# Isomerization of Silylenes: Resolution of Discrepancies between Computer Modeling and Experiment

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It has recently become clear that some early conclusions about the mechanism of isomerization of silylenes were inconsistent with experiment. This paper demonstrates that these inconsistencies are eliminated by taking account of developments in the thermochemistry of organosilicon compounds and of the recent evidence, of considerable general significance in organosilicon chemistry, that the energy barrier for ring closure of long-chain silylenes to form three-membered rings is remarkably low.

## Introduction

Some fascinating reactions in organosilicon chemistry result from intramolecular rearrangements of silylenes. In 1984 we published our first attempts[1,2] to use kinetic estimates and computer modeling by numerical integration to complement experimental studies of some of these rearrangements, beginning with the isomerization of tetramethyldisilene to methyl(trimethylsilyl)silylene,[1] which leads ultimately to the formation of two isomeric 1,3-disiletanes as shown in Scheme I. Reactions 1–9 in Scheme I were suggested by Barton[3] to account for the fact that the two isomeric disiletanes **6** and **7** are the products when either the disilene[4] **1** or the silylsilylene[3] **2** is generated thermally. Irrespective of the precursor, the ratio [**7**]:[**6**] was at least 2, even although the silylene **5** would be formed from the disilirane **3** by a 1,2-methyl shift, whereas the silylene **4** leading to the minor disiletane **6** would be formed by the more favorable 1,2-hydrogen shift. This remarkable result was explained[3] by rapid equilibration between **3** and **4**. However, when we attempted to model the reactions in Scheme I, using the best kinetic estimates available at the time, we were unable to reproduce the experimental ratios of [**7**]:[**6**] without invoking the additional reactions 10–12 involving the silene **8**; these reactions also had sound precedents in organosilicon chemistry and appeared from our calculations to be the major route to the main disiletane **7**. That conclusion has recently been vitiated by the work of Gaspar and co-workers,[5] who obtained convincing evidence, by generating the deuteriated silylsilylene $Me_3SiSi(CD_3)$:, that the main route from **2** to **5** is via the disilirane **3** as originally suggested,[3] not via the silene **8**. They also found that the isomerization of **1** to **2** was reversible. Drastic revision of our kinetic estimates is therefore necessary, in relation both to the original study of methyltrimethylsilylene[1] and to that on bis(trimethylsilyl)silylene,[2] which was based on similar assumptions. We now report such a revision, made possible by recent developments in the understanding of the kinetics and thermodynamics of silylene chemistry. The implications for the mechanism of thermal reactions of silicon intermediates, especially disiliranes, are of some general interest.

Considering Scheme I, the energetics and kinetics of reactions 10–12, now known to be the minor route from **2** to **5**, require no revision from the 1984 estimates.[3] 1,2-Silyl shift from silicon to carbon, reaction 12, was first suggested by Barton 10 years ago and is now well established as a rapid reaction. The silylene ⇄ silene isomerization, reactions 10 and 11, has attracted the interest of both experimentalists[7,8] and theoreticians.[9] When Conlin and Wood[7] pyrolyzed 1-methylsiletane in the presence of butadiene, the only intermediate that they trapped was dimethylsilylene, $:SiMe_2$, leading them to conclude that the initially-produced silene isomerized rapidly and irreversibly to the silylene.

$$HMeSi{=}CH_2 \rightarrow :SiMe_2 \qquad (15)$$

This conclusion was at odds with theoretical calculations,[9] which would predict that reaction 15 was approximately thermoneutral, with an energy barrier in either direction of ca. 40.5 kcal mol$^{-1}$. Subsequent experiments in which $HMeSi{=}CH_2$ and $:SiMe_2$ were generated separately from different precursors in the presence of butadiene[8] gave results entirely consistent with the theoretical predictions, showing that the apparent irreversible isomerization to $:SiMe_2$ observed previously[7] was an artifact caused by differential rates of trapping of the silene and silylene intermediates by butadiene. Consequently, the original estimates of $\log A = 13.5$ and $E = 40.6$ kcal mol$^{-1}$ for the Arrhenius parameters of reaction 10 are still valid. It follows that the erroneous estimates of rate constants were in the other pathway through reactions 2–5. Reasons may be found in recent developments in organosilicon thermochemistry and in the energetics and kinetics of reactions involving silicon-containing three-membered rings.

Reaction 2, in which the disilirane **3** is formed, is an intramolecular insertion of a silylene into a C–H bond, with concomitant ring closure. In the absence of direct kinetic data for this type of reaction, the Arrhenius parameters could be estimated by taking the experimentally-measured Arrhenius parameters for a simple bimo-

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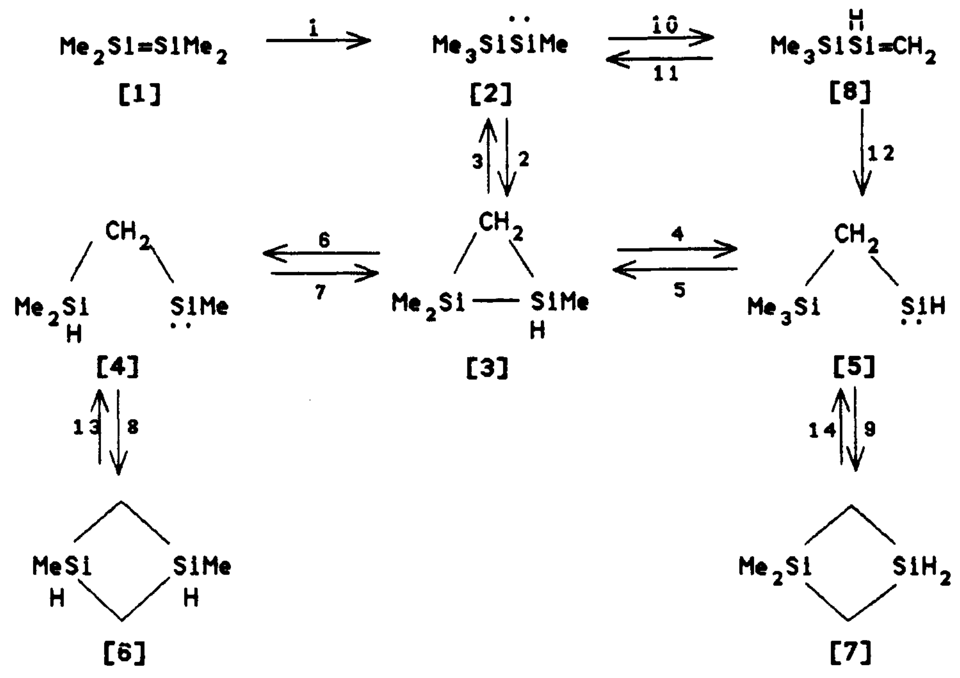
**Scheme I. Isomerization of $Me_2Si{=}SiMe_2$**



lecular silylene-forming reaction, e.g.

$$MeSiH_3 \rightarrow :SiH_2 + CH_4 \tag{16}$$

and then calculating Arrhenius parameters for the reverse insertion reaction from thermodynamic data, modified to take account of the constraints associated with intramolecular formation of a cyclic product. However, this calculation is not straightforward. There are very few reliable enthalpies of formation of silicon compounds; the best compilations are those made by Walsh, who has critically combined experimentally-measured dissociation energies with such calorimetric data as were available to produce series of self-consistent thermochemical tables.[10-13] Furthermore, experimental measurement of the kinetics of reaction 16 is complicated by the fact that it is not the main primary process in the pyrolysis of $MeSiH_3$; the main product is not $CH_4$ but $H_2$, formed in two parallel primary processes,[14] reactions 17 and 18; further complications arise from secondary reactions involving the reactive intermediates produced in reactions 16–18.

$$MeSiH_3 \rightarrow :(Me)SiH + H_2 \tag{17}$$

$$MeSiH_3 \rightarrow CH_2{=}SiH_2 + H_2 \tag{18}$$

From the best data available at the time,[10,14,15] the activation energy for insertion of $:SiH_2$ in the C–H bond of methane was estimated[1,14] to be ca. 19 kcal $mol^{-1}$. No ring strain values were available for disiliranes, but a figure of ca. 37.5 kcal $mol^{-1}$ had been calculated[16] for silirane; there was evidence that more strain was released on opening small silicon-containing rings than had to be overcome on ring-closure,[8] but it was assumed that the latter was appreciable and that the transition state for ring closure was quite tight.[17] Our calculations based on the foregoing gave $\log A = 12.6$ and $E = 39.4$ kcal $mol^{-1}$ for the Arrhenius parameters of reaction 2, thus making $k_2$ smaller than $k_{10}$ and favoring the route via 8 over that via 3 in Scheme I.

Several pieces of independent evidence now point to the conclusion that the formation of three-membered silicon-containing rings is substantially easier than was implied by these calculations. The only significant product when *n*-butylmethylsilylene was generated at 680 °C was 1-butene, with no ethene, propene, or any silacycloalkane.[18] Hence, as shown in Scheme II, cyclization to form a three-membered ring, reaction 19, is favored over formation of larger rings, reactions 21 and 22.

Further evidence comes from studies of the mechanism of addition of silylenes to dienes,[19] where the reaction of dimethylsilylene ($:SiMe_2$) with substituted 1,3-butadienes to form silacyclopentenes does not proceed by 1,4-addition but by concerted 1,2-addition to form a vinylsilirane, which then rearranges by bond homolysis and possibly also by a 1,3-silyl shift.[20]

Ring, O'Neal, and co-workers investigated the shock-induced decomposition of propylsilane and butylsilane.[21] These pyrolyses were at high temperature, forming a number of cyclic products, but those resulting from the formation of silirane intermediates were prominent. When thermally generated $:SiH_2$ was added to 1-butene at much

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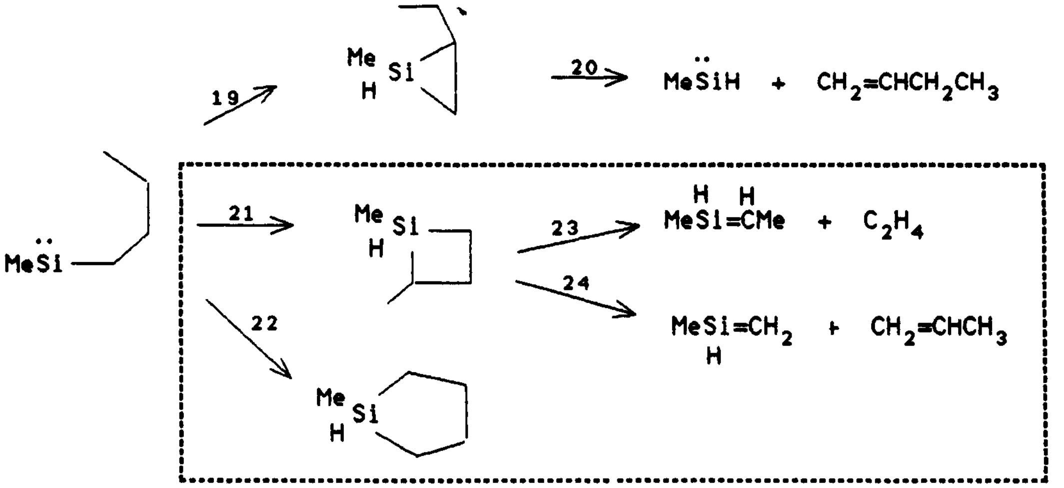
**Scheme II. Cyclization Reactions of a Butylsilylene**



**Scheme III. Silylene Addition to 1-Butene**

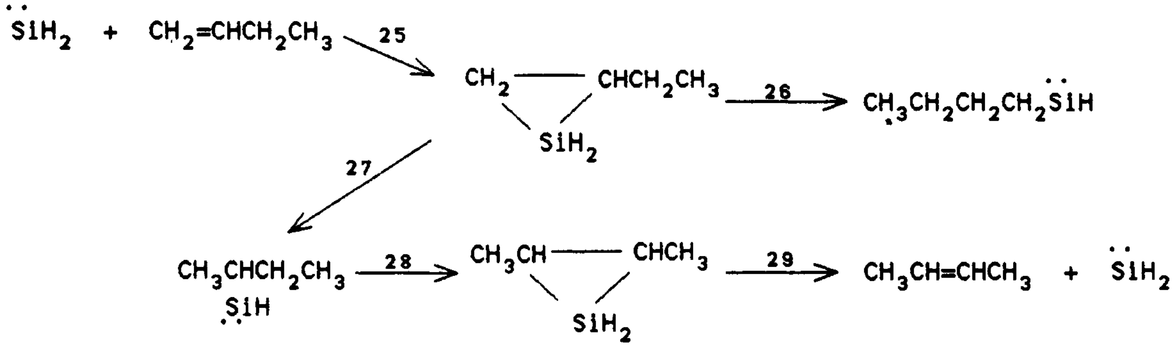


Table I. Arrhenius Parameters for Generic Reactions

| process | log $A/\mathrm{s}^{-1}$ | $E$/kcal mol$^{-1}$ |
|---|---|---|
| c | 12.3 | 10.4 |
| o | 14.0 | $14.7 + \Delta E$ |
| d | 16.9 | $26.1 + \Delta E$ |

Table II. Arrhenius Parameters for Reactions in Scheme I

| | calcd in this work | | taken from ref 1 | |
|---|---|---|---|---|
| reacn | log $A_{633\mathrm{K}}$ | $E$/kcal mol$^{-1}$ | log $A$ | $E$/kcal mol$^{-1}$ |
| 30 | 13.06 | 48.5 | | |
| 2 | 12.94 | 10.4 | 12.6 | 39.4 |
| 3 | 13.52 | 12.3 | 14.0 | 32.3–52.1 |
| 4 | 12.75 | 17.6 | 14.0 | 27.7–47.6 |
| 5 | 11.70 | 17.0 | 12.6 | 34.7 |
| 6 | 13.52 | 2.8 | 13.0 | 7.6–27.5 |
| 7 | 11.99 | 0 | 12.6 | 22.7 |
| 8 | 12.00 | 32.4 | 13.5 | 32.5 |
| 9 | 12.18 | 32.4 | 13.5 | 32.5 |
| 10 | 13.5 | 40.6 | 13.5 | 40.6 |
| 11 | 13.5 | 40.6 | 13.5 | 40.6 |
| 12 | 12.3 | 28.7 | 12.3 | 28.7 |
| 13 | 14.13 | 61 | 13.5 | 61 |
| 14 | 14.13 | 61.2 | 13.5 | 61 |

lower temperatures around 380 °C, all of the products were consistent with the formation of silirane intermediates as shown in Scheme III.[22,23] There were no products indicative of the formation of siletanes or larger rings, in agreement with Barton's results by flash vacuum pyrolysis.[18] Since such products were formed in the shock-induced experiments at higher temperatures,[21] it was concluded[22] that the activation energy for ring closure of a silylene by intramolecular hydrogen abstraction to form a silirane is lower than the activation energies for the equivalent processes forming larger rings by at least 10 kcal mol$^{-1}$. While considerable new information about the kinetics of the reactions in Scheme III was obtained from these experiments at lower temperature,[22] ambiguities and uncertainties remained, largely because the experiments were still in the unimolecular falloff region, as were the earlier shock tube studies.[14,21] Further experiments were therefore undertaken at high and constant total pressure. These experiments, complemented by computer modeling by numerical integration and consideration of the latest developments in the thermochemistry of silicon compounds and intermediates, gave clearer conclusions about the kinetics and energetics of the reactions involving siliranes in Scheme III.[23] Generic high-pressure Arrhenius parameters were derived for the three processes: ring-opening (o) to form a silyene, e.g. reactions 26 and 27, ring-closing (c) by silylene insertion into C–H, e.g. reaction 28, and decomposition (d) to form an alkene and a smaller silylene, e.g. reaction 29. These generic Arrhenius parameters are in Table I. $\Delta E$ is a ring strain correction factor, defined by $\Delta E = (49.6 - E_s)$ kcal mol$^{-1}$, where $E_s$ is the ring strain in the silirane ring, estimated to be 49.6 kcal mol$^{-1}$, whence $\Delta E = 0$; but if $E_s$ is lower, as indicated by theory,[16,24] then $\Delta E > 0$, requiring consequential adjustment of $E_o$ and $E_d$.

There are some striking features in Table I necessitating

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**Table III. Arrhenius Parameters for Reactions in Scheme IV**

| | calcd in this work | | taken from ref 2 | |
|---|---|---|---|---|
| reacn | log $A_{773K}$ | E/kcal·mol$^{-1}$ | log A | E/kcal·mol$^{-1}$ |
| 31 | 13.33 | 48.5 | | |
| 32 | 13.35 | 10.4 | 12.6 | 39.4 |
| 33 | 13.62 | 11.0 | 14.0 | 25.6 |
| 34 | 12.86 | 14.7 | 13.7 | 18.6 |
| 35 | 11.33 | 15.0 | 12.6 | 34.7 |
| 36 | 11.52 | 26.0 | 13.0 | 21.5 |
| 37 | 13.16 | 19.9 | 13.7 | 21.0 |
| 38 | 11.33 | 17.0 | 12.6 | 34.7 |
| 39 | 11.52 | 26.0 | 13.0 | 21.5 |
| 40 | 13.62 | 0.2 | 13.0 | 5.7 |
| 41 | 12.09 | 0 | 12.6 | 19.8 |
| 42 | 12.11 | 32.4 | 12.7 | 32.5 |
| 43 | 11.63 | 17.0 | 12.9 | 34.7 |
| 44 | 12.86 | 17.5 | 13.4 | 21.0 |
| 45 | 13.62 | 2.2 | 12.6 | 19.8 |
| 46 | 12.09 | 0 | 13.0 | 1.0 |
| 47 | 12.29 | 10.4 | | |
| 48 | 13.92 | 11.3 | | |
| 49 | 13.92 | 1.4 | | |
| 50 | 12.09 | 0 | | |
| 51 | 12.11 | 32.4 | | |
| 52 | 11.52 | 32.4 | | |
| 53 | 12.87 | 10.4 | | |
| 54 | 13.92 | 12.7 | | |
| 55 | 13.92 | 1.4 | | |
| 56 | 12.09 | 0 | | |
| 57 | 10.76 | 31.0 | | |
| 58 | 13.92 | 61.0 | | |
| 59 | 13.92 | 57.8 | | |
| 60 | 14.22 | 80.0 | | |
| 61 | 13.92 | 58.4 | | |
| 62 | 13.92 | 72.3 | | |
| 63 | 13.62 | 74.6 | | |

substantial revision of earlier kinetic estimates.[1,14] The high *A* factor for the decomposition process (d) implies a very loose transition state for that process and for the reverse one, the addition of a silylene to an alkene, in keeping with earlier evidence;[25] the transition state is envisaged as some kind of long-range complex in which the silylene is quite free to rock against the alkene. The consequences for the kinetics of addition of silylene to an alkene to form a silirane are that the *A* factor will be unusually high, accounting for Gaspar's observation that 1,2-addition to form a silirane is favored over 1,4-addition in the reaction of silylenes with 1,3-butadienes.[19]

The activation energy for the ring-closure process (c) is very much less than the value of 39.4 kcal mol$^{-1}$ arrived at previously[1] for reaction 2, because recent developments profoundly affect both the assumptions about thermochemistry and those about ring strain. Early estimates[1,14] of the thermochemistry of reaction 16 used −8.3 and 58 kcal mol$^{-1}$, respectively, for the enthalpies of formation of $MeSiH_3$ and $:SiH_2$; the most recent thermochemical estimates[12,13] now give −7.4 and 64.1 kcal mol$^{-1}$, respectively,[23] reducing the activation energy for the insertion of $:SiH_2$ into an acyclic carbon–hydrogen bond from ca. 19 kcal mol$^{-1}$ to ca. 10 kcal mol$^{-1}$. As this new value is essentially equal to $E_c$ in Table I, it follows that the ring-closure process (c) is also rather unusual, with no developments of ring strain in the transition state.

## Results and Discussion

**Table IV. Comparison of Calculated and Experimental Product Yields**

| | product | | | | | |
|---|---|---|---|---|---|---|
| | **5** | **7** | **10** | **13** | **14** | **17** |
| exptl[29] | 60 | ? | ? | 5 | 5 | ≤5 |
| calcd | 62.7 | 23.9 | 2.7 | 4.4 | 1.1 | 4.5 |

**Isomerization of Methyl(trimethylsilyl)silylene.** In recalculating the rate constants in Scheme I in the light of these developments, we simulated Gaspar's experiments by replacing reaction 1 with reaction 30, estimating its

$$(Me_3Si)_2\overset{H}{Si}Me \longrightarrow Me_3Si\ddot{Si}Me + Me_3SiH \qquad (30)$$

Arrhenius parameters by analogy with similar silylene-forming reactions.[26] Arrhenius parameters for the remaining reactions 2–14 were then recalculated using the methods of *Thermochemical Kinetics*,[27] taking into account the results in Table I. The original experimental results to be simulated were that [**7**]:[**6**] was[3] 1.9:1 at 973 K, rising[4] to 3:1 at 633 K; Arrhenius *A* factors were therefore calculated over this temperature range. The results are in Table II, with the original Arrhenius parameters for comparison.[1] *A* factors for each reaction were calculated by the standard methods of *Thermochemical Kinetics*,[27] while additivity tables developed by O'Neal[23] were used to calculate enthalpy changes. The value of $E_2$ was taken directly from Table I, while $E_5$ and $E_7$ were estimated as discussed above, taking into account the latest thermochemistry[12,13,28] and the negligible ring strain associated with silirane formation (disiliranes were assumed to be analogous to siliranes in this respect). First estimates of $E_3$, $E_4$, and $E_6$ were then made from the calculated $\Delta H$ values for each reversible reaction; minor adjustments not exceeding 2.5 kcal mol$^{-1}$ were made in $E_6$, to achieve agreement with the experimental values for [**7**]:[**6**]. The starting point for reactions 8, 9, 13, and 14 was the experimental value[1] of 61 kcal mol$^{-1}$ for $E_{13}$; activation energies for the other reactions were then calculated from the $\Delta H$ values, giving ca. 32 kcal mol$^{-1}$ for closure to form a siletane ring, in keeping with the somewhat surprising conclusion from Ring and O'Neal's work that the activation energies for closure to four- and five-membered rings are higher than for closure to three-membered rings.[23] As explained above, no changes were required in the Arrhenius parameters for reactions 10–12.

The new estimates in Table II reproduced the experimental ratios [**7**]:[**6**] very well, giving 3.0 at 633 K and 1.7 at 973 K. Sensitivity analysis confirmed that reactions 10–12 are of negligible importance, in complete agreement with Gaspar's experimental results;[5] reaction 10 is ca. $10^6$ times slower than the reversible reactions 2 and 3 at 973 K and nearly $10^{10}$ times slower at 633 K. Likewise, although reaction 12 is substantially more important than reaction 11, reaction 4 is more than $10^4$ times faster than reaction 12 at 973 K and more than $10^6$ times faster at 633 K. A further point revealed by the sensitivity analysis is that, in the pairs of reversible reactions involving the disilirane intermediate **3**, the model is much more sensitive to the activation energy *difference* (i.e. $\Delta H$ for each reaction pair) than to the absolute values of the activation energies; thus, varying $E_5$ between 6 and 17 kcal mol$^{-1}$ had little effect provided that $E_4 - E_5$ was kept at 0.6 kcal mol$^{-1}$.

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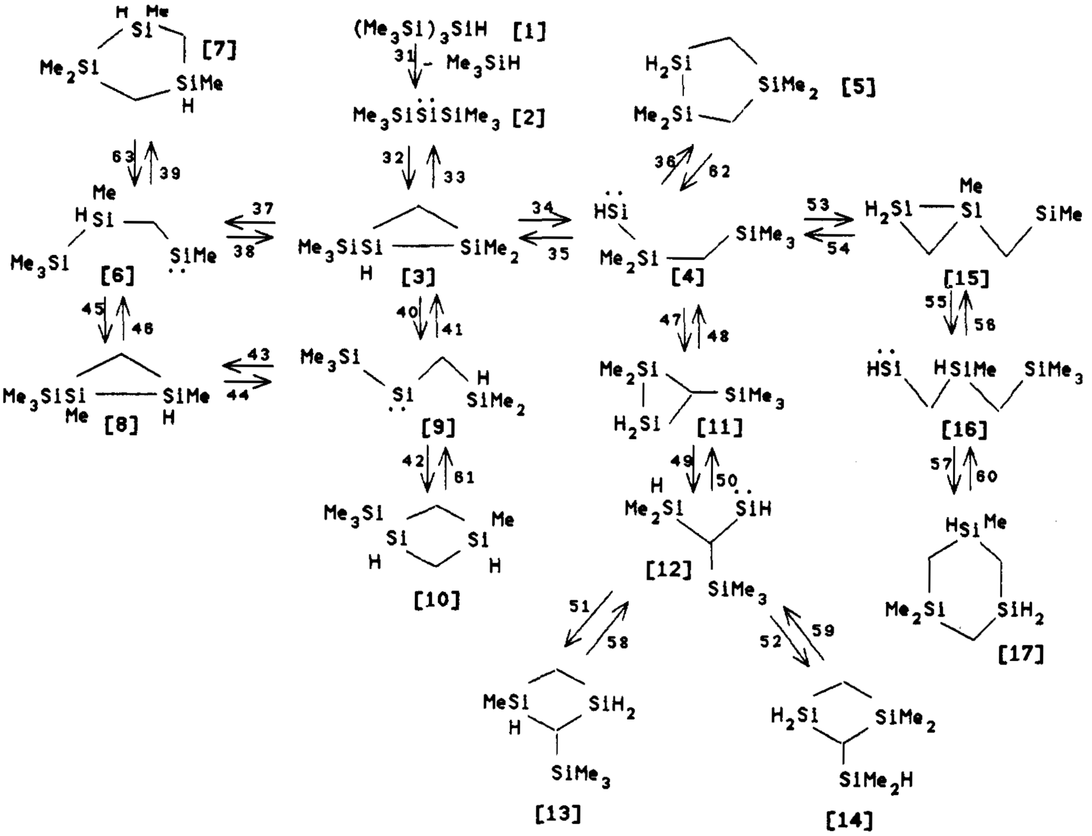
**Scheme IV. Isomerization of $(Me_3Si)_2Si$:**



**Isomerization of Bis(trimethylsilyl)silylene.** Thermal isomerization of this silylene in the gas phase at low pressure is remarkably specific;[29] although several products are formed, one of these was produced in 60% yield at 773 K.

Scheme IV is a modified and extended version of our original scheme, incorporating the relatively simple route to this product shown in the original[2] Scheme II (reactions 32–36 in ref 2), but that modeling must also now be revised in the light of the developments discussed above. The Arrhenius parameters are in Table III, calculated in the same way as for Scheme I, and consistent with those in Table II. Reaction 34, being in effect a trimethylsilyl shift from silicon to carbon, is a somewhat different process from the methyl shifts from silicon to silicon, reactions 37 and 44, and was given a slightly lower activation energy; it should be noted that this model, like the previous one, was much more sensitive to the activation energy differences for pairs of opposing reactions involving disilirane intermediates than to the absolute values of these activation energies.

The original parameters for the route to the main product, reactions 32–36, and for the other reactions in the earlier less comprehensive scheme are included in Table III for comparison.[2] The activation energies for silylene ring closure to siletanes, $E_{42}$, $E_{51}$, and $E_{52}$, were all set at 32.4 kcal mol$^{-1}$, as in Scheme I. Activation energies for the formation of the larger, less strained rings were set at 26 kcal mol$^{-1}$ for $E_{36}$ and $E_{39}$ and at 31 kcal mol$^{-1}$ for $E_{57}$. Activation energies for ring-opening were then calculated from the corresponding $\Delta H$ values. The results of these estimates are in Table IV. As with Scheme I, these revised Arrhenius parameters are consistent with the experimental results, reproducing very satisfactorily the formation of the main product **5** and the minor products.

Thus, the revised thermochemistry, and more particularly the revised estimates for the kinetics of ring closure of silylenes to form three-membered rings, remove the discrepancies between earlier calculations and experiment, providing a quantitative basis for understanding the intriguing reaction mechanisms discussed and referred to in this paper.

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