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SOME MECHANISTIC SUGGESTIONS FOR SILYLENE TO SILYLENE INTERCONVERSIONS

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Summary

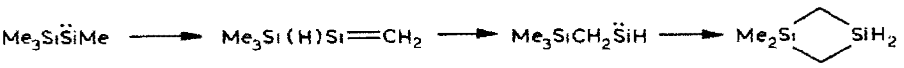
A quantitative model recently developed for some silylene isomerisation reactions has been successfully extended to account for the remarkably specific thermal isomerisation of bis(trimethylsilyl)silylene to 1,1,4,4-tetramethyl-1,2,4-trisilolane; it is suggested that this isomerisation occurs via a trimethylsilyl shift.

Introduction

We have recently investigated the interconvertibility of silylenes and silenes in the gas phase, by generating dimethylsilylene (Me_2Si:) over a wide range of temperature, with and without trapping by added butadiene [1]. We concluded that these experiments, and earlier ones by others in which 1-methylsilene ($HMeSi{=}CH_2$) was generated [2,3], could all be interpreted in terms of a reversible unimolecular silylene ⇌ silene isomerisation with an equilibrium constant close to unity:

$$\mathrm{Me_2Si:} \underset{(2)}{\overset{(1)}{\rightleftharpoons}} \mathrm{HMeSi{=}CH_2}$$

For both k_1 and k_2, we estimated $\log A \approx 13.5$ and $E \approx 170$ kJ mol^{-1}. Subsequently, we have refined our conclusions by numerical integration [4], producing a quantitative model for the foregoing experiments and for related ones on the rearrangement reactions of tetramethyldisilene ($Me_2Si{=}SiMe_2$), **1**, produced directly [5] or by dimerisation of dimethylsilylene [6], and of methyltrimethylsilylsilylene [7] ($Me_3Si\ddot{S}iMe$), **2**. Our model confirmed earlier suggestions [7], but revealed that they were incomplete; additional reactions were clearly necessary to account for the experimental results. We suggested that these were the isomerisation of **2**, analogous to reaction 1, followed by the well-established [3] trimethylsilyl shift:



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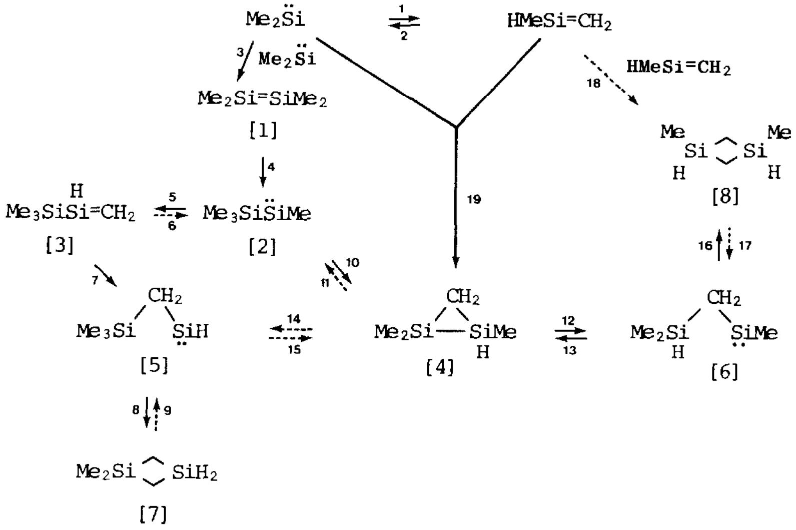
With these additional reactions, our model satisfactorily reproduced all of the foregoing experimental results. The full sequence of reactions is in Scheme 1, where minor reactions are denoted by dotted arrows. An additional point of interest to emerge from our calculations is that dimerisation of Me_2Si: and addition of Me_2Si: to $HMeSi{=}CH_2$ (reactions 3 and 19) were much more important than dimerisation of $HMeSi{=}CH_2$ (reaction 18).

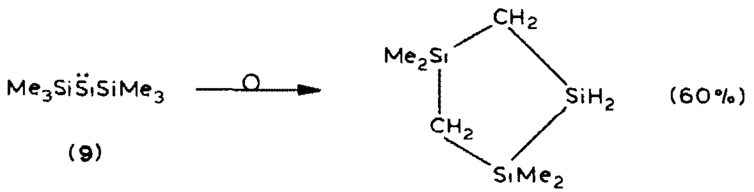
The sensitivity of our model to individual Arrhenius parameters varied considerably from one reaction in Scheme 1 to another. A major contributor to the energetics of the reactions involving the disilirane **4** is the element of ring strain overcome on closing the three-membered ring, or released on opening it, denoted by EC3 and EO3 respectively. EC3 + EO3 = ES3, the total ring strain, the value of which is unknown for **4**. The model was sensitive to the value of EC3 used in reactions 10, 13 and 15 (EC3 did not influence reaction 19, which was strongly exothermic), but extremely insensitive to the value of EO3, which features in reactions 11, 12 and 14. EC3 had to be 83 kJ mol^{-1}, but EO3 was varied between 83 and 166 kJ mol^{-1} without affecting the results. The model was also quite insensitive to the Arrhenius parameters for the ring-closure reactions 8 and 16.



SCHEME 1

Discussion

A fascinating rearrangement related to those in Scheme 1 is that of bis(trimethylsilyl)silylene ($Me_3Si\ddot{S}iSiMe_3$), **9**. Gaspar and co-workers [8] found that pyrolysis of a precursor to **9** at 773 K, under low-pressure conditions favouring unimolecular reactions, led to a 60% yield of the trisilolane **10**. Whilst there were several other products, none was formed in more than 10% yield. Much valuable mechanistic information must be latent in a rearrangement combining complexity with specificity to such a remarkable extent.



(9)

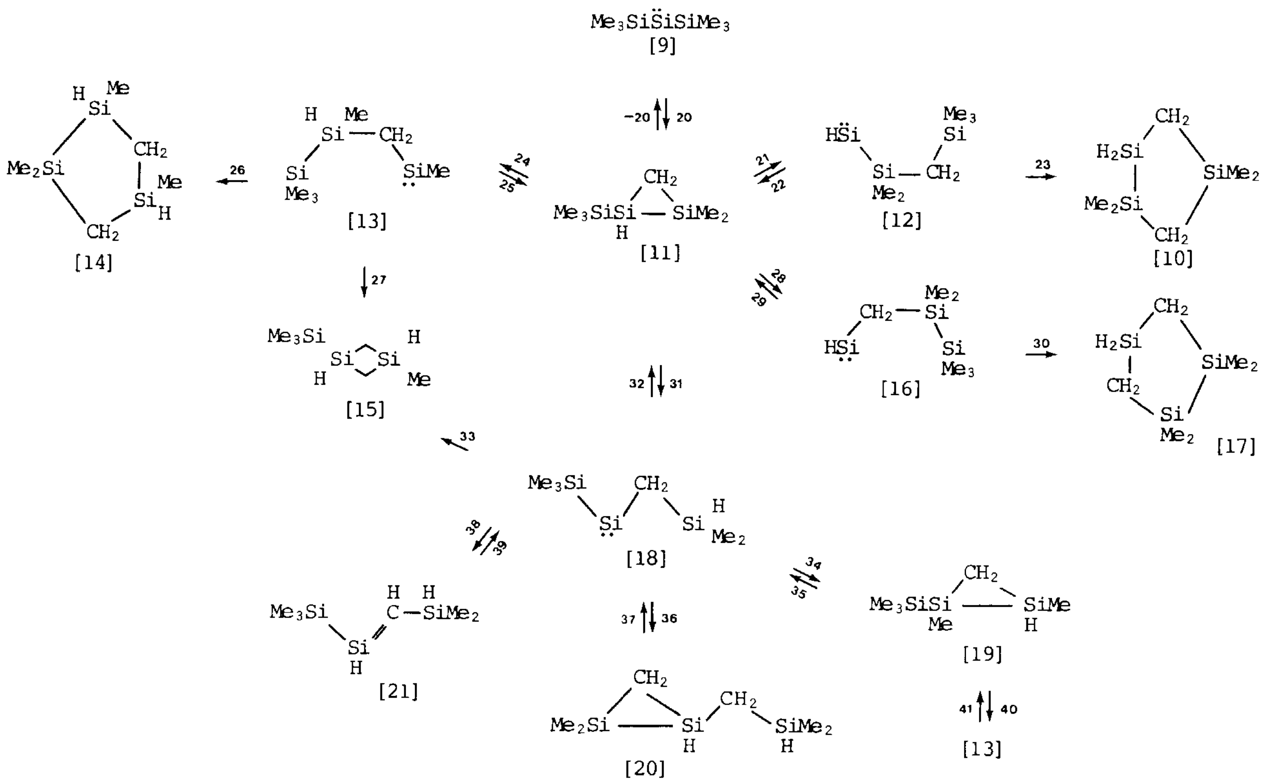
(10)

Accordingly, it is appropriate to seek to extend our model to account for the predominant formation of **10** from **9**. It was very reasonably suggested [8] that the first step in the rearrangement was the formation of disilirane **11** by a reaction exactly analogous to reaction 10 in Scheme 1. By comparison with **4**, disilirane **11** could then undergo H and Me shifts and their reverse insertions, analogous to reactions 12 to 15 in Scheme 1, but could also undergo Me_3Si shifts to carbon or silicon. All of these reactions and some of their consequences are in Scheme 2.

The analogies to reactions 12 to 15 are 31, 32, 24 and 25; reactions 21 and 22 are the Me_3Si shift from silicon to carbon and the reverse silylene insertion into silicon–carbon; reactions 28 and 29 are the Me_3Si shift from silicon to silicon and the reverse silylene insertion into silicon–silicon. The scheme suggested by Gaspar and co-workers [8] included reactions 20, 24, 31, 32, 33 and 36, but attached no importance to Me_3Si shifts. Our route in Scheme 2 to the main product **10** has not previously been suggested, but we think it worthy of serious consideration.

Activation energies for bimolecular insertion reactions of a simple silylene are, in kJ mol^{-1}: 0–12 into silicon–hydrogen, ca. 62 into silicon–carbon, and ca. 82 into carbon–hydrogen bonds [4]. For intramolecular insertions forming n-membered rings, an element of ring strain ECn has to be overcome. We have estimated [4] EC3 $\simeq$ 83 and EC4 $\simeq$ 54 kJ mol^{-1}; the value of EC5 is unknown, but may be set arbitrarily at ca. 8 kJ mol^{-1} in view of the low strain energy in a five-membered ring. If the terminal silylenes **12**, **13** and **16** are to undergo ring-closure by intramolecular insertion into carbon–hydrogen bonds, the reactions of lowest activation energy are those forming trisilolanes. So far as the Arrhenius A factors are concerned, these may tend to be low for small rings because of the tightness of the transition state, and for large rings because of the loss of more free rotations; consequently, large variations in A factors for the formation of rings between $n = 3$ and $n = 5$ are not to be expected, and the trisilolanes **10**, **14** and **17** are the most likely products from the terminal silylenes **12**, **13** and **16**. Reaction 27, which would therefore be of minor importance compared to reaction 26, is included in Scheme 2 simply to show how **13** and **18** are linked by formation of **15**.

The non-terminal silylene **18** cannot form a silolane. Options open to it, with activation energies in kJ mol^{-1} based on our earlier arguments [4], are: silicon–hydrogen insertion, $E_{32} \simeq 83$ (taking the minimum feasible value); carbon–hydrogen insertion, $E_{33} \simeq 136$; silicon–carbon insertion, $E_{34} \simeq 145$; carbon–hydrogen insertion, $E_{36} \simeq 165$; and isomerisation analogous to reaction 1, $E_{38} \simeq 170$. Whilst intriguing reactions of silene **21** may be written, including a further route to **10**, the isomerisation reactions 38 and 39 are minor, and **21** is clearly not an important intermediate in the rearrangement of **9**. Gaspar and co-workers [8] favoured **20** as the precursor to the main product **10**, but reaction 36 is likewise seen to be



SCHEME 2

energetically unfavourable, as is reaction 34. By far the major reaction of silylene **18** is likely to be reversion to disilirane **11**, reaction 32.

These ideas were tested by numerical integration, using programs based on the Gear method provided by the University of Leicester Computer Laboratory. As noted above, the original model in Scheme 1 allowed some flexibility in the values of k_8 and k_{16}, and considerable flexibility in the value of EO3. As a preliminary to estimating Arrhenius parameters for the reactions in Scheme 2 which are still consistent with Scheme 1, we determined limiting values for the latter. We found that $\log A_8$ and $\log A_{16}$ could be reduced to 12.9, while EO3 could be increased to $\leqslant 198$ kJ mol^{-1}, without destroying the agreement found earlier between calculation and experiment [4].

An important reference reaction is the elimination of dimethylsilylene from hexamethyldisilane [9] ($\log A = 13.7$, $E = 282$ kJ mol^{-1}):

$$\mathrm{Me_3SiSiMe_3 \rightarrow Me_2Si\!:+ Me_4Si} \qquad (42)$$

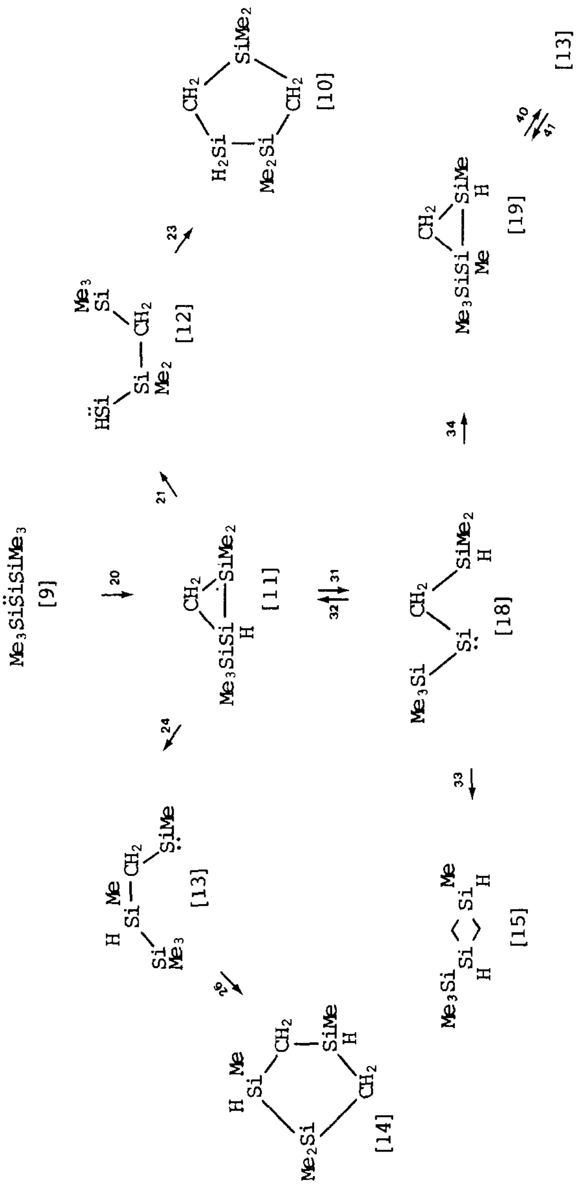
Reaction 42 may be thought of as a $\mathrm{Me_3Si}$ shift from silicon to carbon or as a Me shift from silicon to silicon; it is therefore the model for both reactions 21 and 24, but it does not follow that these have identical Arrhenius parameters. From studies of the kinetics of dissociation of the silicon–allyl bond in allyltrimethylsilane [10] and allylpentamethyldisilane [11], we found that the former dissociation energy is 305 ± 8 while the latter is 287 ± 6 kJ mol^{-1}, corresponding to a stabilisation energy of ca. 18 kJ mol^{-1} in the pentamethyldisilanyl radical. Walsh has noted a very similar effect in the unsubstituted disilanyl radical [12]. In reaction 24 both of the bonds broken and also the bond formed would be weakened by this disilanyl stabilisation, while in reaction 21 the bonds broken would be weakened but the bond

TABLE 1

ESTIMATED ARRHENIUS PARAMETERS FOR REACTIONS OF SCHEME 2

Reaction	$\log A$	E(kJ)	Rel. rate	Analogous reaction	Comments
20	12.6	165	1.66	10	$E = 82 + \mathrm{EC3}$
−20	14	107	0.02	11	$E = 301 - \mathrm{EO3}$
21	13.7	78	1.00	42	$E = 281 - \mathrm{EO3} - 10$
22	12.6	145	8×10^{-5}	15	$E = 62 + \mathrm{EC3}$
23	13	90	1.00		$E = 82 + \mathrm{EC5}$
24	13.7	88	0.21	42	$E = 282 - \mathrm{EO3}$
25	12.6	145	3×10^{-5}	22	
26	13	90	0.33	23	
27	12.4	136	7×10^{-5}	8,16	$\log A < 12.9$ [a]
31	13	24	891	12	$E > 198 - \mathrm{EO3}$ [a]
32	12.6	83	891	13	$E = 0 + \mathrm{EC3}$
33	12.7	136	0.31	8,16	$\log A < 12.9$ [a]
34	12.9	145	0.12	22	$\log A > \log A_{22}$ [a]
35	13.4	88	3×10^{-6}	24	$\log A < \log A_{24}$ [a]
36	12.6	165	3×10^{-3}	19	
37	14	107	3×10^{-3}	20	
38	13.5	170	9×10^{-3}	1	
39	13.5	170	3×10^{-3}	2	
40	13	4	0.50	12	$E = 198 - \mathrm{EO3}$
41	12.6	83	0.39	13	

[a] See text.



Me$_3$SiS̈iSiMe$_3$
[9]
20
[11]
21
HS̈i
[12]
23
[10]
24
[13]
26
[14]
31
32
[18]
33
[15]
34
[19]
40
41
[13]

SCHEME 3

formed would not. Hence, if E_{24} is given by (282 − EO3), then E_{21} would be lower by up to 18 kJ mol^{-1}.

Similar arguments apply to E_{28}, but it would be even higher than E_{24} because there would be more strain energy to be overcome in forming a cyclic transition state with three silicon atoms than there is in reaction 42; furthermore, reaction 29, involving silylene insertion into a silicon–silicon bond, would have a substantially lower activation energy [4] than reaction 22, where insertion is into silicon–carbon. Hence, k_{28} would be less than k_{21}, while k_{29} would be much greater than k_{22}, with the result that formation of 17 by reactions 28 to 30 would be substantially slower than formation of **10** by reactions 21 to 23.

Reactions 28 to 30 were therefore ignored, but all of the remaining reactions in Scheme 2 were included in the model for numerical integration. EC3 and EC4 were kept at their original values, E_{32} was set at (83 + 0) as noted above, and minor adjustments were made to *A* factors relative to analogous reactions in Scheme 1 to take account of differences in the number of available bonds. The main variable was then EO3, which features in reactions −20, 21, 24, 31, 35, 37 and 40. When EO3 was increased to 194 kJ mol^{-1}, with E_{21} less than E_{24} by 10 kJ mol^{-1} for the reasons discussed above, the calculated yield of **10** from the reactions in Scheme 2 was 60.7%, in excellent agreement with experiment. Our simple, relatively direct route to **10** may therefore be quite plausible, provided that it is reasonable for the total ring strain in **11** to be (83 + 194), i.e. 277 kJ mol^{-1}. The ring strain in a substituted monosilirane has been estimated [13] as ca. 226 kJ mol^{-1}, while it is known that further silicon-substitution in the ring increases the strain [14].

The estimated Arrhenius parameters for the reactions in Scheme 2 are in Table 1. To reduce "stiffness" in the numerical integration, E_{31} was arbitrarily increased from 4 to 24 kJ mol^{-1}, which had no adverse effect, because k_{31} and k_{32} were still much the largest rate constants in the Scheme. This expedient was unnecessary for the relatively minor reaction 40.

Table 1 also contains rates for each reaction at 773 K, calculated relative to unity for reaction 21. From these relative rates, the main reactions in Scheme 2 may be identified; these are in Scheme 3.

Scheme 3 is, of course, incomplete. We have shown that our quantitative model can explain the predominant formation of the trisilolane, **10**, but the model has not been extended to cover minor products because the nature and yields of these are as yet unspecified [8]. It should be noted, for example, that silylene **13** and disilirane **19** are interconvertible, while the latter could undergo an analogous series of reactions to its isomer **11**, thus leading to a greater variety of minor products.

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