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Review

Silicon knocked into a cocked hat *

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Abstract

The propensity of silicon to form a three-membered ring intermediate (the "cocked hat" of the title) in preference to larger cyclic intermediates in many thermal reactions of organosilicon compounds is discussed in the light of recent developments in organosilicon kinetics and thermochemistry.

Introduction

In 1983 Alwyn Davies and his co-workers published two elegant contributions to the literature of organosilicon chemistry in which they used ESR spectroscopy to study the mechanism of cyclisation of alkenylsilyl radicals [1] and the ring-opening of silyl-substituted cyclopropylmethyl radicals [2]. The former study elucidated the factors controlling homolytic *exo* : *endo* cyclisation rates of radicals with the radical centre located on a second row element, while the latter gave valuable insight into the regioselectivity of ring-opening reactions in these three-membered ring systems.

Shortly afterwards, we described our first attempt to use kinetic estimates and computer modelling by numerical integration to complement our own experimental studies and those of others of reaction mechanisms in organosilicon chemistry [3]. We were also involved in the chemistry of three-membered rings in that work, because reactions forming and opening a simple disilirane were of central importance (the only stable disiliranes known at that time were highly substituted [4], but there was good indirect evidence for the involvement of simple disiliranes as short-lived intermediates in gas-phase thermolyses at high temperature [5,6]). The reactions involving the disilirane intermediate are shown in Scheme 1.

Reactions 1–9 in Scheme 1 are those suggested by Barton [7] to account for the experimental observation that the two isomeric disiletanes **6** and **7** are the products when either the disilene **1** [6] or the silylsilylene **2** [7] is generated thermally. In

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* Dedicated to Professor Alwyn G. Davies, a distinguished organometallic chemist and an admirable fellow-scientist.

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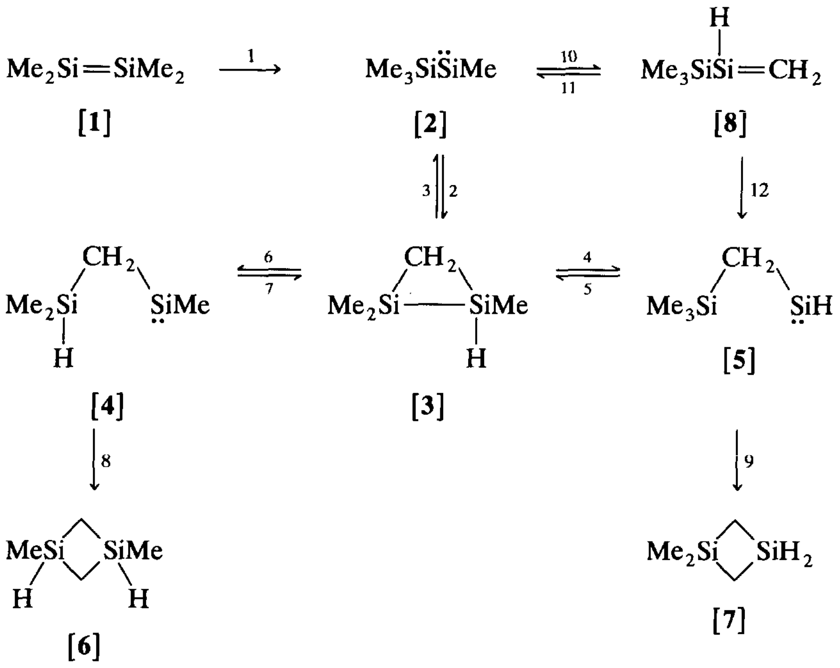

Scheme 1. Disilirane reactions.

either case, the ratio [7]:[6] ≥ 2. Barton pointed out [7] that this result was surprisingly since the silylene precursor **5** of the major disiletane **7** would be formed from the disilirane **3** by a 1,2-methyl shift, whereas the silylene precursor **4** of the minor disiletane **6** would be formed by the more favourable 1,2-hydrogen shift; he suggested that the explanation lay in a very rapid equilibration between **3** and **4**. However, when we attempted to model the reactions in Scheme 1, using the best kinetic estimates available at the time, we were unable to reproduce the experimental ratios [7]:[6] without invoking the additional reactions 10–12, involving the silene **8**; these reactions also had sound precedents in organosilicon chemistry and according to our calculations they were the major route to the main disiletane 7. Very recently, Gaspar and co-workers [8], by generating the deuterated silylsilylene $Me_3SiSi(CD_3)$:, obtained convincing contrary evidence that the main route from **2** to **5** is indeed *via* the disilirane **3** as originally suggested [7], and not *via* the silene **8**; incidentally, they also found evidence for the reversibility of the isomerisation of **1** to **2**.

There have been substantial advances in understanding the kinetics and thermodynamics of organosilicon reactions since 1984, especially in the last few years, with the result that if the calculations on the reactions in Scheme 1 were repeated today no conflict between experiment and calculation would be expected. * Although this is not an outstandingly important example in itself, it provides a

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* Note added in proof: this expectation has now been fulfilled (I.M.T. Davidson and C.H. Morgan, to be published).

convenient framework for reviewing these advances, especially as it is now such a simple matter to carry out numerical integrations on a microcomputer; if reasonably reliable kinetic estimates are available, computer modelling can be recommended as a valuable adjunct to experiment which deserves to be more widely used. This small review discussing some quantitative aspects of reaction mechanisms in organosilicon chemistry is offered as a tribute to the distinguished work on reaction mechanisms in Group IV chemistry undertaken by Alwyn Davies.

Discussion

The energetics and kinetics of reactions 10–12, now known to be the minor route from **2** to **5** in Scheme 1, require no revision from the 1984 estimates [3]. The 1,2-silyl shift from silicon to carbon, reaction 12, was first suggested by Barton 10 years ago [9], and is now well established as a rapid reaction. The silylene $\leftrightarrows$ silene isomerisation, reactions 10 and 11, attracted the interest of experimentalists and theoreticians around the same time. In 1982 Schaefer published his stimulating review "The Silicon–Carbon Double Bond: A Healthy Rivalry between Theory and Experiment" [10]. The title was well chosen, and still has continuing echoes [11], because silicon chemistry has benefited from lively and constructive exchanges between theoreticians and experimentalists. When Conlin and Wood [12] pyrolysed 1-methylsiletane in the presence of butadiene, the only intermediate which they trapped was dimethylsilylene, $:SiMe_2$; they concluded that a silene was produced initially, which isomerised rapidly and irreversibly to the silylene, thus:

$$HMeSi{=}CH_2 \longrightarrow :SiMe_2 \qquad (13)$$

Schaefer [10] pointed out that this conclusion was at odds with theoretical calculations, which would predict that reaction 13 was approximately thermoneutral, with an energy barrier in either direction of *ca.* 170 kJ mol^{-1}. Subsequent experiments in which $HMeSi{=}CH_2$ and $:SiMe_2$ were generated separately from different precursors in the presence of various amounts of butadiene over a wide temperature range resolved this paradox [13]. These later experiments gave results which were entirely consistent with the theoretical predictions, and which showed that the apparent irreversible isomerisation to $:SiMe_2$ observed previously [12] was an artefact caused by differential rates of trapping of the silene and silylene intermediates by butadiene. Consequently, the original estimates of $\log A = 13.5$, $E = 170$ kJ mol^{-1} for the Arrhenius parameters of reaction 10, the rate-determining step of this pathway in Scheme 1, are still valid. It follows that the estimates of rate constants for the other pathway through reactions 2–5 were erroneous. Reasons may be found in recent developments in organosilicon thermochemistry and in some unforeseen features of the energetics and kinetics of reactions involving silicon-containing three-membered rings.

A crucial step in the whole series of reactions 2–7 is reaction 2, in which the disilirane **3** is formed. This reaction involves an intramolecular insertion of a silylene into a C–H bond, with concomitant ring closure. Estimates of its Arrhenius parameters could in principle be made from the Arrhenius parameters of a "normal" bimolecular silylene insertion into C–H, modified to take account of the energetic and entropic constraints of forming a cyclic product intramolecularly. Since 1985, some absolute rate constants for reactions of photolytically-generated silylene, $:SiH_2$, have been obtained from fast time-resolved studies by Inoue and Suzuki [14], Jasinski and co-workers [15], and Frey, Walsh and their co-workers [16]. However, most of these measurements were at room temperature only, and in any case none was available in 1984; at that time, the only possibility was to estimate Arrhenius parameters for a silylene insertion reaction by combining thermodynamic data with the experimentally-measured Arrhenius parameters for the reverse silylene-forming reaction, *e.g.*:

$$MeSiH_3 \longrightarrow :SiH_2 + CH_4 \tag{14}$$

Neither step in this calculation is straightforward. There are very few reliable experimentally-measured enthalpies of formation of silicon compounds, and it has been difficult to deduce the thermochemistry of organosilicon compounds and intermediates from these limited data and from bond dissociation energies; much the most successful efforts over the past decade have been made by Walsh, who has carefully and critically combined the most reliable experimentally-measured dissociation energies, largely from his own laboratory, with such calorimetric data as were available to produce valuable series of self-consistent thermochemical tables which have been the best available at the time in question [17–20].

Experimental measurement of the kinetics of reaction 14 is complicated by the fact that it is not the main primary process; the main product is not CH_4 but H_2, formed in two parallel primary processes [21], reactions 15 and 16; further complications arise from secondary reactions involving the reactive intermediates produced in reactions 14–16.

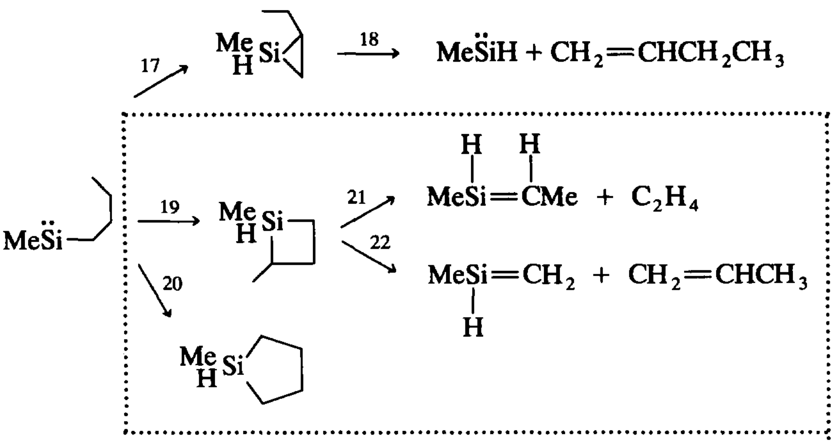
$$MeSiH_3 \longrightarrow :(Me)SiH + H_2 \tag{15}$$

$$MeSiH_3 \longrightarrow CH_2{=}SiH_2 + H_2 \tag{16}$$

The earliest kinetic studies of the pyrolysis of $MeSiH_3$ attempted to circumvent the problem of secondary reactions by quenching them with ethene in pyrolyses at low conversion [22], or by carrying out the pyrolysis at low pressure [23]. The most complete study [21] was done in a shock tube, using a competitive technique with very low partial pressures of $MeSiH_3$.

From the best data available at the time [17,21,23], we [3] and others [21] estimated that the activation energy for insertion of $:SiH_2$ in the C–H bond of methane was *ca.* 80 kJ mol^{-1}. To estimate Arrhenius parameters for reaction 2, we had then to take account of ring strain; no values were available for disiliranes, but a figure of *ca.* 157 kJ mol^{-1} for the ring strain of silirane had been calculated by Gordon [24], who has continued to produce valuable information derived from *ab initio* calculations [25]. There was evidence that more strain was released on opening small silicon-containing rings than had to be overcome on ring-closure [13], but it was assumed that the latter factor was not negligible, and that the transition state for ring closure was quite tight [26]. Our calculations based on the foregoing gave $\log A = 12.6$, $E = 165$ kJ mol^{-1} for the Arrhenius parameters of reaction 2, thus making k_2 smaller than k_{10} and favouring the route *via* **8** over that *via* **3** in Scheme 1.

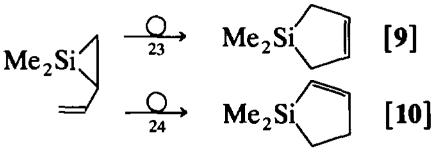
Subsequently, evidence has accumulated that the formation of three-membered silicon-containing rings is substantially easier than was implied by these calculations. A striking example comes from the work of Barton and Burns, who found



Scheme 2. Cyclisation reactions of a butylsilylene.

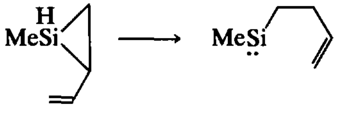
that the only significant product when *n*-butylmethylsilylene was generated at 680°C was 1-butene, with no ethene, propene, or any silacycloalkane [27]. As shown in Scheme 2, that result clearly shows that cyclisation to form a three-membered ring, reaction 17, is favoured over formation of larger rings, reactions 19 and 20, notwithstanding the greater thermal stability and lower ring strain of the latter.

Further important evidence comes from studies of the mechanism of addition of silylenes to dienes. Seminal work by Gaspar has elegantly demonstrated that 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 followed by rearrangement of the resulting vinylsilirane as summarised in Scheme 3 [28].



Scheme 3. Isomerisation of a vinylsilirane.

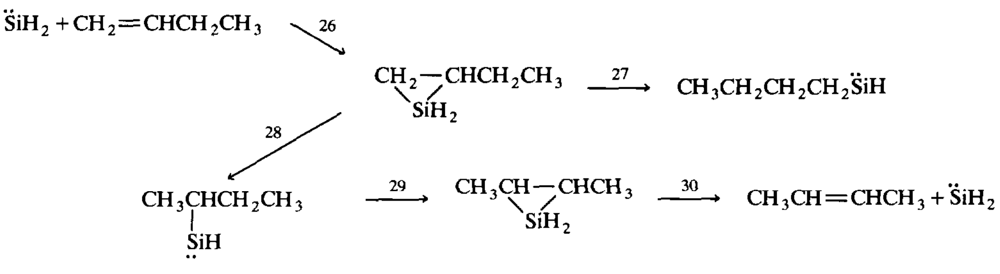
Product **10** may be envisaged as being formed by C–C bond rupture in the silirane followed by ring-closure of the resulting biradical; a similar process initiated by Si–C bond rupture would give product **9**, but **9** was the major product whereas there is no doubt that the Si–C bond is stronger than C–C, at least in acyclic organosilicon compounds [17]; a direct 1,3-silyl shift has therefore been suggested as an alternative [29]. Addition of :(Me)SiCl proceeds similarly, but there are new reaction pathways with :(Me)SiH because siliranes with hydrogen attached to silicon, like the corresponding siletanes [13], can undergo [29] an alternative ring-opening by a 1,2-hydrogen shift to form a silylene, thus:



(25)

It has recently been shown that the Gaspar mechanism [28] is also followed by silylenes with bulky mesityl [30] and adamantyl [31] groups attached to silicon, notwithstanding some earlier indications to the contrary [32], in keeping with calculations suggesting that silylenes with bulky alkyl substituents will continue to have the singlet as their ground state; the most likely silylenes to have triplet ground states are bis(trialkylsilyl)silylenes with alkyl groups larger than methyl [33]. It was possible to prepare stable 2-vinylsiliranes by adding dimesitylsilylene to dienes [34], and stable 1,1-di-tert-butyl siliranes have also been synthesised, including the first silirane with no substituents on carbon. Interestingly, neither photolysis nor thermolysis of the latter disilirane generated free di-tert-butyl silylene, while the homologue with one methyl group attached to carbon gave di-tert-butyl silylene on photolysis only [35].

As part of their extensive gas kinetic studies in organosilicon chemistry, Ring, O'Neal and co-workers investigated the shock-induced decomposition of propylsilane and butylsilane [36]. These pyrolyses were complex, not surprisingly in view of the high temperature range of 830–980°C, but products resulting from the formation of silirane intermediates were prominent. Further insights into the cyclisation of silylenes were obtained by generating long-chain silylenes by the addition of $:SiH_2$ to alkenes at much lower temperatures, around 380°C [37,38]. Thus, when thermally generated $:SiH_2$ was reacted with 1-butene, all of the products were consistent with the formation of silirane intermediates as shown in Scheme 4.



Scheme 4. Silylene addition to 1-butene.

There were no products indicative of the formation of siletanes or larger rings, in agreement with Barton's results by flash vacuum pyrolysis [27]. Such products were formed in the shock-induced experiments at higher temperatures [36]. It was therefore concluded [37] that the activation energy for ring closure of a silylene by intramolecular hydrogen-abstraction to form a silirane, *e.g.* reaction (17) in Scheme 2, is lower than the activation energies for the equivalent processes forming larger rings, *e.g.* reactions (19) and (20). Whilst considerable new information about the kinetics of the reactions in Scheme 4 was obtained from these experiments at lower temperature [37], some ambiguities and uncertainties remained, largely because the experiments were still in the unimolecular falloff region, as were the earlier shock tube studies [21,36]. Further experiments were therefore undertaken at high and constant total pressure. These experiments, complemented by computer modelling 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 4 [38]. It must be noted that Scheme 4 was not intended [37] to be

Table 1

Process (see text)	log A (s^{-1})	E (kJ mol^{-1})
c	12.3	43.5
o	14.0	$61.5+\Delta E$
d	16.9	$109\ +\Delta E$

exhaustive; for instance, all of the reactions in it are reversible, and both butylsilylenes could be formed by ring-opening of either silirane.

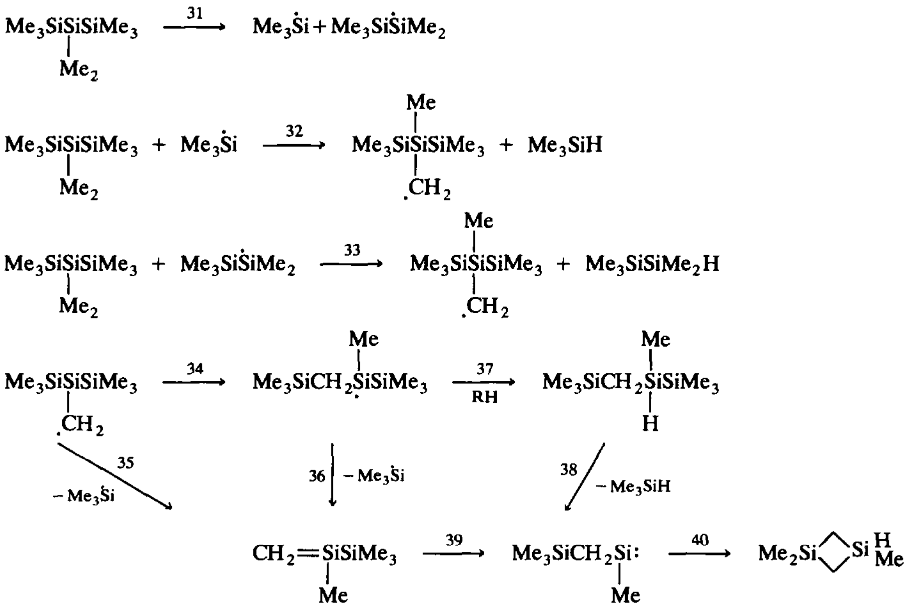
Generic high-pressure Arrhenius parameters were derived for the three processes involved and are presented in Table 1: ring-opening (o): to form a silylene, *e.g.* reactions 27 and 28, ring-closing (c): the reverse process, *e.g.* reaction 29, and decomposition (d): to form an alkene and a smaller silylene, *e.g.* reaction 30.

ΔE is a ring strain correction factor, defined by $\Delta E = (207.5 - E_s)$ kJ mol^{-1}, where E_s is the ring strain in the silirane ring. Ring and O'Neal estimate E_s to be 207.5 kJ mol^{-1}; if so, then $\Delta E = 0$, but if E_s is lower, as indicated by theory [24,25], then $\Delta E > 0$ requiring consequential adjustment of E_o and E_d.

There are some striking features in Table 1 necessitating substantial revision of earlier kinetic estimates [3,21]. 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; 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, discussed above, that 1,2-addition to form a silirane is favoured over 1,4-addition in the reaction of silylenes with 1,3-butadienes [28]. The unusual nature of the transition states in these reactions (*vide supra et infra*) may also be a contributory factor in resolving the paradox that reaction 23 is faster than reaction 24 in Scheme 3 [28,29].

The activation energy for the ring-closure process (c) is very much less than the value of 165 kJ mol^{-1} arrived at previously [3] for reaction 2, because recent developments profoundly affect both the assumptions about thermochemistry and those about ring strain. Early estimates [3,21] of the thermochemistry of reaction 14 used -34.7 and 243 kJ mol^{-1} respectively for the enthalpies of formation of $MeSiH_3$ and $:SiH_2$; as a result of the refinements in thermochemistry in which Walsh has played a leading part [19,20], these values were replaced by -31 and 268 kJ mol^{-1} respectively [38]. The result was to reduce the activation energy for the insertion of $:SiH_2$ into an acyclic carbon-hydrogen bond from *ca.* 80 kJ mol^{-1} to *ca.* 42 kJ mol^{-1}. As this new value is essentially equal to E_c in Table 1, it follows that the ring closure process (c) is also rather unusual, with no development of ring strain in the transition state. Similar arguments applied to the formation of the disilirane ring in reaction 2 would increase k_2 very substantially over the earlier value [3], making it bigger than k_{10} and thus favouring the route in Scheme 1 via **3** over that *via* **8**, in accordance with the experimental results [8].

Some interesting cyclisation reactions, some of which lend themselves to testing the general applicability of the Arrhenius parameters in Table 1, featured in our recent work on the kinetics and mechanism of pyrolysis of trisilanes in the gas phase. Pyrolysis of octamethyltrisilane, Me_8Si_3, gave cyclic products with four- and



Scheme 5. Formation of a disiletane in the pyrolysis of Me_8Si_3.

five-membered silicon-containing rings [39]. The main four-membered ring product, 1,1,2-trimethyl-1.3-disiletane, was formed in a series of well-precedented reactions [9,40,41] resulting from radical attack on a methyl group attached to the central silicon atom, as shown in Scheme 5.

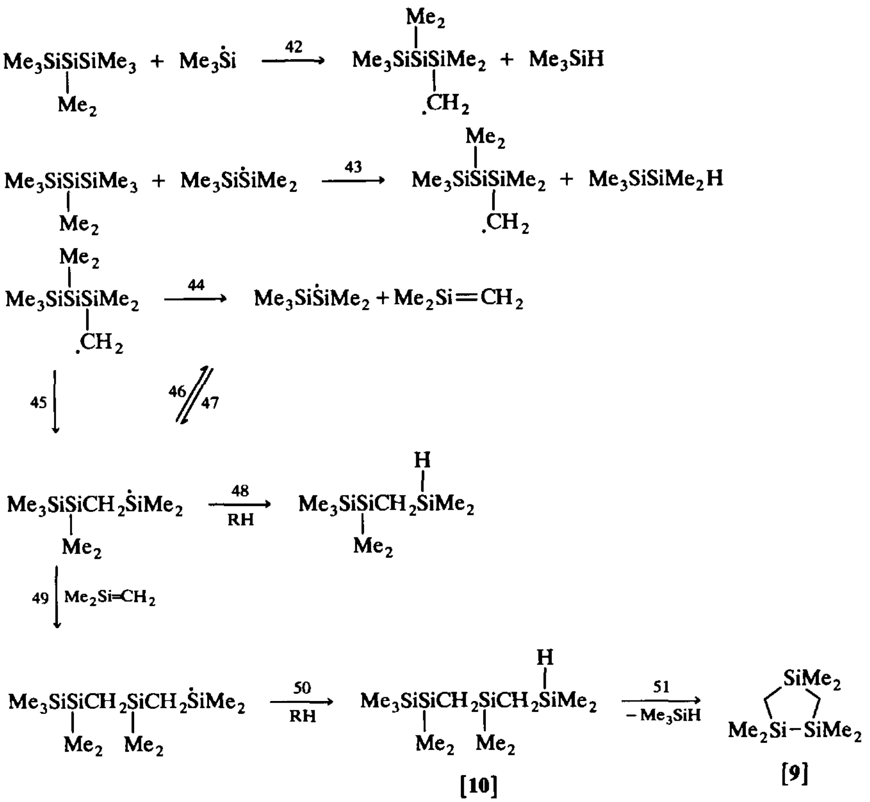
Scheme 5 is unexceptionable, but a considerably more significant product was 1,1,2,2,4,4-hexamethyl-1,2,4-trisilacyclopentane (**9**), which was believed to be produced in a sequence initiated by radical attack on a methyl group attached to a terminal silicon atom, culminating in a novel cyclisation with elimination of Me_3SiH, somewhat analogous to the well known silylene-forming elimination of Me_3SiH from pentamethyldisilane:

$$Me_3SiSiMe_2H \longrightarrow :SiMe_2 + Me_3SiH \qquad (41)$$

This reaction sequence is in Scheme 6; it was shown by pyrolysis of **10** and an isomer that having the components of the eliminated Me_3SiH (*i.e.* Me_3Si and H) both attached to silicon, as they are in reaction (41), was a prerequisite for reaction 51 as well [39].

On the other hand, no cyclic products were obtained in the pyrolysis of 2,2-diethylhexamethyltrisilane, $(Me_3Si)_2SiEt_2$ [42]. At 580°C, the major products were C_2H_4 (46%), Me_3SiH (36%), and vinyltrimethylsilane, $Me_3SiCH{=}CH_2$ (9%). Formation of these products was kinetically complex, with orders of reaction of *ca.* 1.6. We proposed the following reaction sequences involving silirane intermediates to account for this striking difference, resulting from radical attack on the ethyl groups, either at the β-position (Scheme 7) or at the α-position (Scheme 8).

Schemes 7 and 8 describe the results of hydrogen abstraction from the ethyl groups, but abstraction could also occur from the methyl groups, leading to a series of reactions analogous to Scheme 6, giving the corresponding cyclic product.

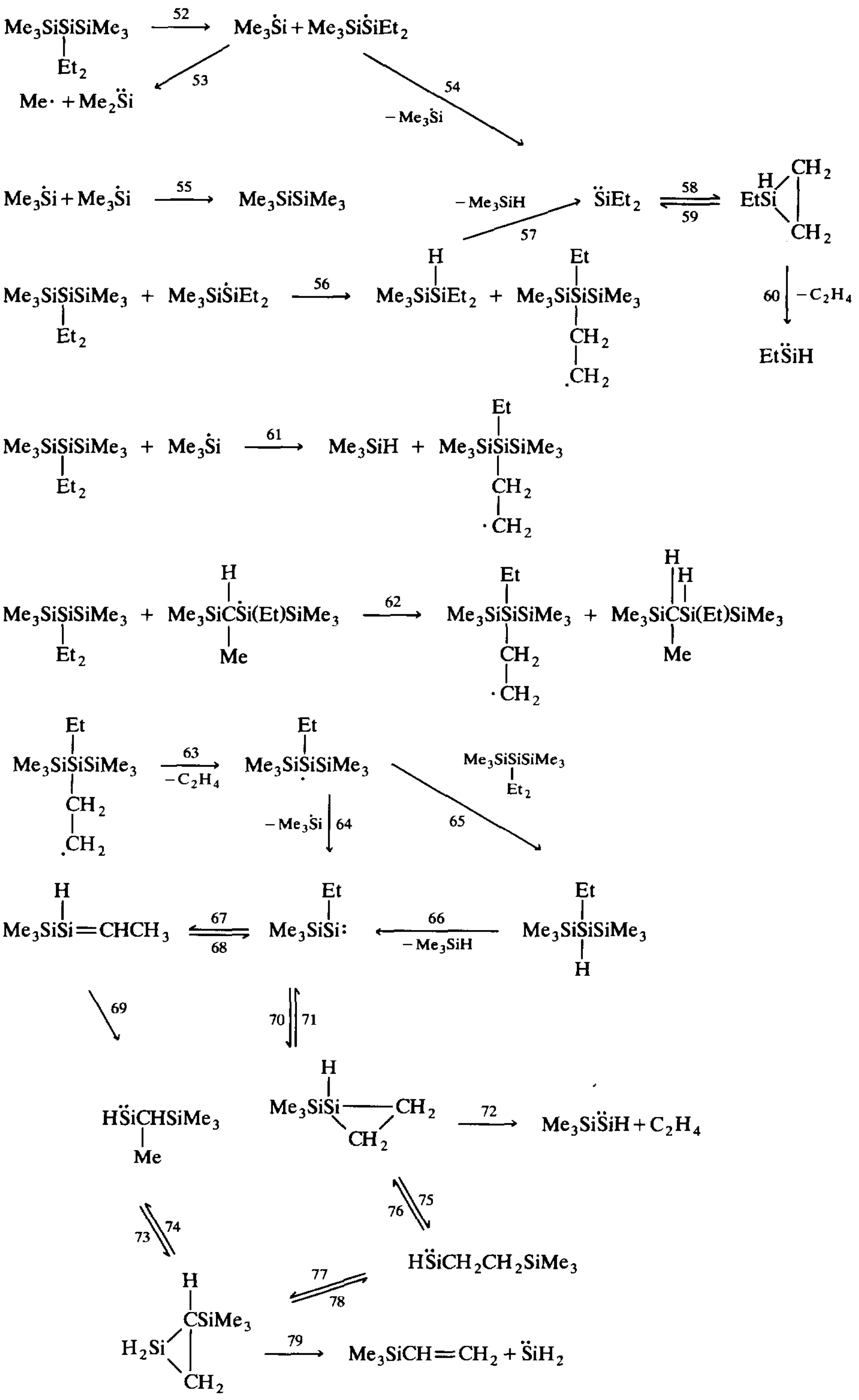


Scheme 6. Formation of a trisilacyclopentane in the pyrolysis of Me_8Si_3.

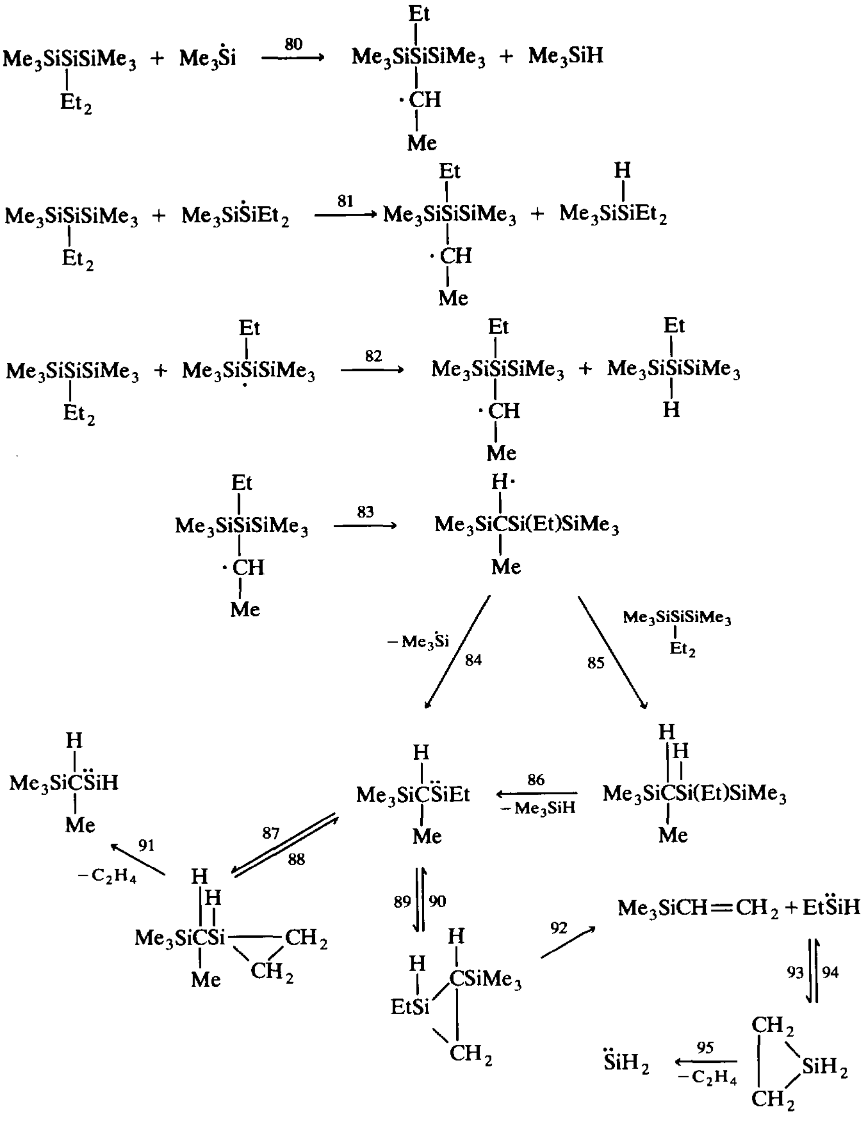
Failure to observe cyclic products in the pyrolysis of $(Me_3Si)_2SiEt_2$ indicates that the reactions in Schemes 7 and 8 are faster, a conclusion supported by subsequent kinetic studies on Me_8Si_3 [43]. Reaction orders were again complex, varying between 1 and *ca.* 1.5; combined 1.5 order rate constants for the formation of all products in the pyrolysis of Me_8Si_3 at 620°C were *ca.* 40 times lower than the corresponding rate constants for the $(Me_3Si)_2SiEt_2$ pyrolysis under the same conditions.

We modelled an overall reaction mechanism for the pyrolysis of $(Me_3Si)_2SiEt_2$ (comprising Schemes 7 and 8 plus some other minor reactions, including those resulting from abstraction at a methyl group) by numerical integration, using the Arrhenius parameters in Table 1 for all of the generic reactions of siliranes, with $\Delta E = 0$. The resulting comparison of calculated and experimental Arrhenius parameters based on 1.6 order rate constants is shown in Table 2. It should be noted that orders of reaction close to 1.5 are not surprising; in Scheme 6 for instance, formation of C_2H_4 by reaction 60 would have an order of exactly 1.5 if $Me_3Si.$ radicals are lost mainly by reaction 55.

Considering the complexity of the overall mechanism, the agreement between calculation and experiment is encouraging (since $Me_3SiCH{=}CH_2$ was a relatively minor product, the poorer agreement in that case is not surprising), indicating that



Scheme 7. Pyrolysis of $(Me_3Si)_2SiEt_2$ (β-hydrogen abstraction).



Scheme 8. Pyrolysis of $(Me_3Si)_2SiEt_2$ (α-hydrogen abstraction).

Table 2

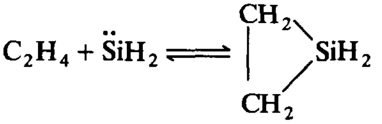
Kinetics of formation of products. Arrhenius parameters for 1.6 order rate constants

Product	C_2H_4		Me_3SiH		$Me_3SiCH{=}CH_2$	
	log A [a]	E (kJ mol^{-1})	log A	E (kJ mol^{-1})	log A	E (kJ mol^{-1})
Experiment	20.8 ± 0.5	308 ± 9	20.8 ± 0.6	310 ± 9	18.0 ± 0.6	274 ± 10
Calculated	20.7 ± 1.6	318 ± 27	19.5 ± 1.4	303 ± 23	19.6 ± 1.4	312 ± 23

[a] A factors calculated using mol dm^{-3} as the unit of concentration.

Ring and O'Neal's kinetic estimates [38] are transferable to a substantially different chemical system, and providing further evidence of the importance of silirane intermediates.

Independent evidence for loose transition states in reactions involving siliranes has recently come from time-resolved studies on the prototype reaction 96 and −96 by Frey, Walsh and co-workers [44]; from RRKM modelling of their experimental results and calculated values of ring strain, they estimated that log $A_{-95} \geq 17.5$.



$$C_2H_4 + \ddot{\mathrm{S}}iH_2 \rightleftharpoons \begin{array}{l} CH_2 \\ \,|\quad \rangle SiH_2 \\ CH_2 \end{array} \qquad (96)$$

Furthermore, confirmation of the unconventional nature of transition states in these reactions came from the finding that reaction 96 had a negative activation energy.

A quantitative explanation of the predominance of silirane-forming pathways, as exemplified by the result in Scheme 2, is now possible. Loss of internal rotors on forming the transition state causes the A factor for ring closure to *decrease* regularly with increasing ring size in steps of about 3.5 entropy units, while the activation energy for ring closure has been found to *increase* with increasing ring size relative to the relatively low value for silirane formation [38]. Thus, both factors would combine to reduce k_{19} and k_{20} relative to k_{17}.

Acknowledgments

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