) was recrystallized from a mixture of ether and pentane (1:10) to give 6.1 g of **6c** as off-white crystals, mp 103.5–104.5 °C. The analytical sample was obtained from an additional recrystallization from diethyl ether–*n*-pentane (1:10) as fine white needles: mp 105.5–106 °C; ir (KBr) 3210 (m, NH), 1545 (s), 1214 (s), 1168 (s), 1021 (s), 852 and 836 (m, $SiMe_3$), and 738 cm^{-1} (s); NMR ($CDCl_3$) δ 8.61–8.30 (br, 1 NH), 7.27 (s, 10, aromatic), 5.95 (m, 1, $-CH_2O$), 3.11 (m, 2, $PhCH_2-$), 1.19 (m, 2, $-CH_2Si$), and 0.14 (s, 9, $SiMe_3$).

Anal. Calcd for $C_{19}H_{25}NOSSI$: C, 66.42; H, 7.33; N, 4.08; S, 9.33; Si, 8.17. Found: C, 66.56; H, 7.45; N, 4.05; S, 9.15; Si, 8.09.

The thiocarbamate **6c** (5.8 g, 17 mmol) was placed in a 25-ml round-bottom flask which was then fitted with a reflux condenser and a drying tube. The flask was heated to 125 °C for 1 h. The reaction mixture was worked up by adding 50 ml of *n*-pentane and extracting with two 50-ml portions of 2 N hydrochloric acid followed by one 50-ml portion of water. The pentane layer was dried ($MgSO_4$) and evaporated to leave 3.5 g of crude product. The crude product was vacuum distilled and the fraction of bp 49–53 °C (0.13 Torr) collected, 2.7 g (84%). This fraction was determined to be a mixture of three components with retention times of 7.0, 7.9, and 9.5 min in the ratio 50:8:42, respectively, by analytical GLC at 170 °C on a 10-ft 20% SE-30 on Chromosorb W column. Preparative GLC at 135 ° was performed and the two major components collected. The product with the shortest retention time was the vinylsilane **13**: ir (neat) 1619 (w), 1608 (w), 1247 (s), 990 (m), 864 (s), 837 (s), and 696 cm^{-1} (s); NMR ($CDCl_3$) δ 7.16 (br s, 5, aromatic), 6.05 (doublet of triplets, 1, J = 4.8 and 16.0 Hz, $PhCH_2CH=$), 5.70 (d, 1, J = 16.0 Hz, $=CHSi$), 3.41 (d, 2, J = 4.8 Hz, $PhCH_2-$), and 0.07 (s, 9, $SiMe_3$); mass spectrum *m/e* (rel intensity) 190 (15), 175 (23), 117 (7), 116 (7), 115 (11), 93 (15), 91 (4), 77 (11), 75 (10), 74 (11), 73 (100), 65 (14), 59 (43), 45 (18), and 43 (15).

Anal. Calcd for $C_{12}H_{18}Si$: C, 75.72; H, 9.53; Si, 14.75. Found: C, 75.52; H, 9.41; Si, 14.64.

The product with the longest retention time was the allylsilane **14**, identified by comparing its ir, NMR, and mass spectra with those reported in the literature.[21]

Preparation and Thermolysis of 1-Trimethylsilyl-2-octyl *S*-Methyl Xanthate (7d). The procedure employed was similar to that used for **1a** except that in this case the xanthate was sufficiently stable to be isolated as a light yellow liquid. From 5.00 g (24.8 mmol) of **7a** was obtained 6.91 g (95%) of **7d**: NMR (CCl_4) δ 0.10 (s, 9, $SiMe_3$), 0.5–2 (m, 15), 2.58 (s, 3, SCH_3), 5.5–5.9 (m, 1, CHO).

Elimination occurred on distilling through a short-path apparatus (bath temperature 216 °C) to give 3.29 g (72%) of product. This material was predominantly *trans*-1-trimethylsilyl-1-octene (**15**) as evidenced by its 100-MHz NMR spectrum, which exhibited signals for the vinyl protons consistent with this structure. The vinyl H at C(1) appeared as a doublet (J = 18 Hz) at δ 5.5 and the vinyl proton at C(2) appeared as a doublet of triplets (J = 18, 6 Hz) at δ 5.95. An additional multiplet at δ 5.25 was present corresponding to a smaller, but undetermined, amount of an impurity presumed to be 1-trimethylsilyl-2-octene (**16**).[22]

A pure sample of **15** was obtained by treating 15.7 g of a similar reaction mixture with 17.4 g of *m*-chloroperoxybenzoic acid in dichloromethane (180 ml) for 11 h. Workup and distillation at 0.01 Torr afforded 3.0 g of a fraction (bp 30–37 °C) which by NMR was cleanly **15**: NMR (CCl_4) δ 0.16 (s, 9, $SiMe_3$), 0.6–1.6 (m, 11, C_5H_{11}), 2.1 (m, 2, $CH_2C{=}$), 5.6 (d, 1, $J = 18$ Hz, $=CHSiMe_3$), 6.0 (d, t, 1, $J = 18, 6$ Hz, $HC{=}CHSiMe_3$).

Anal. Calcd for $C_{11}H_{24}Si$: C, 71.65; H, 13.12; Si, 15.23. Found: C, 71.54; H, 13.14; Si, 15.15.

Preparation and Thermolysis of 1-Phenyl-2-trimethylsilylethyl *N*-Phenylcarbamate (8b). By the usual procedure 15.2 g (78 mmol) of **8a** was converted to its *N*-phenylcarbamate. The crude product (25.4 g) was recrystallized from absolute ethanol to afford 11.3 g (46%) of **8b**: mp 89.5–90.5 °C; ir (KBr) 3270 (s, NH), 1690 (s, C=O), 1309 (s, C–N), 1240 (s br, C–O), 876 (s, $SiMe_3$), and 849 cm^{-1} (s, $SiMe_3$); NMR ($CDCl_3$) δ 6.91–7.47 (m, 10, aromatic), 6.60 (br, 1, NH), 5.84 (doublet of doublets, 1, $J = 7.0$ and 8.4 Hz, methine), 1.37 (d, 1, $J = 7.0$ Hz) and 1.33 (d, 1, $J = 8.4$ Hz) (both methylene), and −0.10 (s, 9, $SiMe_3$).

Anal. Calcd for $C_{18}H_{23}NO_2Si$: C, 68.97; H, 7.40; N, 4.47; Si, 8.96. Found: C, 68.89; H, 7.52; N, 4.53; Si, 8.94.

A flask containing 11.16 (35.6 mmol) of **8b** was placed in an oil bath preheated to 197 °C. The carbamate melted rapidly with gas evolution. After heating for 15 min the resulting liquid was cooled and filtered (removing 0.18 g of *N,N'*-diphenylurea) and washed with 20 ml of 2 N HCl. Addition of the hydrochloric acid caused the precipitation of a large amount of white hydrochloride salt. This was removed by filtration, dried under vacuum, then shaken vigorously with 150 ml of 20% sodium hydroxide and 200 ml of diethyl ether. The ether layer was washed with 100 ml of water, dried ($MgSO_4$), and evaporated to give 3.2 g (33%) of 1-phenyl-*N*-phenyl-2-trimethylsilylethylamine (**18**) as a white solid, mp 56–58 °C. The analytical sample was recrystallized from diethyl ether–*n*-pentane: mp 58–59 °C; ir (KBr) 3420 (s, NH), 1602 (s), 1505 (s), 1320 (s, C–N), 1246 (s), 868 (s, $SiMe_3$), 846 (s, $SiMe_3$), 750 (s), 704 (s), and 693 cm^{-1} (s); NMR ($CDCl_3$) δ 6.38–7.43 (m, 10, aromatic), 4.44 (t, 1, $J = 7.0$ Hz, PhCHN), 4.00 (br, 1, NH), 1.19 (d, 2, $J = 7.0$ Hz, $-CH_2SiMe_3$), and 0.01 (s, 9, $SiMe_3$); mass spectrum *m/e* (rel intensity) 269 (11), 182 (12), 177 (22), 165 (14), 150 (25), 104 (11), 93 (14), and 73 (100).

Anal. Calcd for $C_{17}H_{23}NSi$: C, 75.78; H, 8.60; N, 5.20; Si, 10.42. Found: C, 75.82; H, 8.63; N, 5.15; Si, 10.36.

The ether solution of that portion of the thermolysis product which did not dissolve in the 2 N hydrochloric acid and which was not precipitated as the hydrochloride salt was extracted once more with 10 ml of 2 N hydrochloric acid to ensure that all of the amines had been removed. The ether solution was washed with 10 ml of water, dried ($MgSO_4$), and the ether removed by distillation at atmospheric pressure. The residue was distilled and 2.7 g (43%) of *trans*-β-trimethylsilylstyrene (**17**) was collected, bp 45–46 °C (0.25 Torr) [lit. 80–83 °C (3 Torr),[10b] 98 °C (10.5 Torr)[23]]; the ir[10b] and NMR[10f] corresponded to those reported.

Chugaev Reaction Applied to 8a. When the Chugaev process was carried out on 10.5 g (50 mmol) of **8a** according to the usual procedure and the crude residue distilled at 0.005 Torr, 2.6 g of a fraction, bp 56–61 °C, was obtained. This fraction was identified as 1-methylthio-1-phenyl-2-trimethylsilylethane (**19**) and was obtained in a 25% yield: ir (neat) 3045 (w), 2970 (m), 2930 (m), 1730 (w), 1610 (w), 1500 (w), 1460 (m), 1248 (s), 1132 (br w), 861, (s, $SiMe_3$), 850 (sh s, $SiMe_3$), 726 (m), 720 (m), 710 (m), and 699 cm^{-1} (s); NMR ($CDCl_3$) δ 7.39 (br s, 5, aromatic), 3.90 (t, 1, $J = 8.2$ Hz, $CHSCH_3$), 1.95 (s, 3, $-SCH_3$), 1.39 (d, 2, $J = 8.2$ Hz, $-CH_2SiMe_3$), and 0.16 (s, 9, $SiMe_3$).

Anal. Calcd for $C_{12}H_{20}SSi$: C, 64.21; H, 8.98; S, 14.29; Si, 12.52. Found: C, 64.27; H, 8.74; S, 14.10; Si, 12.32.

Acknowledgments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. In addition, J.R.T. was an NDEA Title IV Fellow during the period 1971–1974.

Registry No.—**1a**, 58540-98-0; **1b**, 58540-99-1; **1c**, 58541-00-7; **1d**, 58541-01-8; **1e**, 58541-02-9; **1f**, 58541-03-0; **3**, 58541-04-1; **4a**, 58541-05-2; **4b**, 58541-06-3; **4c**, 58541-07-4; **5a**, 55287-96-2; **5b**, 58541-08-5; **6a**, 58541-09-6; **6c**, 58541-10-9; **7a**, 58541-11-0; **7d**, 58541-12-1; **8a**, 17993-97-4; **8b**, 58541-13-2; **12**, 58541-14-3; **13**, 58541-15-4; **15**, 57365-47-6; **18**, 58541-16-5; **19**, 58541-17-6; methanesulfonyl chloride, 124-63-0; phenyl isothiocyanate, 103-72-0.

References and Notes

(1) (a) C. R. Hauser and C. R. Hance, *J. Am. Chem. Soc.*, **74,** 5091 (1952); (b) D. J. Peterson, *J. Org. Chem.*, **33,** 780 (1968).

(2) (a) A. W. P. Jarvie, *Organomet. Chem. Rev., Sect. A*, **6,** 153 (1970); (b) P. F. Hudrlik and D. Peterson, *J. Am. Chem. Soc.*, **97,** 1464 (1975).

(3) (a) H. Gilman, D. Aoki, and D. Wittenberg, *J. Am. Chem. Soc.*, **81,** 1107 (1959); (b) I. M. T. Davidson, M. R. Jones, and C. Pelt, *J. Chem. Soc. B*, 937 (1967); (c) W. K. Musker and G. L. Larson, *J. Am. Chem. Soc.*, **91,** 514 (1969); (d) C. Eaborn and R. W. Bott in "Organometallic Compounds of the Group IV Elements", Vol. I, Part I, A. G. MacDiarmid, Ed., Marcel Dekker, New York, N.Y., 1968, pp 380–386.

(4) (a) T. H. Chan, E. Chang, and E. Vinokur, *Tetrahedron Lett.*, 1137 (1970); (b) T. H. Chan and E. Chang, *J. Org. Chem.*, **39,** 3264 (1974); (c) I. Fleming and A. Pearce, *J. Chem. Soc., Chem. Commun.*, 633 (1975); (d) K. Utimoto, M. Kitai, and H. Nozaki, *Tetrahedron Lett.*, 2825 (1975); (e) J.-P. Pillot, J. Dunoges, and R. Calas, *Bull. Soc. Chim. Fr.*, 2143 (1975).

(5) G. Stork and E. Colvin, *J. Am. Chem. Soc.*, **93,** 2080 (1971).

(6) (a) B.-T. Gröbel and D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **13,** 83 (1974); (b) R. K. Boeckman, Jr., and K. J. Bruza, *Tetrahedron Lett.*, 3365 (1974).

(7) R. B. Miller and T. Reichenbach, *Tetrahedron Lett.*, 543 (1974).

(8) (a) G. Stork and B. Ganem, *J. Am. Chem. Soc.*, **95,** 6152 (1973); (b) G. Stork and M. E. Jung, *ibid.*, 3682 (1974); (c) R. K. Boeckman, Jr., *ibid.*, **95,** 6867 (1973); **96,** 6179 (1974); (d) G. Stork and J. Singh, *ibid.*, **96,** 6180 (1974)

(9) (a) G. R. Buell, R. Corriu, C. Guerin, and L. Spialter, *J. Am. Chem. Soc.*, **92,** 7424 (1970); (b) W. P. Weber, R. A. Felix, A. K. Willard, and K. E. Koenig, *Tetrahedron Lett.*, 4701 (1971); (c) K. E. Koenig and W. P. Weber, *ibid.*, 2533 (1973); (d) K. E. Koenig and W. P. Weber, *J. Am. Chem. Soc.*, **95,** 3416 (1973); R. F. Cunico, *J. Organomet. Chem.*, **60,** 219 (1973); (e) K. Yamamoto, K. Shinohara, T. Ohuchi, and M. Kumada, *Tetrahedron Lett.*, 1153 (1974).

(10) For syntheses of vinylsilanes see ref 4–8 and (a) H. Sakurai, K. Nishiwaki, and M. Kira, *Tetrahedron Lett.*, 4193 (1973); (b) D. Seyferth, L. G. Vaughn, and R. Suzuki, *J. Organomet. Chem.*, **1,** 437 (1964); (c) ref 3d, Chapter 2; (d) B. Martel and M. Varache, *J. Organomet. Chem.*, **40,** C53 (1972); (e) G. Stork, M. E. Jung, E. Colvin, and Y. Noel, *J. Am. Chem. Soc.*, **96,** 3684 (1974); (f) J. J. Eisch and M. W. Foxton, *J. Org. Chem.*, **36,** 3520 (1971).

(11) For reviews see (a) C. H. DePuy and R. W. King, *Chem. Rev.*, **60,** 431 (1960); (b) H. R. Nace, *Org. React.*, **12,** 58 (1962); (c) W. H. Saunders, Jr., and A. F. Cockerill, "Mechanisms of Elimination Reactions", Wiley-Interscience, New York, N.Y., 1973, Chapter VIII.

(12) E. M. Burgess, H. R. Penton, Jr., and E. A. Taylor, *J. Org. Chem.*, **38,** 26 (1973).

(13) P. S. Skell and W. L. Hall, Jr., *J. Am. Chem. Soc.*, **85,** 2851 (1963).

(14) (a) T. G. Traylor, W. Hamstein, M. J. Berwin, N. A. Clinton, and R. S. Braun, *J. Am. Chem. Soc.*, **93,** 5715 (1971); (b) L. H. Sommer and G. A. Baughman, *ibid.*, **83,** 3346 (1961).

(15) J. L. Fry, E. M. Engler, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **94,** 4628 (1972).

(16) (a) H. Kwart and J. Slutsky, *J. Chem. Soc., Chem. Commun.*, 552 (1972); (b) N. J. Daly and F. Ziolkowski, *ibid.*, 911 (1972); (c) N. J. Daly and F. Ziolkowski, *Aust. J. Chem.*, **24,** 2541 (1971).

(17) (a) E. Dyer and G. C. Wright, *J. Am. Chem. Soc.*, **81,** 2138 (1959); (b) A. F. McKay and G. R. Vavasour, *Can. J. Chem.*, **31,** 688 (1953).

(18) R. C. Fort, Jr., and P. v. R. Schleyer, *J. Org. Chem.*, **30,** 789 (1965).

(19) E. Block and H. W. Orf, *J. Am. Chem. Soc.*, **94,** 8438 (1972).

(20) W. P. Weber, A. K. Willard, and H. G. Boettger, *J. Org. Chem.*, **36,** 1620 (1971).

(21) (a) J. Slutsky and H. Kwart, *J. Am. Chem. Soc.*, **95,** 8678 (1973); (b) R. G. Jones, P. Partington, W. J. Rennie, and R. M. G. Roberts, *J. Organomet. Chem.*, **35,** 291 (1972).

(22) The ratio of **15/16** was determined in a separate experiment to be 2:1.

(23) L. H. Sommer, D. L. Bailey, G. M. Goldberg, C. E. Buck, T. S. Bye, F. J. Evans, and F. C. Whitmore, *J. Am. Chem. Soc.*, **76,** 1613 (1954).