Journal of Organometallic Chemistry, 271 (1984) 249–260
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

QUANTITATIVE ASPECTS OF SOME UNIMOLECULAR ISOMERIZATION REACTIONS OF ORGANOSILICON INTERMEDIATES *

IAIN M.T. DAVIDSON* and ROBERT J. SCAMPTON

Department of Chemistry, The University, Leicester, LE1 7RH (Great Britain)

(Received February 22nd, 1984)

Summary

Estimates of rate constants are deduced for several reactions of silylenes. These estimates, applied to experimental results for some intriguing silylene isomerization reactions, are shown to reconcile some apparent conflicts in the literature and to draw attention to hitherto unnoticed mechanistic features.

Introduction

It is becoming increasingly apparent that there is a very rich variety of reactions undergone by organosilicon intermediates. Particularly interesting are the unimolecular isomerization and intramolecular insertion reactions of these intermediates which occur in gas phase thermolyses, where the low-pressure conditions favour unimolecular processes over bimolecular. We hope to show in this paper that the measurement and estimation of rate constants for individual elementary reactions have now progressed sufficiently to be useful in explaining the course of some of these thermolyses and in providing some simple guidelines, with particular reference to the reactions of silylenes. An early example of our interest in this topic, stimulated by the work of Kumada, was the disilanyl radical isomerization reaction (eq. 1):

$$Me_3SiSi(Me_2)\dot{C}H_2 \rightarrow Me_3SiCH_2\dot{S}iMe_2 \qquad (1)$$

This reaction was ingeniously suggested by Kumada [1] as the key step in the isomerization of $Me_3SiSiMe_3$ to $Me_3SiCH_2Si(Me_2)H$, which occurs in high yield at high pressure. From gas kinetic studies over a range of pressure [2,3] we were able to confirm the mechanism he proposed and to account for the different course of the thermolysis at low pressure. Rate constants were subsequently [4] measured for the main reactions, giving $\log A_1 = 12.3$ and $E_1 = 92$ kJ mol^{-1}. Another point of interest in the thermolysis of disilanes is that for some the main primary reaction is

---

* Dedicated with profound admiration and respect to Professor Makoto Kumada.

0022-328X/84/$03.00 © 1984 Elsevier Sequoia S.A.

TABLE 1

ARRHENIUS PARAMETERS FOR PRIMARY REACTIONS IN THE PYROLYSIS OF METHYL DISILANES

Reaction	log A [a]	E (kJ mol^{-1})	$k_{900\ \mathrm{K}}$ (s^{-1})	Ref.
$Me_3SiSiMe_2H \rightarrow Me_2\ddot{Si} + Me_3SiH$ (2)	12.93 ± 0.31	198 ± 3.9	2.70×10^{1}	7
$Me_3SiSiMe_3 \rightarrow Me_2\ddot{Si} + Me_4Si$ (3)	13.7 ± 0.7	282 ± 12	2.15×10^{-3}	3
$Me_3SiSiMe_3 \rightarrow Me_3Si\cdot + Me_3Si\cdot$ (4)	17.2 ± 0.3	337 ± 4	4.37×10^{-3}	3

[a] First-order A factors and rate constants are in s^{-1} and second-order in dm^3 mol^{-1} s^{-1}.

dissociation into radicals, while for others it is formation of a silylene and a monosilane. An early suggestion [5] was that the activation energy for the reverse of the latter process, i.e. insertion of a silylene into its concomitant molecular product, was the vital factor in determining which route was favoured. Whilst that is broadly true, it is an oversimplification. Now that Arrhenius parameters have been measured for the primary reactions in the thermolysis of several disilanes [3,6–8] and monosilanes [9–11] a clearer understanding of the factors involved is possible. These may be illustrated for disilanes by reference to the pyrolysis of hexamethyldisilane and pentamethyldisilane; Arrhenius parameters for the primary reactions in these pyrolyses are in Table 1.

Thus, although k_3 is indeed much less then k_2 because it has a higher activation energy [5], it is less than k_4 primarily because it has a lower A factor. So far as the methylmonosilanes are concerned, tetramethylsilane and trimethylsilane decompose by radical mechanisms [12], but the primary reactions in the pyrolysis of methylsilane and dimethylsilane produce silylenes with the Arrhenius parameters given in Table 2.

It is of particular interest to estimate the kinetic parameters for typical silylene insertion reactions, which have not been directly measured, but which are the reverse of some of the silylene-forming reactions in Tables 1 and 2. For reaction (−2), log A_{-2} has been estimated [13] and 9.0 and E_{-2} as 0; slightly different estimates of 9.5 and 12 kJ mol^{-1} respectively are favoured by Ring, O'Neal and co-workers [14] for this type of reaction. Activation energies for reactions (−3) and (−6) may be estimated from E_3, E_6, and thermochemical data. Whilst there are problems with thermochemical data in silicon chemistry, the estimates compiled by Walsh [15] are both reasonable and self-consistent. Using these, one obtains ~ 220 and ~ 197 kJ mol^{-1} for ΔH_3 and ΔH_6 respectively. Hence $E_{-3} = (282 - 220) = 62$ kJ mol^{-1} and $E_{-6} = (279 - 197) = 82$ kJ mol^{-1}. The latter is in good agreement with another

TABLE 2

ARRHENIUS PARAMETERS [a] FOR PRIMARY REACTIONS IN THE PYROLYSIS OF METHYLSILANES

Reaction	log A	E (kJ mol^{-1})	Ref.
$MeSiH_3 \rightarrow Me\ddot{Si}H + H_2$ (5)	15.2	271	9, 10, 11
$MeSiH_3 \rightarrow \ddot{Si}H_2 + CH_4$ (6)	14.7	279	9, 10
$Me_2SiH_2 \rightarrow Me_2\ddot{Si} + H_2$ (7)	14.3	285	10, 11
$Me_2SiH_2 \rightarrow Me\ddot{Si}H + CH_4$ (8)	15.0	301	10

[a] For consistency, all Arrhenius parameters are from ref. 10; concordant parameters are given in the other references cited.

estimate [37]. Thus, activation energies for bimolecular insertions of simple silylenes may be taken to be ~ 0–12 into silicon–hydrogen, ~ 62 into silicon–methyl, and ~ 82 kJ mol^{-1} into carbon–hydrogen bonds. It was anticipated some time ago [16] that silylenes should also insert into silicon–silicon bonds, and this has been shown to occur [17]. It is a reasonable inference that the activation energy for silylene insertion into silicon–silicon bonds should be between 12 and 62 kJ mol^{-1}.

Excellent evidence exists in the literature that hydridosilenes, $RHSi{=}CH_2$, isomerize thermally to methylsilylenes [18]. The possibility of the reverse reaction has also been noted [19], while theoretical calculations indicate that such isomerizations should indeed be thermoneutral with an energy barrier in either direction of 170 or 180 kJ mol^{-1}, depending on the details of the calculation [20]. The foregoing expectations having recently been confirmed experimentally [21], silylene and silene chemistry are closely linked in thermolysis reactions in which either intermediate of the above type is formed.

A further important reaction [22] linking silylenes with silenes is the 1,2-silyl shift converting silylsilenes to silylenes:

$$Me_3Si(Me)Si{=}CH_2 \rightarrow Me\ddot{S}iCH_2SiMe_3 \qquad (9)$$

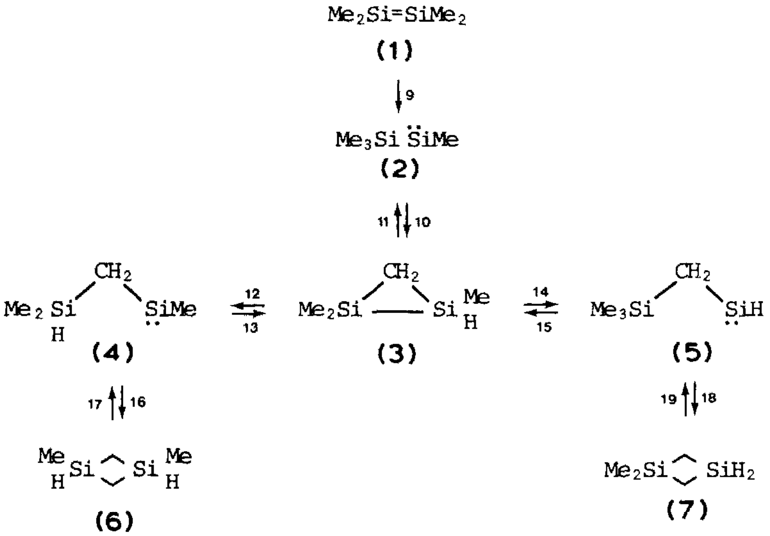
Whilst this reaction may be estimated [19] to be endothermic by some 20 kJ mol^{-1}, the experimental evidence [22] is that the resulting silylene goes on to other products instead of reverting to the silene.

Discussion

A suitable starting point for applying and extending the above kinetic estimates is the intriguing isomerization of tetramethyldisilene to two isomeric 1,3-disiletans, observed by Roark and Peddle [23], who invoked the intermediacy of disiliran, as did Barton and co-workers [24], who suggested the more refined mechanism in Scheme 1. Although there was earlier indirect evidence for the existence of disilirans [25], the first stable disilirans were prepared and characterized by Kumada and his co-workers [26], who have been responsible for much of our knowledge of the chemistry of three-membered rings containing silicon, and likewise for much of our knowledge of silyl, alkyl, and hydrogen shifts in organosilicon chemistry [27].

Estimated Arrhenius parameters for the reactions in Scheme 1 are in Table 3. Reaction 3 is not a close analogy to reaction 9, the thermochemistry being uncertain in the absence of a reliable estimate of the π-bond energy in disilenes; but the estimated parameters agree with the overall rate of decomposition of the disilene precursor used by Roark and Peddle [23] at 633 K. We know of no kinetic data relating directly to the intramolecular silylene insertion reactions 10, 13 and 15; the closest analogy comes from the recent results of Ring, O'Neal and co-workers, who obtained Arrhenius parameters of log $A \sim 12.6$ and $E \sim 139$ kJ mol^{-1} for the decomposition of n-propylsilylene to propene and silylene. This may have occurred via a siliran intermediate, with ~ 50 kJ of ring strain energy to be overcome in the transition state [10]. The ring strain in siliran has been calculated [28] as ~ 157 kJ mol^{-1}, and approximately estimated as ~ 226 kJ mol^{-1} in a substituted siliran from some experimental evidence [29]. We have found [21] that a 1,2-hydrogen shift with ring-opening in 1-methylsiletan releases ~ 59 kJ mol^{-1} out of a total ring strain of ~ 80 kJ mol^{-1}. If the calculated ring strain [28] for siliran is accepted, it thus

SCHEME 1. Isomerization of tetramethyldisilene.



appears in both of these cases that the element of ring strain released on ring-opening is approximately twice that which has to be overcome on closure. However, the ring strain for 1,3-disiletans has been estimated [30] as ~ 100 kJ mol^{-1} which, in conjunction with our preliminary measurements [31] for reaction 17 of log A ~ 13.5 and E ~ 255 kJ mol^{-1}, would indicate approximately equal elements of ring strain in either direction for reactions 16 and 17, as noted in Table 3. It seems to us that the experimentally-determined A factors for reactions 2, 3, 8 and 17 are mutually inconsistent; a compromise value was therefore chosen for A_{11}, which could be refined once confusion in the experimental results has been resolved, although it will be shown below that reaction 11 is kinetically unimportant.

TABLE 3

ESTIMATED ARRHENIUS PARAMETERS FOR REACTIONS IN SCHEME 1

Reaction	log A	E (kJ mol^{-1})	Analogous reaction	Comments
9	13.5	180	3	See text
10	12.6	82 + EC_3	−6	A factor from Ref. 10 for reactions 10, 13 and 15
11	14	301 − EO_3	8	A factor is compromise, cf. A_2, A_3, A_8 and A_{17}
12	13	198 − EO_3	2	
13	12.6	12 + EC_3	−2	
14	14	282 − EO_3	3	
15	12.6	62 + EC_3	−3	
17, 19	13.5	301 − EO_4	8	$E_{17} = 255$ (Ref. 31) $\therefore EO_4 = 301 - 255 = 46$
16, 18	13.5 [a]	82 + EC_4	−6	$ES_4 \sim 100$ (Ref. 30) $\therefore EC_4 = 100 - 46 = 54$

EC_n and EO_n are the elements of strain energy overcome or released respectively on forming transition states for closing or opening a n-membered ring; $EC_n + EO_n = ES_n$, the total strain energy of the n-membered ring.

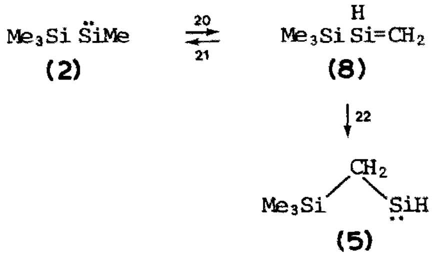
[a] *Note added in proof*: from subsequent work on a related rearrangement we now favour a lower value, down to 12.9; this change has only a minor effect on the relative rates in Table 6, and none on the results in Table 5.

When **1** was generated at 633 K, **7** and **6** were produced [23] in the ratio of 3/1, while generation of **2** at 973 K [24] gave **7**/**6** = 1.9. At the latter temperature, **6** and **7** would decompose appreciably. We have taken account of that in a simple way with reactions 17 and 19, based on our experience of the thermolysis of hydridosiletans [21] and disiletans [31]. However, that is only likely to be satisfactory at relatively low temperature, because we would expect [31] **7** to be significantly more unstable thermally than **6**.

Barton [24] drew attention to the discrepancy between the observed yields of **6** and **7** and the expected migratory aptitudes of H (reaction 12) and Me (reaction 14), explaining it in terms of rapid equilibration of reactions 12 and 13. Whilst that is undoubtedly an important factor, others are revealed by our estimates.

We attempted to simulate the results at 633 K by numerical integration [32] of Scheme 1. EO_4 and EC_4 were set at 46 and 54 kJ mol^{-1} respectively, as explained above; but EC_3 (which features in reactions 10, 13 and 15) and EO_3 (in reactions 11, 12 and 14) had to be set by trial and error. 50 kJ mol^{-1} was taken as the starting point for EC_3, but that value related to a siliran [10], whereas **2** is a disiliran. As silicon substitution increases strain energy in cyclopropane rings [28] 50 kJ mol^{-1} was likely to be a lower limit. For the reasons given above, EO_3 was made twice EC_3. With these values, the anticipated equilibration [24] between **3** and **4** occurred to such effect that **3** and **6** were the only significant products! Increasing EC_3 and EO_3 reduced the build-up of **3**, but it was not possible to increase the **7**/**6** ratio above ~ 0.05; an additional route to **7** is clearly required. It has only recently been realised [21] that the methylsilylene **2** would isomerize reversibly to a silylsilene. The latter would then undergo the well-established [22] 1,2-silyl shift to give silylene **5**. These reactions, with their estimated Arrhenius parameters, are in Scheme 2. It is not necessary to include similar reactions for the silylenes **4** and **5**; like **2**, they could isomerize to silenes, but the latter could not rearrange like **8**, but would simply revert to **4** and **5**.

SCHEME 2. Additional reactions in the isomerization of tetramethyldisilene.



Estimated Arrhenius parameters

Reaction	log *A*	*E*(kJ mol^{-1})	Comments
20, 21	13.5	170	Ref. 21 and references therein
22	12.3	120	Like reaction 1, but endothermic

With the addition of the reactions in Scheme 2, it was then possible to reproduce the experimental results at 633 K by varying EC_3 and EO_3 to adjust the balance between k_{10}–k_{15} and k_{20}. The results were very sensitive to the value of EC_3, which had to be 83 kJ mol^{-1} to achieve agreement with experiment. However, it made no difference whether EO_3 was twice EC_3 (i.e. 166 kJ mol^{-1}, giving ES_3 249 kJ mol^{-1}), or equal to EC_3 at 83 kJ mol^{-1} (giving ES_3 166 kJ mol^{-1}), as suggested by analogy with our estimates for reactions 16 and 17 in Table 3. Over that wide range, reactions 11 and 14 were relatively slow, as were 15 and 21, while reactions 12 and 13 were essentially equilibrated, as anticipated [24]. The observed **7**/**6** ratio [24] at the rather high temperature of 973 K could also be reproduced with these values of EC_3 and EO_3, provided that k_{19} was increased to be the same as that found [31] for 1,3-disiletan itself.

Thus, although our kinetic estimates are of necessity rather approximate, they have improved understanding of the mechanism of isomerization of **1**, by demonstrating the need to invoke the new reactions in Scheme 2.

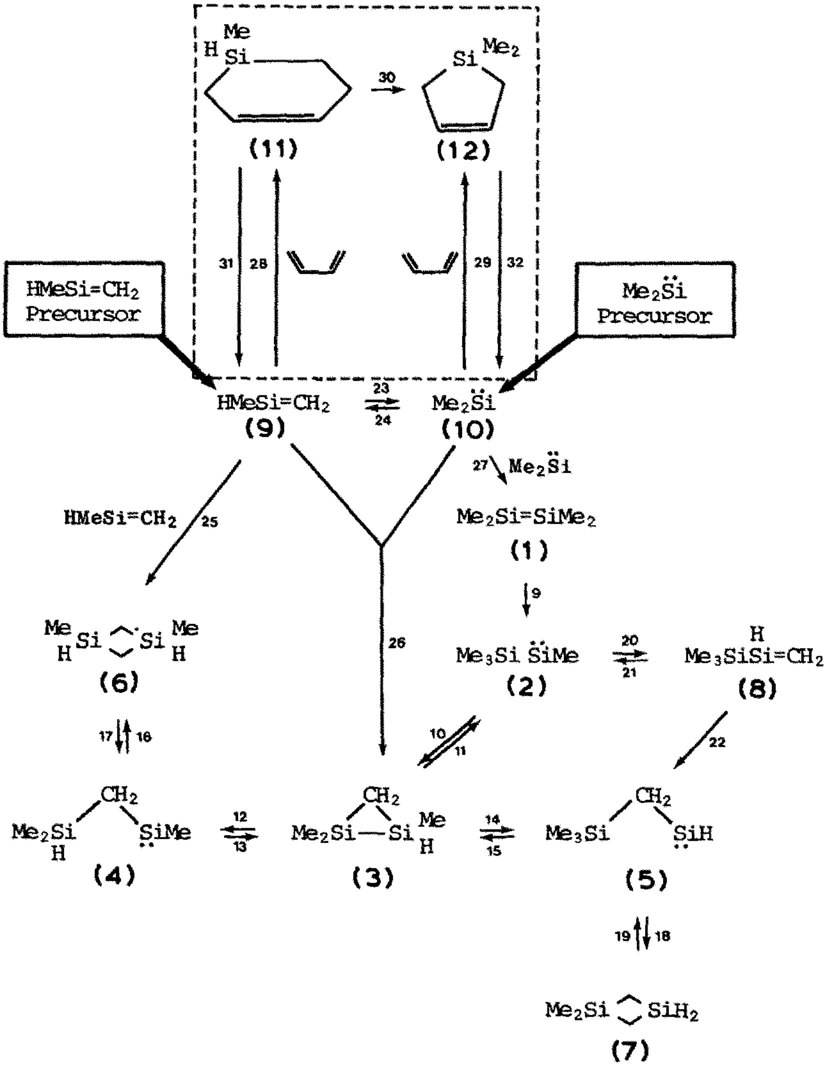
All of the reactions in Schemes 1 and 2 are relevant to the thermal silylene-silene isomerization, reactions 23 and 24, which is of some considerable current interest [18,20–22,33].

$$\underset{(\mathbf{9})}{HMeSi{=}CH_2} \rightleftharpoons \underset{(\mathbf{10})}{Me_2\ddot{S}i} \qquad (23),(24)$$

We have recently suggested that several earlier experiments [18,19,22] and some new ones [21], in which **9** or **10** was generated thermally with or without added butadiene, could be interpreted in terms of the thermoneutral reversible isomerization reactions 23 and 24, as predicted theoretically [20]. That conclusion was not obvious previously [18] mainly because of the differential reactivity of **9** and **10** towards butadiene, although the first suggestion of the silylene-silene isomerization, reaction 24, was made in relation to experiments on thermally-produced dimethylsilylene **10** [19]. The quantitative estimates developed here may now be used to refine, extend, and partially modify our suggestions. The full reaction sequence is in Scheme 3.

The earlier experiments by others, although they yielded much useful information and prompted ingenious mechanistic explanations, were done under widely different conditions which were not entirely suitable for kinetic analysis. In particular, flash vacuum pyrolysis (FVP) experiments were likely to be in the unimolecular fall-off region. Accordingly, we undertook some experiments [21] in a stirred-flow apparatus where the temperature, reaction time, and reactant pressures were all known, and where fall-off was obviated by use of nitrogen carrier gas at ~ 2.5 atmospheres [34]. By generating **10** between 720 and 860 K, and between 720 and 924 K with added butadiene, we were able to offer a broad explanation for the effect of butadiene and to conclude that in the absence of butadiene, **9** and **10**, equilibrated by reactions 23 and 24, were withdrawn from the equilibrium by the dimerization reactions 25 and 27. In order to probe the mechanism in the absence of butadiene more fully we have done some further experiments [35] by the same technique, separately generating **9** from 1-methylsiletan and **10** from methoxypentamethyldisilane between 760 and 850 K; within that temperature range **6** and **7** would be thermally stable. The results were most illuminating. Starting from the silylene precursor we obtained a ratio of **7**/**6** of ~ 0.6 at 850 K, increasing to ~ 1.4 at 760 K; while starting from the silene precursor we obtained **7**/**6** ~ 0.5 at 850 K decreasing to ~ 0.4 at 760 K. The striking difference in the ratio of **7** to **6** at 760 K and the opposing trends with temperature towards approximate parity at 850 K reflect the interplay between dimerization and

SCHEME 3. The silylene-silene isomerization (with and without trapping).



cross-combination of **9** and **10**, reactions 25–27. The rate constant [36] for dimerization of $Me_2Si{=}CH_2$ should be a reasonable analogy for k_{25}. Rate constants have been estimated [37] for the dimerization of $\ddot{S}iH_2$ and $Me\ddot{S}iH$ as log A ~ 11.88 and ~ 10.99 respectively, both with zero activation energy, thus giving a good indication of the likely size of k_{27}. In carbene chemistry, addition of a singlet carbene to a π-bond is competitive with the most favourable σ-bond insertions; therefore, reaction 26 would likewise be expected to have a large rate constant.

An obvious, but previously unforeseen, conclusion from these estimates is that reaction 25 is of negligible importance relative to reactions 26 and 27; **6**, the "dimer" of **9**, is in fact produced entirely from reaction 16 in these thermolyses. The variations in **7**/**6** noted above result from the balance between reactions 26 and 27;

TABLE 4

ESTIMATED ARRHENIUS PARAMETERS FOR REACTIONS IN SCHEME 3

Reaction	log A	E (kJ mol^{-1})	Source
9	13.5	180	Table 3 and text
10	12.6	165	
11	14	$\leqslant 218$	
12	13	$\leqslant 115$	
13	12.6	95	
14	14	$\leqslant 199$	
15	12.6	145	
16, 18	13.5[a]	136	
17, 19	13.5	255	
20, 21	13.5	170	Scheme 2
22	12.3	120	
23, 24	13.5	170	Ref. 21 and refs. therein
25	6.6	0	Ref. 36
26	10	0	See text
27	10	0	
28	7	10	Ref. 21
29	9.5	12	Ref. 14
30	13.5	252	Ref. 31 and text
31	14.4	252	
32	13.5	255	

[a] Now 12.9–13.5, see footnote *a* to Table 3.

TABLE 5. TESTS OF SCHEME 3 AGAINST EXPERIMENTAL RESULTS

Initial intermediate	Experimental conditions	Ref.	T (K)	7/6	
				Observed	Calculated
(a) Experiments without added butadiene					
9	Stirred flow in 2.5 atm. of nitrogen	35	760	0.4	0.46
9			850	0.5	0.56
10			760	1.4	1.3
10			850	0.6	0.67
9	Flow, 1–5 Torr	18	898	0.53	0.56
9			925	0.56	0.57
9	Nitrogen flow	22	673	~ 0	0.005
10	Vacuum flow	19	873	0.86	0.64
10	< 0.1 Torr		973	~ 0.6	0.62
1	Sealed tube	23	633	3	3
(b) Experiments with added butadiene					
	Excess of butadiene and conditions			**11/12**	
10	×10; stirred flow	21	720	<1 %	0.0003
10			924	<1 %	0.003
9	×8	18	829	~ 0.8	0.6
9			898	~ 0	0.067
9			925	~ 0	0.014
9	N_2 flow	22	673	[11] ≫ [12]	20
9	~ 1 atm	21	873	[11] ≫ [12]	12

reaction 27 leads directly to **2**, and thence to the reactions in Scheme 2, whereas reaction 26 does not. With all other Arrhenius parameters set at the previously estimated values given in Table 4, k_{26} and k_{27} were varied systematically. Reasonably satisfactory agreement with our latest experimental results [35] was obtained when both were 10^{10} dm^3 mol^{-1} s^{-1}. This full Scheme, like Scheme 1 augmented by Scheme 2, was insensitive to the chosen value of EO_3. For simplicity, we favour $EO_3 = EC_3 = 83$ kJ mol^{-1}, giving a total ring strain of 166 kJ mol^{-1}, close to the calculated value in siliran [28].

Interpretation of the results of trapping experiments with butadiene is complicated by the differential thermal stability of the adducts **11** and **12**. The Arrhenius parameters for reaction 32 are based on a few experiments which we have done on the thermolysis of **12**, while those for reactions 30 and 31 are estimates based on our results [31] for the thermolysis of the dimethylsilyl homologue of **11**. Scheme 3 was then tested against the earlier experiments; the results of all of these tests are in Table 5.

In view of the uncertain reaction time, pressure, temperature, and rôle of the surface in many of the earlier experiments, we consider the agreement in Table 5 to be sufficiently good for Scheme 3 to be realistic. It should be stressed that the computer-aided speculations in this paper are no substitute for experimental work, but they are of some value if they focus attention on some mechanistic features, such as the need to include the reactions in Scheme 2, the importance of reaction 26, or the unimportance of reaction 25.

A clearer indication of the main reactions in Scheme 3 in the absence of added

TABLE 6

RELATIVE RATES[a] IN SCHEME 3 FOR A TYPICAL THERMOLYSIS WITHOUT ADDED BUTADIENE

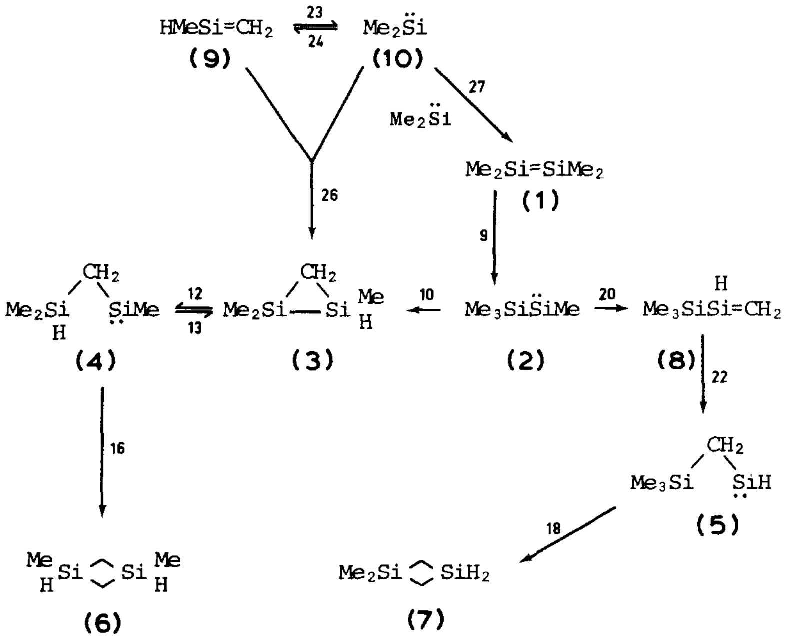
Reaction	Relative rate
23	5.0
24	6.1
25	4.2×10^{-4}
26	1.2
27	1.3
9	1.3
10	0.26
11	3.1×10^{-4}
20	1.0
21	0.014
22	1.0
12	60.1
13	58.7
14	4.5×10^{-3}
15	0.035
16	1.5
17	1.0×10^{-3}
18	1.0
19	6.9×10^{-4}

[a] Conditions simulated were production of **10** at 850 K after ~ 20% decomposition of precursor. Rates are in arbitrary units, relative to rate 18 = 1.0.

butadiene may be gleaned from Table 6, in which we list relative rates for a typical thermolysis at an intermediate temperature.

Exactly the same rates are obtained for all reactions if EO_3 is increased to 166 kJ mol^{-1}, thus reducing the activation energies for reactions 11, 12 and 14 by a further 83 kJ mol^{-1}. Because the other rate constants dependent on EC_3 are unchanged, all that happens is that the concentration of **3** falls to maintain the rates of reactions 11, 12 and 14 at the same values. Hence, irrespective of the true value of EO_3, the reactions in the abbreviated Scheme 4 are the only important ones.

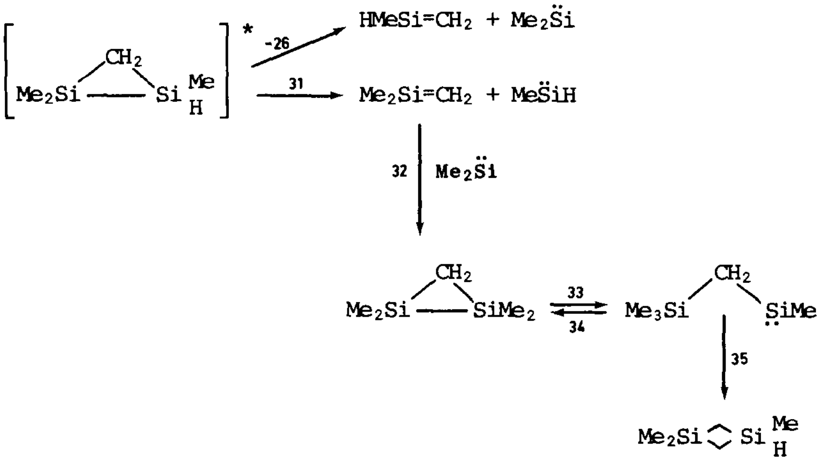
SCHEME 4. Main reactions from Scheme 3.



It should be noted that reactions 23 and 24 are essentially equilibrated, as are reactions 12 and 13; but reactions 20 and 21 are not because reaction 22 is so relatively fast. Reactions 11, 14 and 15 being unimportant, there is no route to **7** from **3**, but only from **2** via **8**.

Thermolyses of low pressures of precursors in the absence of a carrier gas may be further complicated by the formation of chemically-activated "hot" molecules. The conditions most conducive to that possibility were those used by Conlin and Gaspar [19], who generated **10** by vacuum flow thermolysis below 0.1 Torr. Uniquely, they found up to 8% of a third disiletan, 1,1,3-trimethyl-1,3-disiletan. It is tempting to suggest that under these conditions reaction 26 gave "hot" disilacyclopropane **3**, which could then decompose by additional routes not accessible to the unactivated species. The equivalent reaction to 26 in hydrocarbon chemistry is a classic way of producing "hot" cyclopropanes. A suggested sequence of additional reactions is in Scheme 5. Reaction 32 is plausible because there is a relatively high concentration of **10** present, while reaction 35 is known to occur very cleanly [22]. Of course, if this suggestion is correct, it follows that there would be similar minor reactions between **9** or **10** and Me$\ddot{S}$iH or its isomer $H_2Si{=}CH_2$, leading to formation of 1-methyl-1,3-

SCHEME 5



disiletan, but that disiletan would probably be substantially more unstable than the others, as is 1,3-disiletan itself [31].

Acknowledgements

We thank our co-workers, A. Fenton, K.J. Hughes, and Dr. S. Ijadi-Maghsoodi for valuable discussions, M.J. Blades for help with the numerical integrations, and the SERC for financial support.

References

1 K. Shiina and M. Kumada, J. Org. Chem., 23 (1958) 139.
2 I.M.T. Davidson, C. Eaborn and J.M. Simmie, J. Chem. Soc., Faraday Trans. I, 70 (1974) 249.
3 I.M.T. Davidson and A.V. Howard, J. Chem. Soc., Faraday Trans. I, 71 (1975) 69.
4 I.M.T. Davidson, P. Potzinger and B. Reimann, Ber. Bunsenges Phys. Chem., 86 (1982) 13.
5 I.M.T. Davidson, J. Organomet. Chem., 24 (1970) 97.
6 A.J. Vanderwielen, M.A. Ring and H.E. O'Neal, J. Amer. Chem. Soc., 97 (1975) 993.
7 I.M.T. Davidson and J.I. Matthews, J. Chem. Soc., Faraday Trans. I, 72 (1976) 1403.
8 I.M.T. Davidson and M.E. Delf, J. Chem. Soc., Faraday Trans. I, 72 (1976) 1912.
9 I.M.T. Davidson and M.A. Ring, J. Chem. Soc., Faraday Trans. I, 76 (1980) 1520.
10 M.A. Ring, H.E. O'Neal, S.F. Rickborn and B.A. Sawrey, Organometallics, 2 (1983) 1891.
11 P.S. Neudorfl and O.P. Strausz, J. Phys. Chem., 82 (1978) 241.
12 A.C. Baldwin, I.M.T. Davidson and M.D. Reed, J. Chem. Soc., Faraday Trans. I, 74 (1978) 2171.
13 I.M.T. Davidson, F.T. Lawrence and N.A. Ostah, J. Chem. Soc., Chem. Commun., (1980) 859.
14 B.A. Sawrey, H.E. O'Neal, M.A. Ring and D. Coffey, Int. J. Chem. Kinetics, in press.
15 R. Walsh, Acc. Chem. Res., 14 (1981) 246.
16 P.P. Gaspar, Reactive Intermediates, 1 (1978) 229.
17 H. Sakurai, T. Kobayachi and Y. Nakadaira, J. Organomet. Chem., 162 (1978) C43.
18 R.T. Conlin and D.L. Wood, J. Amer. Chem. Soc., 103 (1981) 1843; R.T. Conlin and R.S. Gill, J. Amer. Chem. Soc., 105 (1983) 618.
19 R.T. Conlin and P.P Gaspar, J. Amer. Chem. Soc., 98 (1976) 868.
20 H.F. Schaefer III, Acc. Chem. Res., 15 (1982) 283; S. Nhease and T. Kudo, J. Chem. Soc., Chem. Commun., (1984) 141.

21 I.M.T. Davidson, S. Ijadi-Maghsoodi, T.J. Barton and N. Tillman, J. Chem. Soc., Chem. Commun., (1984) 478.
22 T.J. Barton, S.A. Burns and G.T. Burns, Organometallics, 1 (1982) 210.
23 D.N. Roark and G.J.D. Peddle, J. Amer. Chem. Soc, 94 (1972) 5837.
24 W.D. Wulff, W.F. Goure and T.J. Barton, J. Amer. Chem. Soc., 100 (1978) 6236.
25 D. Seyferth and D.P. Duncan, J. Organomet. Chem., 111 (1976) C21.
26 M. Ishikawa, H. Sugisawa, M. Kumada, T. Higuchi, K. Matsui, K. Hirotsu and J. Iyoda, Organometallics, 2 (1983) 174.
27 M. Ishikawa, K-I. Nakagawa and M. Kumada, J. Organomet. Chem., 131 (1977) C15; M. Ishikawa, T. Fuchikami and M. Kumada, J. Organomet. Chem., 142 (1977) C45; M. Ishikawa, T. Fuchikami and M. Kumada, J. Amer. Chem. Soc., 99 (1977) 245; M. Ishikawa, H. Sugisawa, K. Yamamoto and M. Kumada, J. Organomet. Chem., 179 (1979) 377; M. Ishikawa, K.-I. Nakagawa and M. Kumada, J. Organomet. Chem., 190 (1980) 117; M. Ishikawa, K. Nishimura, H. Sugisawa and M. Kumada, J. Organomet. Chem., 194 (1980) 147; M. Ishikawa, K-I. Nakagawa, S. Katayama and M Kumada, J. Amer. Chem. Soc., 103 (1981) 4170; M. Ishikawa, H. Sugisawa, T. Fuchikami, M. Kumada, T. Yamabe, H. Kawakami, K. Fukui, Y. Ueki and H. Shizuka, J. Amer. Chem. Soc., 104 (1982) 2872.
28 M.S. Gordon, J. Amer. Chem. Soc., 102 (1980) 7419.
29 D. Seyferth, D.C. Annarelli, S.C. Vick and D.P. Duncan, J. Organomet. Chem., 201 (1980) 179.
30 H.E. O'Neal and M.A. Ring, J. Organomet. Chem., 213 (1981) 419.
31 N. Auner, T.J. Barton, I.M.T. Davidson and S. Ijadi-Maghsoodi, unpublished.
32 Numerical integrations made use of programs based on the Gear method provided by the University of Leicester Computer Laboratory; we thank Dr. K.F. Brodlie for help and encouragement.
33 R. Walsh, J. Chem. Soc., Chem. Commun., (1982) 1415.
34 A.C. Baldwin, I.M.T. Davidson and A.V. Howard, J. Chem. Soc., Faraday Trans. 1, 71 (1975) 972.
35 M.J. Blades, I.M.T. Davidson, K.J. Hughes, S. Ijadi-Maghsoodi and R.J. Scampton, to be published.
36 L.E. Gusel'nikov, K.S. Komoboeyevsky, V.M. Vdovin and N.S. Nametkin, Dokl. Akad. Nauk SSSR, 235 (1977) 1086.
37 B.A. Sawrey, H.E. O'Neal, M.A. Ring and D. Coffey, Int. Jnl. Chem. Kinetics, 16 (1984) 7, 23, 31.