distribution pattern was established by GC–MS analyses using electron-impact (EI), chemical-ionization (CI), and negative CI (NCI) techniques.

Table IV shows the typical fragmentation patterns for A–D as determined by the three mass spectral methods. The fragments noted are found in the fragmentation pattern of each member of a specific family.

Conversion of $Ru_3(CO)_{12}$) to $H_4Ru_4(CO)_{12}$. $Ru_3(CO)_{12}$ (200 mg, 0.31 mmol) in 2 mL of hexamethyldisilazane is heated at 135 °C under 1 atm of H_2. After 10 min, the solution color turns red and then back to orange and a yellow-orange precipitate (165 mg) is formed. After 0.5 h the solution is cooled and the precipitate is washed with petroleum ether and identified as $H_4Ru_4(CO)_{12}$ with traces of $H_2Ru_4(CO)_{13}$. (Identified by IR and NMR in comparison with authentic samples.) In the absence of an H_2 atmosphere, $Ru_3(CO)_{12}$ is recovered as the major product even after an 8-h reaction time, although a significant amount of decomposition occurs during the heating period.

Polymerization of Tetramethyldisilazane in the Presence of Ammonia. (a) To 100.0 mmol of tetramethyldisilazane (TDMS, 13.3 g) is added 50.0 μmol of $Ru_3(CO)_{12}$ (32.0 mg), and the solution is heated under ammonia under various reaction conditions as noted in Table III. The volatile oligomers were separated from the solution by vacuum distillation (up to 180 °C (300 μm)). The residue is the nonvolatile fraction. ^1H NMR ($CDCl_3$, δ, reference $CHCl_3$): TDMS, Si–H, 4.46 (m); N–H, 0.50 (br); Si–CH_3, 0.14 (d); Nonvolatile products (for run 3, Table III), Si–H (not evident); N–H 0.52 (br); Si–CH_3, 0.12 (s, 5%), 0.08 (s, 95%). ^{29}Si NMR ($CDCl_3$, δ, reference Me_4Si): −13.99 ppm. We can use the NMR data in conjunction with $\bar{M}_n$ to calculate polymer composition (linear vs. branched species) for simple mixtures. Given (for run 3, Table III) M_n 2024, a completely linear polymer will be H-$[Me_2SiNH]_{27}$–Me_2SiH (M_r 2033) and we can calculate a chemical composition for $Si_{28}C_{56}H_{195}N_{27}$: C, 33.07; H, 9.66; N, 18.60; Si, 38.66; O, 0.00. We find: C, 32.92; H, 8.67; N, 17.65; Si, 40.42; O, 0.40. For a DP of 27, capped at both ends by Me_2SiH groups, we should see two methyl carbon signals in the ratio of 2:26 or 7% vs. 93%. In fact, the ratio of the two signals we observed, δ 0.12 and 0.08, is found to be 5% vs. 95% (TMDS methyl protons are at δ 0.14). The error limits are probably ±2%, and the NMR sensitivity is too low to show SiNH.

We conclude that branching in this oligomer product must be less than 2 per 30 monomer units. The chemical analysis is high for silicon and low for nitrogen. The low nitrogen can be explained by the 0.40% oxygen impurity. The high silicon could result from the formation of some $Me_2SiN(SiMe_2H)$ branches; in fact the GC–MS results for oligomers with a DP of <12 do show approximately 2–3% branching where the branches are of the type $Me_2SiN(SiMe_2H)$. Note that this suggests oligomer uniformity for all the species even for those species we cannot see by GC–MS.

NH_3 pressures: 1 atm is obtained by quickly pressurizing and depressurizing the reactor once before sealing. Repeating this cycle until no more ammonia will dissolve provides 12 atm of pressure at temperature.

(b) To 20.0 mmol of TMDS (2.66 g) is added 23 μmol of $Ru_3(CO)_{12}$ (16 mg), and the solution is heated at 135 °C under 7 atm of ammonia for 20 h. Following distillation a 68% yield of nonvolatile products is obtained with $\bar{M}_n$ = 1200 daltons.

(c) $Ru_3(CO)_{12}$ (25 μmol) is added to 2.40 g of the volatile fraction collected from run 2 (Table III) at 60–80 C (500 μm) which consists of a mixture of cyclomers (*x* = 3–6; 25%) and linear oligomers (*x* = 3–6). The solution is heated for 2 h at 60 °C followed by 2 h at 90 °C under 1 atm of ammonia. Following distillation, a 45% yield of nonvolatile products is obtained (60% yield of the linear oligomers G and H in the starting mixture) with $\bar{M}_n$ = 1000 daltons.

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Registry No. (1)(2) (copolymer), 103692-00-8; $(HSiMe_2NHSiMe_2H)(NH_3)$ (copolymer), 103692-02-0; $Ru_3(CO)_{12}$, 15243-33-1; $H_4Ru_4(CO)_{12}$, 34438-91-0; $Fe(CO)_5$, 13463-40-6; $Fe_3(CO)_{12}$, 17685-52-8; $Os_3(CO)_{12}$, 15696-40-9; $H_2Os_3(CO)_{10}$, 41766-80-7; $Rh_6(CO)_{16}$, 28407-51-4; $Ir_4(CO)_{12}$, 18827-81-1; Pt, 7440-06-4; C, 7440-44-0; PtO_2, 1314-15-4; $AlCo_3$, 7446-70-0; H_2SO_4, 7664-93-9.

Kinetics of the Thermal Rearrangement of Chloromethyldimethylsilane: Some Observations on 1,2-Shifts in Silicon-Containing Radicals

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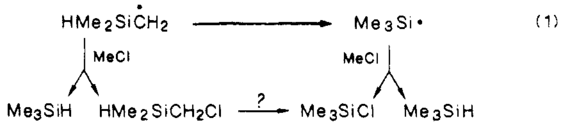
The kinetics of the thermal rearrangement of chloromethyldimethylsilane to trimethylchlorosilane have been measured alone, in the presence of several traps for reactive intermediates and in the presence of a radical source. The role and energetics of 1,2-shifts in α-silylmethyl or silyl radicals in the mechanism of rearrangement of this and other chloromethylsilane are discussed.

Introduction

Gas kinetic measurements in the pyrolysis of allyltrimethylsilane with and without added methyl chloride enabled two concurrent primary processes to be distinguished, viz., radical-forming homolysis and retroene elimination of dimethylsilene.[1] These methods have been applied to the mechanism of pyrolysis of a number of other alkenylsilanes, including 4-(dimethylsilyl)-1-butene;[2] this butenylsilane dissociates to give an allyl radical and

Scheme I



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$\cdot CH_2SiHMe_2$. Trapping with methyl chloride gave significant quantities of Me_3SiCl, suggesting that $\cdot CH_2SiHMe_2$ had rearranged to $Me_3Si\cdot$ but, as shown in Scheme I, that conclusion would only be valid if there was no direct or radical-induced rearrangement of chloromethyldimethylsilane (I) to trimethylchlorosilane. When that question was tested under the conditions used for the pyrolysis of 4-(dimethylsilyl)-1-butene, the amount of Me_3SiCl formed was found to be trivial compared to that formed by the reaction of $Me_3Si\cdot$ radicals with methyl chloride. Computer modeling of the experimental yield of Me_3SiCl then enabled the Arrhenius parameters of reaction 1 to be estimated as log $A \simeq 13.5$ and $E \simeq 41$ kcal·mol^{-1}; a similar energy barrier of 42.6 kcal·mol^{-1} for reaction 1 was deduced from an ab initio calculation.[2]

Although thermal rearrangement of I was unimportant in that context, our interest in it was aroused, prompting the kinetic investigation reported here. Our results complement earlier studies of the radical-induced rearrangement of I[3] and of the thermal rearrangement of other α-substituted silanes,[4] shedding some light on the role and energetics of 1,2-shifts in α-silylmethyl and silyl radicals. The related $AlCl_3$-catalyzed rearrangement of chloromethylsilanes is, of course, a classic reaction in organosilicon chemistry.[5] After this paper was submitted, we learnt that another paper on the thermal rearrangement of I was in press.[6]

Results

Chloromethyldimethylsilane (I) was pyrolyzed in our stirred-flow (SFR) apparatus with nitrogen carrier gas between 467 and 550 °C. The reaction was very clean, with a material balance of ca. 99%; Me_3SiCl was by far the major product, other products (all <2%) being $ClCH_2SiMe_2Cl$, methane, Me_3SiH, and $ClCH_2SiMe_3$. Over a wide range of initial pressure of I, from 0.04 to 15 mmHg, formation of Me_3SiCl closely obeyed first-order kinetics, with Arrhenius parameters given by log $A = 12.5 \pm 0.3$ and $E = 49.5 \pm 1.2$ kcal·mol^{-1}. The kinetics of formation of Me_3SiCl were unaffected by added methanol, methyl chloride, toluene, butadiene, or propene, each in 10-fold excess. No new products were detected in any of these "trapping" experiments nor in others with a 30-fold excess of butadiene or a 200-fold excess of propene. Similar results were obtained in some experiments by low-pressure pyrolysis (LPP); in these experiments added water was also shown to have no effect on the kinetics and product composition.

For comparison with earlier work on the radical-induced decomposition,[3] mixtures of dimethylmercury and I were pyrolyzed at 470 °C. The main effect of the dimethylmercury was to increase the rate of formation of Me_3SiCl, but a small amount of $EtSiMe_2Cl$ was also formed together with more methane and some ethane, both resulting from the presence of methyl radicals. The rate constant for formation of Me_3SiCl in the pyrolysis of I alone was 0.0087 s^{-1} at 470 °C; in a 10:1 mixture of I and dimethylmercury the rate constant was 0.0253 s^{-1}, increasing to 0.0533 s^{-1} in a 1:10 mixture.

A few experiments were done in the SFR on the pyrolysis of chloromethyltrimethylsilane (II), with product analysis by GC/mass spectrometry. II was less thermally labile than I, only undergoing ca. 10% decomposition at 555 °C. The main products were $EtSiMe_2Cl$, Me_4Si, methane, and ethene in comparable proportions; minor products were $ClCH_2SiMe_2Cl$, Me_3SiCl,Me_2SiCl_2, Me_3SiH, $MeSiCl_3$, propene, methyl chloride, and possibly some $ClCH_2SiMeEtCl$.

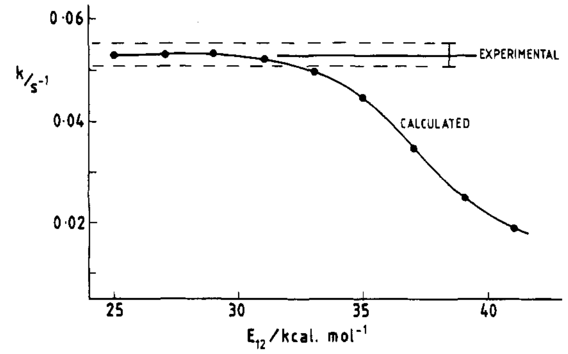
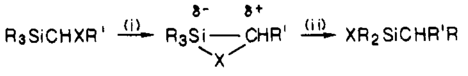


Figure 1. Comparison of experimental and calculated rate constants for formation of Me_3SiCl in copyrolysis of I and Me_2Hg (1:10).

Discussion

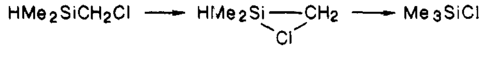
Brook and his co-workers investigated thermal rearrangements of a number of α-substituted silanes, $R_3SiCHXR'$, by pyrolyzing them in sealed tubes at temperatures up to 330 °C. Generally, they found clean exchange of X and R groups between carbon and silicon, although other products indicative of some mechanistic complexity were observed when R was Br.[4] They concluded that the rearrangement was not a radical process but proceeded by the unimolecular formation of an "inverse ylide" by migration of X from carbon to silicon via a cyclic transition state, thus



$$R_3SiCHXR' \xrightarrow{(i)} \overset{\delta-}{R_3Si}\text{—}\overset{\delta+}{CHR'}\ (\text{X bridging}) \xrightarrow{(ii)} XR_2SiCHR'R \qquad (2)$$

The authors envisaged step 2(i) as rate determining, followed by the rapid migration of R from silicon to carbon. They considered the kinetic data and observed migratory aptitudes to be inconsistent with the double-bridged transition state required for simultaneous migration of X and R in a dyotropic rearrangement.[7] They did not study any of the compounds pyrolyzed by us nor any compound with a silicon–hydrogen bond; the closest parallel to our work is Ph_3SiCH_2Cl, which had a rate constant for rearrangement at 330 °C of 4.5×10^{-5} s^{-1}. The migratory aptitude of Ph was found to be greater than that of Me.

We found that the first-order kinetics and product composition for the pyrolysis of I were insensitive to added traps for radicals, silenes, or silylenes; the clear conclusion is that the pyrolysis proceeds mainly by a unimolecular rearrangement. The Arrhenius parameters are similar to those for elimination of a silylene from chlorodisilanes, envisaged as proceeding by Cl migration via a three-center transition state (Arrhenius parameters for that process were in the range of log $A = 11.7$–12.5 and E/kcal·mol^{-1} = 46–50).[8] The simplest conclusion is that formation of Me_3SiCl should be represented by reaction 3, analogous



$$HMe_2SiCH_2Cl \longrightarrow \underset{\text{Cl}}{HMe_2Si\text{—}CH_2} \longrightarrow Me_3SiCl \qquad (3)$$

to reaction 2. Note that H migration occurs rather than

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Table I. Reaction Scheme for Modeling the Radical-Induced Decomposition of I

no.					
a	b	reaction[i]	log A	E/kcal·mol^{-1}	ref
i	3	A → B	12.5	49.5	c
ii		C → D	16.5	59.0	d
iii	4	A + D → E + F	8.1	7.2	e
iv	5	A + F → G + H	7.6	4.1	e, f
v	1	H → I	13.5	41.0	e
vi	10	A + I → H + J	7.6	4.1	e
vii	12	F → JJ	13.5	25.0	g
viii	13	A + JJ → Q + F	8.1	7.2	e
ix		F + D → L	9.0	0	h, f
x		JJ + D → M	9.0	0	h
xi		H + D → N	9.0	0	h
xii		I + D → O	9.0	0	h, f
xiii		D + D → P	10.3	0	h
xiv		I → H	13.5	50	e, f
xv		JJ + C → Q	8.8	7.2	e
xvi		A + D → H + T	8.0	9.1	e
xvii		A + D → S + E	8.8	9.6	e
xviii		A + D → R + E	8.5	9.6	e
xix		R → F	13.5	41.0	e, f
xx		F → R	13.5	50.0	e, f
xxi		S → F	13.5	41.0	e
xxii		F → S	13.5	50.0	e, f
xxiii		JJ + A → S + Q	8.8	9.6	e
xxiv		JJ + A → R + Q	8.5	9.6	e, f
xxv		S + Q → JJ + A	8.8	9.6	e
xxvi		R + Q → JJ + A	8.5	9.6	e, f
xxvii		S + A → A + F	8.1	7.2	e
xxviii		A + F → S + A	9.8	14.3	e, f
xxix		S + B → JJ + A	8.98	9.6	e, f
xxx		S + J → JJ + A	8.98	9.6	e, f
xxxi		S + E → A + D	8.5	9.6	e
xxxii		R + D → A + D	8.5	9.6	e, f
xxxiii		S + C → A	8.5	9.6	e
xxxiv		S + A → U + H	8.0	9.1	e
xxxv		S + S → V	9.0	0	h, f
xxxvi		R + A → A + F	8.1	7.2	e
xxxvii		A + F → R + A	9.5	17.9	e, f
xxxviii		R + B → JJ + A	8.5	9.6	e, f
xxxix		R + J → JJ + A	8.5	9.6	e, f
xl		R + C → A	8.8	9.6	e
xli		R + A → W + H	8.0	9.1	e, f
xlii		R + R → X	9.0	0	h, f
xliii		A → H + Y	15.0	81.	h, f
xliv	6	A + H → Z + F	8.1	7.2	e
xlv		A + Y → AA + F	9.0	0	h, f
xlvi		JJ + A → G + H	8.0	9.1	e, f
xlvii		G + H → JJ + A	8.0	9.1	e, f
xlviii		JJ + E → Q + D	8.5	9.6	e, f
xlix		A + H → R + Z	8.5	9.6	e
l		A + H → S + Z	8.8	9.6	e
li		JJ + JJ → BB	9.0	0	h, f
lii		JJ + S → CC	9.0	0	h, f
liii		JJ + R → DD	9.0	0	h, f
liv		JJ + H → EE	9.0	0	h, f
lv		R + S → FF	9.0	0	h
lvi		S + D → GG	9.0	0	h
lvii		S + H → HH	h, f	0.	h, f
lviii		R + H → II	9.0	0	h, f
lix		H + H → JJJ	9.0	0	h, f
lx		R + D → LL	9.0	0	h

[a] Reaction numbers used in computer modeling. [b] Corresponding reaction numbers in text. [c] This work (experimental). [d] Kominar, R. J.; Price, S. J. *Can. J. Chem.* **1969**, *47*, 991 (experimental). [e] Estimated from similar modeling sequence in ref 2. [f] Rate < 10% rate of reaction 3. [g] See text. [h] Estimated from: Benson, S. W. *Thermochemical Kinetics*, 2nd ed; Wiley: New York. [i] A, $ClCH_2SiMe_2H$; B, Me_3SiCl from reaction 3; C, Me_2Hg; D, Me·; E, CH_4; F, $ClCH_2Si(Me_2)\cdot$; G, $ClCH_2SiMe_2Cl$; H, $\cdot CH_2SiMe_2H$; I, $Me_3Si\cdot$; J, Me_3SiCl from reaction 10; JJ, $\cdot CH_2SiMe_2Cl$; L, $ClCH_2SiMe_3$; M, $ClCH_2SiMe_2Et$; N, $EtMe_2SiH$; O, Me_4Si; P, C_2H_6; Q, Me_3SiCl from reactions other than (3) and (10); R, $\cdot CH(Cl)SiMe_2H$; S, $ClCH_2SiHMeCH_2\cdot$; T, MeCl; U, $ClCH_2SiMeHCl$; V, $(ClSiMeHCH_2)_2$; W, $Cl_2CHSiMe_2H$; X, $(HMe_2SiCHCl)_2$; Y, Cl·; Z, Me_3SiH; AA, HCl; BB, $(ClSiMe_2CH_2)_2$; CC, $(ClSiMeClCH_2)_2$; DD, $HSiMe_2CH(Cl)CH_2SiMe_2Cl$; EE, $ClSiMe_2CH_2CH_2SiMe_2H$; FF, $HMe_2SiCH(Cl)CH_2SiMe(H)CH_2Cl$; GG, $ClCH_2SiMeEtH$; HH, $HMe_2SiCH_2CH(Cl)SiMe_2H$; II, $HMe_2SiCH_2CH(Cl)SiMe_2H$; JJJ, $(HMe_2SiCH_2)_2$; LL, $MeCH(Cl)SiMe_2H$.

Me migration. Our experiments do not enable us to comment on the charge separation in the transition state, which might simply be thought of as involving pentacoordinate silicon.

In contrast to the foregoing, our experiments on the radical-induced decomposition of I gave significantly different results from those of Jung and Weber.[3] In sealed-tube experiments at 136 °C these authors found that the main initial products were equimolecular amounts of $\mathrm{Me_3SiH}$ and $\mathrm{ClCH_2SiMe_2Cl}$; later in the reaction these products decreased while $\mathrm{Me_3SiCl}$ became the main product. Their results were very reasonably interpreted in terms of two consecutive radical chain sequences, reactions 4–6 being followed by reactions 7–9. Under these

$$\mathrm{ClCH_2SiMe_2H + R\cdot \rightarrow ClCH_2\dot{S}iMe_2 + RH} \quad (4)$$

$$\mathrm{ClCH_2SiMe_2H + ClCH_2\dot{S}iMe_2 \rightarrow ClCH_2SiMe_2Cl + \cdot CH_2SiMe_2H} \quad (5)$$

$$\mathrm{ClCH_2SiMe_2H + \cdot CH_2SiMe_2H \rightarrow ClCH_2\dot{S}iMe_2 + Me_3SiH} \quad (6)$$

$$\mathrm{Me_3SiH + R\cdot \rightarrow Me_3Si\cdot + RH} \quad (7)$$

$$\mathrm{ClCH_2SiMe_2Cl + Me_3Si\cdot \rightarrow \cdot CH_2SiMe_2Cl + Me_3SiCl} \quad (8)$$

$$\mathrm{Me_3SiH + \cdot CH_2SiMe_2Cl \rightarrow Me_3Si\cdot + Me_3SiCl} \quad (9)$$

conditions were was no need to postulate 1,2-shifts in α-silylmethyl or isomeric silyl radicals in either direction:

$$\mathrm{\cdot CH_2SiMe_2R \rightleftharpoons RCH_2\dot{S}iMe_2} \quad (\mathrm{R = H, Cl})$$

Such shifts have been shown by Wilt et al.[9] not to occur in $\mathrm{Ph_3SiCH_2\cdot}$, $\mathrm{PhMe_2SiCH_2\cdot}$, and $\mathrm{Me_3SiCH_2\cdot}$ radicals generated in the liquid phase at 150 °C. In an ingenious competitive experiment on a cyclic biradical generated between 205 and 235 °C, Ashe[10] found that a 1,2-H shift from carbon to carbon did not occur, while a 1,2-$\mathrm{SiMe_3}$ shift did; he estimated that the activation energy for the latter was at least 13 kcal·mol^{-1} lower than that for the H shift. We suggest that the size of the activation energy for 1,2-shifts is the key to explaining the difference between earlier results[3] and ours.

There is no doubt that $\mathrm{Me_3SiCl}$ was the predominant product at all stages in our radical-induced decomposition of I at 470 °C. One reason for the difference from earlier results[3] is that reactions 4 and 5 would be followed by the new chain sequence, reactions 1 and 10. Our estimated

$$\mathrm{\cdot CH_2SiMe_2H \rightarrow Me_3Si\cdot} \quad (1)$$

$$\mathrm{ClCH_2SiMe_2H + Me_3Si\cdot \rightarrow \cdot CH_2SiMe_2H + Me_3SiCl} \quad (10)$$

Arrhenius parameters for the 1,2-H shift, reaction 1, give $k_1 = 27.5\ \mathrm{s^{-1}}$ (i.e., a half-life of 25 ms) at 470 °C, as opposed to a negligibly low value ($4 \times 10^{-9}\ \mathrm{s^{-1}}$) at 136 °C, illustrating our point that such reactions are important at high temperature but not at low.[3,9]

An alternative reaction of the $\mathrm{\cdot CH_2SiMe_2H}$ radical is unimolecular dissociation:

$$\mathrm{\cdot CH_2SiMe_2H \rightarrow CH_2{=}SiMeH + Me\cdot} \quad (11)$$

Arrhenius parameters for this type of reaction have been estimated[11] as $\log A = 15$ and $E = 50$ kcal·mol^{-1}, giving $k_{11} = 1.96\ \mathrm{s^{-1}}$ at 470 °C, 14 times smaller than k_1. Reaction 11 is therefore relatively unimportant.

A further possibility in the radical-induced decomposition of I is that the $\mathrm{ClCH_2Si(Me_2)\cdot}$ radical formed in reaction 4 may undergo a 1,2-Cl shift from carbon to silicon (reaction 12). A few experiments on the radical-induced

$$\mathrm{ClCH_2\dot{S}iMe_2 \rightarrow \cdot CH_2SiMe_2Cl} \quad (12)$$

decomposition of I some years ago[12] prompted us to draw attention to the possible occurrence of reaction 12.

In the formation of silylenes from disilanes by 1,2-shifts, Cl migration is ca. 100 times slower than H migration.[8] ΔH is approximately constant in those reactions, but while $\Delta H_1 \simeq -8$ kcal·mol^{-1}, $\Delta H_{12} \simeq -30$ kcal·mol^{-1}, from bond dissociation energies.[13] A second chain sequence forming $\mathrm{Me_3SiCl}$ by reactions 12 and 13 should therefore be considered, especially as $\mathrm{ClCH_2SiMe_2Cl}$ (the product of reaction 4) was not detected in significant amount.

$$\mathrm{ClCH_2SiMe_2H + \cdot CH_2SiMe_2Cl \rightarrow Me_3SiCl + ClCH_2\dot{S}iMe_2} \quad (13)$$

This possibility was investigated by numerical integration of the extensive sequence of reactions given in Table I. Reactions with rates < 10% rate of reaction 3, identified by footnote *f* in Table I, did not affect the results; an abridged sequence omitting these reactions satisfactorily accounted for the observed product formation in the copyrolysis of I with dimethylmercury and was also consistent with our conclusion that radical reactions are trivial compared to reaction 3 in the absence of dimethylmercury.

Not only was reaction 12 found to be necessary in order to model the experimental results for the copyrolysis of I with dimethylmercury, but a lower limit could be calculated for k_{12}. Assuming that A_{12} was lower than A_1, by analogy with silylene formation from disilanes,[8] the activation energy for reaction 12 was estimated to be ≤30 kcal·mol^{-1} by matching the computed and experimental effects of dimethylmercury on the rate constant for formation of $\mathrm{Me_3SiCl}$, as shown in Figure 1. Similar calculations relating to the 10:1 mixture gave the same result.

The activation energies for 1,2-shifts from silicon to carbon in α-silylmethyl radicals are comparable to those for silenes isomerizing to silylenes:

$$\mathrm{RHSi{=}CH_2 \rightarrow H\ddot{S}iCH_2R}$$

For R = $\mathrm{SiH_3}$, H, and Me, activation energies have been calculated to be 26, 42, and 55 kcal·mol^{-1}, respectively.[14] The activation energy for the 1,2-$\mathrm{SiMe_3}$ shift in reaction 14 has been measured[15] as 22 kcal·mol^{-1}, while E_1, as noted

$$\mathrm{\cdot CH_2Si(Me_2)SiMe_3 \rightarrow Me_3SiCH_2\dot{S}iMe_2} \quad (14)$$

above, is 41 kcal·mol^{-1}. A 1,2-Me shift in an α-silylmethyl radical is likely to have an activation energy significantly greater than 41 kcal·mol^{-1}. With that possibility in mind, we may comment on our few experiments with II.

In the pyrolysis of II, the equivalent to reaction 2 would give $\mathrm{EtSiMe_2Cl}$, which was indeed a major product. However, as there were comparable amounts of several other products, it is likely that $\mathrm{EtSiMe_2Cl}$ was formed mainly or entirely in a radical sequence involving the 1,2-Me shifts, reactions 17 and 19, and the 1,2-Cl shift, reaction 20. In the radical-induced decomposition of I,

$$\mathrm{ClCH_2SiMe_3 \rightarrow \cdot CH_2SiMe_3 + Cl\cdot} \quad (15)$$

$$\mathrm{ClCH_2SiMe_3 + \cdot CH_2SiMe_3 \rightarrow Me_4Si + ClCH_2Si(Me_2)\dot{C}H_2} \quad (16)$$

$$\mathrm{\cdot CH_2SiMe_3 \rightarrow Et\dot{S}iMe_2} \quad (17)$$

$$\mathrm{ClCH_2SiMe_3 + Et\dot{S}iMe_2 \rightarrow EtSiMe_2Cl + \cdot CH_2SiMe_3} \quad (18)$$

$$\mathrm{ClCH_2Si(Me_2)\dot{C}H_2 \rightarrow ClCH_2\dot{S}iMeEt} \quad (19)$$

$$\mathrm{ClCH_2\dot{S}iMeEt \rightarrow \cdot CH_2SiMeEtCl} \quad (20)$$

$$\mathrm{ClCH_2SiMe_3 + \cdot CH_2SiMeEtCl \rightarrow EtSiMe_2Cl + ClCH_2Si(Me_2)\dot{C}H_2} \quad (21)$$

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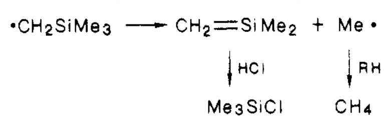
reaction 11 could be ignored relative to reaction 1. However, as reactions 17 and 19 would be significantly slower than reaction 1, unimolecular dissociation of α-silylmethyl radicals would contribute to the formation of products, e.g., eq 22. The most likely reaction of $CH_2{=}SiMe_2$ is addition



$$\begin{array}{ccccc} \cdot CH_2SiMe_3 & \longrightarrow & CH_2{=}SiMe_2 & + & Me\cdot \\ & & \downarrow{\scriptstyle HCl} & & \downarrow{\scriptstyle RH} \\ & & Me_3SiCl & & CH_4 \end{array} \qquad (22)$$

to the adventitious HCl invariably present in the pyrolysis of silicon–chlorine compounds.[16] Analogous reactions of $\cdot CH_2Si(Me_2)CH_2Cl$ and $\cdot CH_2SiMeEtCl$ would give rise to other observed products, viz., MeCl, $ClCH_2SiMe_2Cl$, C_2H_4 (from dissociation of Et· radicals), and Me_2SiCl_2. Another possible source of C_2H_4 is the 1,2-alkyl shift that competes with reaction 19, followed by a β-elimination:[17]

$$ClCH_2Si(Me_2)\dot{C}H_2 \rightarrow Me_2\dot{S}iCH_2CH_2Cl \rightarrow Me_2\dot{S}iCl + C_2H_4$$

The very minor amounts of other products in the pyrolysis of I would result from similar radical reactions, but the contrast between our detection of virtually a single product in the pyrolysis of I and a complex mixture including several products in comparable amounts in the pyrolysis of II provides clear evidence that unimolecular rearrangement was fast enough to compete successfully with radical processes in the case of I but not in the case of II under the experimental conditions used by us. As we found that Me_3SiCl did not react with water or methanol under these conditions, we were very probably observing homogeneous gas-phase reactions with no surface catalysis. As noted above, the size of the *A* factor and the close similarity of both Arrhenius parameters to those for the formation of a three-center transition state in the pyrolysis of chlorodisilanes seem to support the conclusion by Brook and co-workers that the unimolecular rearrangement of I to Me_3SiCl is rate-determined by a 1,2-Cl shift from carbon to silicon, as shown in eq 3. By analogy with the rearrangements in radicals discussed above, that strongly exothermic Cl shift would be expected to have a higher rate constant than the 1,2-H shift from silicon to carbon, which would in turn have a higher rate constant than the corresponding Me shift. The latter difference may have some bearing on our finding that I rearranged unimolecularly faster than II, but further work is needed to produce a clearer picture of the reaction coordinate for these interesting reactions; Brook and his co-workers[4] only studied R_3Si compounds, so the effect of substituents at silicon on the unimolecular rearrangement did not come to light in their work. Our Arrhenius parameters for the rearrangement of I give a rate constant at 330° C about one-tenth of that found by Brook for the rearrangment of Ph_3SiCH_2Cl; if that difference is significant, it may be a further pointer to substituent effects, but it may simply reflect the substantial difference in conditions between sealed-tube experiments and ours, whih were undertaken in a flow system with dry de-oxygenated nitrogen at ca. 1.5 atm as carrier gas.

Martin, Ring, and O'Neal[6] investigated the pyrolysis of I in a static system over a lower temperature range than ours, 363–417 °C. Our results are in substantial agreement with theirs, but they found that the radical chain sequence, induced in our experiments by added dimethylmercury, occurred concurrently with the unimolecular rearrangement in the pyrolysis of neat I under their conditions. They obtained separate Arrhenius parameters for each process by inhibiting the chain sequence with added propene and showed that the residual reaction in the presence of propene was unimolecular, being unaffected by added methyl bromide and hydrogen chloride. They also estimated from their results that $(E_{12} - E_5)$ was ca. 11 $kcal{\cdot}mol^{-1}$; as E_5 would be expected[18] to be ca. 4 kcal, that gives an estimate for E_{12} of ca. 15 $kcal{\cdot}mol^{-1}$, considerably less vague than ours of ≤ 30 $kcal{\cdot}mol^{-1}$.

Experimental Section

Chloromethyldimethylsilane was prepared by $LiAlH_4$ reduction of chloromethyldimethylchlorosilane (Cambrian Chemicals). Chloromethyltrimethylsilane was obtained commercially (Lancaster Synthesis). Purity was checked by gas chromatography and mass spectrometry. The SFR and LPP apparatus used for the kinetic experiments have been described previously.[1]

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