Concerning the Isomerization of Sila-olefins to Silylenes. Some Thermochemical Kinetic Arguments

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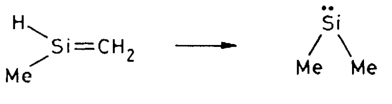
Some apparently conflicting results on the mechanistic behaviour of sila-olefins and their precursors may be resolved by taking account of the different conditions of the experiments and these considerations lead to a plausible activation energy for isomerisation of the sila-olefin.

There is considerable current interest[1,2] in the reactions of sila-olefins both from the mechanistic and kinetic viewpoints. Although the first stable sila-olefin has recently been prepared[3] sila-olefins are in general very reactive species. It is now known, with reasonable assurance, that they may be trapped in bimolecular reactions with a variety of other molecules such as alcohols, hydrogen halides and dienes. In the last two years rate constants and Arrhenius parameters have been determined for some of these processes.[4] Another possible reaction of sila-olefins, that of unimolecular rearrangement to the isomeric divalent organo-silicon species, silylenes (*via* 1,2-H shift) is currently the focus of considerable attention and some apparent controversy. This may be illustrated by the example of reaction (1), the isomerisation of 2-silapropene to dimethylsilylene. Theoretical calculations first by Gordon[5] and then by Schaefer and

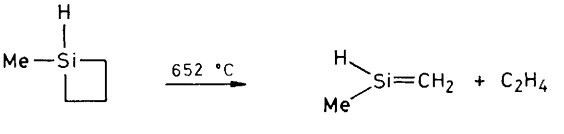


(1)

(2)

co-workers,[6] suggested that the prototype reaction (2) is slightly exothermic (but almost thermoneutral). A cruder but simpler thermochemical estimate supports this.[7] The thermodynamic feasibility of this reaction has encouraged experimental tests to try to observe reaction (1).

Conlin and Wood[8] using the pyrolysis of 1-methylsilacyclobutane as a rational source of $MeSiH{=}CH_2$ [reaction (3)] obtained substantial yields of 1,1-dimethyl-1-silacylopent-3-ene, when butadiene was added as a trapping agent. This product, a known adduct of *dimethylsilylene* with butadiene, was taken as evidence that the isomerisation reaction (1) had occurred. Drahnak, Michl, and West[9] have observed by spectroscopic means both Me_2Si and $MeSiH{=}CH_2$ in matrix-isolation studies, and obtained evidence that at 100 K reaction (1) is occurring in an isopentane matrix.



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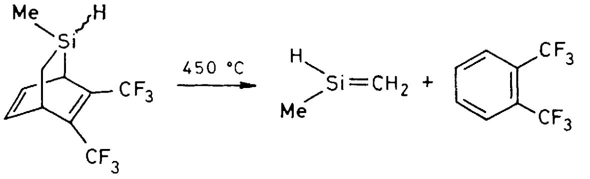
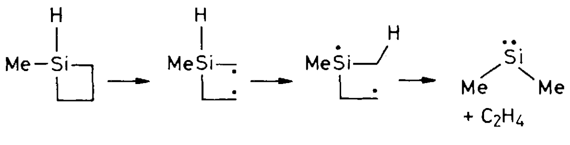


(4)

Barton, Burns, and Burns[10] using the retrodiene reaction of a derivative of silabicyclo[2.2.2]octadiene as a source of $MeSiH{=}CH_2$ [reaction (4)] obtained reasonable yields of 1,3,4-trimethyl-1-silacyclohex-3-ene, when 2,3-dimethylbuta-1,3-diene was used as a trapping agent. This product is the Diels–Alder adduct of the *unrearranged* 2-silapropene, which indicates that in these experiments reaction (1) has *not* occurred. The seeming contradiction between this result and that of Conlin and Wood[7] led Barton *et al.*[9] to question whether 1-methylsilacyclobutane was a reliable source of 2-silapropene. They pointed out the possibility of direct formation of dimethylsilylene *without* the intermediacy of 2-silapropene *via* the sequence shown in Scheme 1. In further support of the case against the facile occurrence of reaction (1) is the recently calculated activation barrier of *ca.* 170 kJ mol^{-1} for reaction (2).[11] Other matrix experiments[12] offer a miscellany of confusing evidence. Auner and Grobe[12a] claim that both $SiH_2{=}CH_2$ and $MeSiH{=}CH_2$ can be trap-to-trap distilled at low temperature, while Maier, Mihm, and Reisenauer[12b] who also observed $SiH_2{=}CH_2$, see only its dimerisation on matrix warming. Differences in conditions may explain this but neither group offers any evidence for *rearrangements* of the sila-olefins.

The purpose of this communication is to point out, by use of a simple kinetic argument, combined with reasonable thermochemical estimates, that the results of the experiments of Conlin and Wood on the one hand and Barton *et al.* on the other are not in conflict and that reaction (1) [and by analogy reaction (2)] may well occur in the former's experiments (but with a high activation energy). The key to the argument presented below concerns the competition between the isomerisation step (i) potentially present in both sets of experiments and the trapping process (t). This is shown in Scheme 2.† Assuming that there is no reverse isomerisation [step (–i)] and that step (t2) is efficient then the ratio of trapping products P_i and P_t is given by equation (5).



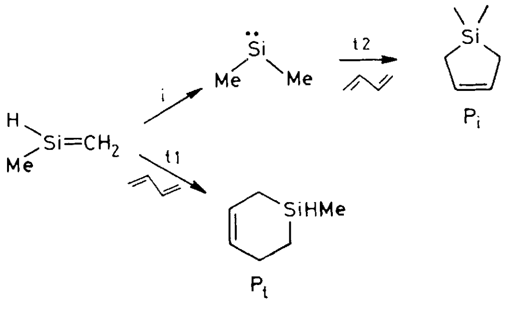
Scheme 1

$$\frac{P_i}{P_t} = \frac{k_i}{k_{t1}\,[\text{butadiene}]} \qquad (5)$$

The non-observation of P_t by Conlin and Wood and of P_i by Barton *et al.* may be expressed by the (cautious) inequalities $[P_i]/[P_t] > 10$ and $[P_i]/[P_t] < 10$, respectively. Both sets of workers carried out their experiments in fast-flow systems with at most a few Torr pressure of diene. From a reasonably assumed concentration of butadiene of $10^{-4.5}$ mol dm^{-3} the limiting rate constant ratios, k_i/k_{t1} may be obtained under each set of conditions. These are shown in Table 1.‡ Arrhenius A factors for reactions i and t1 may be reasonably established both by analogy with structurally similar processes and from transition state theoretical arguments[13] as A_i *ca.* $10^{13.5\pm1}$ s^{-1} and A_{t1} *ca.* $10^{7\pm1}$ dm^3 mol^{-1} s^{-1} and thus $A_i/A_{t1} = 10^{6.5\pm1.4}$ mol dm^{-3}. The use of this ratio in combination with k_i/k_{t1} enables limiting $(E_i - E_{t1})$ (E = activation energy) values to be calculated at each temperature. These are shown in Table 1. Finally although E_{t1} is not known it may be reasonably surmised to lie in the range of 20—40 kJ mol^{-1} from observations of the competition between dimerisation of 2-methyl-2-silapropene and its trapping by butadiene.[14] This enables limiting values for E_i to be determined.§ These are also shown in Table 1.

Table 1

T/K	(k_i/k_{t1})/ mol dm^{-3}	$(E_i - E_{t1})/RT$	$E_i - E_{t1}$/ kJ mol^{-1}	E_i/ kJ mol^{-1}
925	$\geqslant 10^{-3.5}$	$\leqslant 23 \pm 3$	$\leqslant 177 \pm 25$	$\leqslant 207 \pm 27$
723	$\leqslant 10^{-3.5}$	$\geqslant 23 \pm 3$	$\geqslant 138 \pm 19$	$\geqslant 168 \pm 22$



Scheme 2. i = isomerisation; t = trapping process.

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† For simplicity the diene trap is shown as butadiene (rather than dimethylbutadiene).

‡ Error estimates in Table 1 have been vectorially combined since it is improbable that all uncertainties will operate in the same direction.

§ Other uncertainties include the possibilities of some reversibility of the isomerisation step (i) and the fact that it will almost certainly not be at its unimolecular high pressure limit. However, these small added uncertainties do not seriously undermine the general argument.

These calculations demonstrate that the experimental results of Conlin and Wood and Barton *et al.* are not in conflict as far as reaction (1) is concerned. It can occur at 925 K, without occurring at 723 K provided that the activation energy E_1 lies (most probably) in the range 168—207 kJ mol^{-1}, although the uncertainties could allow a larger range. Nevertheless this range is encouragingly close to the theoretical barrier height, and lends some credence to these arguments.

Thus, isomerisation of silaethene to silylene could be a reasonable high temperature process. Although this discussion is not a mechanistic proof it does away with the need to invoke the mechanism of Scheme 1 with its unprecedented and in our view, unlikely, 1,2-H migration in the biradical intermediate.¶ Of course these arguments do not explain the apparent observation of reaction (1) at 100 K in a matrix by Drahnak *et al.*[9] On the other hand the later matrix-isolation experiments[12] do not apparently lead to isomerisation of sila-olefins and so there appears to be a contradiction in the matrix-isolation studies.

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References

1 L. E. Gusel'nikov and N. S. Nametkin, *Chem. Rev.*, 1979, **79**, 529.

2 B. Coleman and M. Jones, Jr., *Rev. Chem. Intermediates*, 1981, **4**, 297.

3 A. G. Brook, F. Abdesaken, B. Gutekunst, A. Gutekunst, and R. K. Kallury, *J. Chem. Soc., Chem. Commun.*, 1981, 191.

4 I. M. T. Davidson and I. T. Wood, *J. Chem. Soc., Chem. Commun.*, 1982, 550.

5 M. S. Gordon, *Chem. Phys. Lett.*, 1978, **54**, 9.

6 H. F. Schaefer, III, *Acc. Chem. Res.*, 1979, **12**, 288.

7 R. Walsh, *Acc. Chem. Res.*, 1981, **14**, 246; a recent ion cyclotron resonance experiment, however, suggests this reaction is highly endothermic, W. J. Hehre, personal communication.

8 R. T. Conlin and D. L. Wood, *J. Am. Chem. Soc.*, 1981, **103**, 1843.

9 T. J. Drahnak, J. Michl, and R. West, *J. Am. Chem. Soc.*, 1981, **103**, 1845.

10 T. J. Barton, S. A. Burns, and G. T. Burns, *Organometallics*, 1982, **1**, 210.

11 J. D. Goddard, Y. Yoshioka, and H. F. Schaefer, III, *J. Am. Chem. Soc.*, 1980, **102**, 7644; Y. Yoshioka and H. F. Schaeffer, III, *J. Am. Chem. Soc.*, 1981, **103**, 7366.

12 (a) N. Auner and J. Grobe, *Z. Anorg. Allg. Chem.*, 1979, **459**, 15; (b) G. Maier, G. Mihm, and H-P Reisenauer, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 597.

13 S. W. Benson, 'Thermochemical Kinetics,' 2nd Edn., Wiley, New York, 1976. For a review of Diels–Alder reaction Arrhenius parameters see R. Walsh and J. M. Wells, *Int. J. Chem. Kinetics*, 1975, **7**, 319.

14 H. M. Frey, A. Kashoulis, Lee M-L., S. P. Lodge, I. M. Pidgeon, and R. Walsh, *J. Chem. Soc., Chem. Commun.*, 1981, 915.

¶ 1,4-Biradicals generally react *via* C(2)–C(3) bond rupture or 1,5-H migration (when possible).