Simple Functional Siloles. Kinetics and Mechanism of Pyrolysis of 1-Allyl-1-silacyclopent-3-enes[1]

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1-Allyl-1-silacyclopent-3-enes are shown by trapping with MeOH and MeOD to undergo endocyclic retroene elimination of propene, initially to form 2*H*-siloles, which rapidly isomerize to 1*H*-siloles; additionally, a 1-allyl-1-silacyclopent-3-ene with a substituted allyl group undergoes a 1,3-silyl shift. Kinetics of these processes were measured and found to be faster than in their acyclic counterparts because of lower activation energies. Explanations based on conformation effects are discussed.

Introduction

The chemistry of the metalloles (heterocyclopentadienes) of group 14 has developed considerably in recent years, by the synthesis of siloles,[2,3] germoles,[3,4] and stannoles,[5] unsubstituted or methylated at carbon, and of their π-complexes.[2d,3,4b,c,6] Of the siloles with hydrogen or with functional groups on the heteroatom, only the C-phenylated ones are known.[7] There is good evidence from the work of Barton and Burns[2a] that flash vacuum pyrolysis (FVP) of 1-methyl-1-allylsilacyclopent-3-ene (**1**) gives the 1-methylsilole (**5**), but it was only isolated as the dimer **6** (Scheme I); the simple silole appeared to be unstable in the monomeric state and has not hitherto been definitively characterized.[8]

Since we have shown that methylation of carbon atoms 3 and 4 in the ring stabilizes monomeric metalloles,[2d,e,4c] we thought it worthwhile to study the FVP of 1-allyl-3,4-dimethylsilacyclopent-3-enes.[1] We now report a full account of that work and of gas kinetic studies of the pyrolysis of two 1-allyl-3,4-dimethyl-silacyclopent-3-enes and of the simpler compound **1**; kinetic measurements have proved to be very helpful in elucidating the mechanism of pyrolysis of the acyclic allylsilanes, allyltrimethylsilane,[9a,b] and diallyldimethylsilane.[9c]

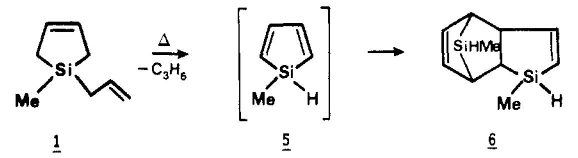
Results

1. FVP of 1-Allyl-3,4-dimethylsilacyclopent-3-enes. FVP experiments were carried out on compounds **2**, **3**, and **4** at 600 °C (Schemes II and III). The pyrolyzate from compound **2**, trapped at −196 °C, consisted of propene and a liquid phase, shown by low-pressure distillation to consist of three components: the original silacyclopentene (**2**, 50%), the 1,3,4-trimethylsilole (**7**, 43%), and its transoid isomer, the 1,3-dimethyl-4-methylenesilacyclopent-2-ene (**8**, 7%) [**2**:**7**:**8** = 1:0.86:0.14]. The combined yield of **7** and **8** was about 80% of the **2** consumed.

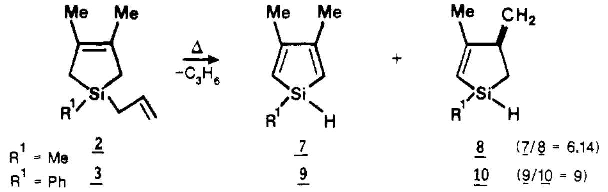
Siladienes **7** and **8** were also formed in the FVP of compound **4** (**7**:**8** = 6.15:1), together with butene and a large amount of "recovered silacyclopentene" (75% of the crude product); GC analysis showed this to be a mixture of three isomers, **4a**:**4b**:**4c** = 1:1.48:1.22, identified by NMR (see Table II in the Experimental Section) as follows: 4a, original compound 4; **4b**, 1-(*trans*-crotyl)-1,3,4-trimethylsilacyclopent-3-ene; **4c**, 1-(*cis*-crotyl)-1,3,4-trimethylsilacyclopent-3-ene. The combined yield of 7 and 8 was about 69% of the 4 transformed.

Compound **3** was more troublesome because of its low volatility and had to be introduced into the FVP apparatus in solution or through a preheater at the entrance to the thermolysis tube; the latter method was more satisfactory.

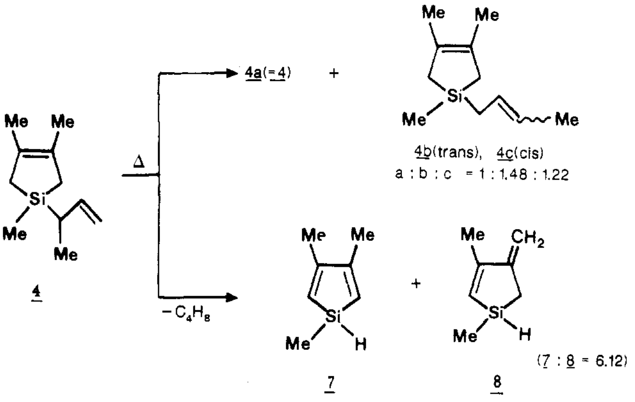
Scheme I



Scheme II



Scheme III



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[‡] The University.

(1) Preliminary communication: Bêteille, J. P.; Manuel, G.; Laporterie, A.; Iloughmane, H.; Dubac, J. *Organometallics* **1986**, *5*, 1742.

(2) (a) Barton, T. J.; Burns, G. T. *J. Organomet. Chem.* **1979**, *179*, C17. (b) Laporterie, A.; Dubac, J.; Mazerolles, P.; Iloughmane, H. *Ibid.* **1981**, *206*, C25; **1981**, *216*, 321. (c) Burns, G. T.; Barton, T. J. *Ibid.* **1981**, *209*, C25. (d) Dubac, J.; Laporterie, A.; Iloughmane, H. *Ibid.* **1985**, *293*, 255. (e) Dubac, J.; Laporterie, A.; Manuel, G.; Iloughmane, H. *Phosphorus Sulfur* **1986**, *27*, 191.

(3) Iloughmane, H. Thèse d'Etat, Université Paul-Sabatier, Toulouse, 1986, No. 1247.

(4) (a) Laporterie, A.; Manuel, G.; Dubac, J.; Mazerolles, P.; Iloughmane, H. *J. Organomet. Chem.* **1981**, *210*, C33. (b) Laporterie, A.; Iloughmane, H.; Dubac, J. *Ibid.* **1983**, *244*, C12. (c) Guimon, C.; Pfister-Guillouzo, G.; Dubac, J.; Laporterie, A.; Manuel, G.; Iloughmane, H. *Organometallics* **1985**, *4*, 636.

(5) (a) Ashe, A. J., III; Diephouse, T. R. *J. Organomet. Chem.* **1980**, *202*, C95. (b) Ashe, A. J., III; Drone, F. J. *Organometallics* **1984**, *3*, 495.

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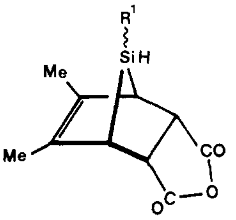
The 1-phenyl-3,4-dimethylsilole (**9**) and its transoid isomer (**10**) were recovered in the ratio **9**:**10** = 9:1, with a combined yield that was about 40% of compound **3** consumed (Scheme II).

The siloles **7** and **9**, and their respective isomers, were identified by NMR, MS, and IR spectroscopy (details in the Experimental Section) and by their maleic anhydride adducts[10] **11** and **12**.



R^1 = Me (**11**), Ph (**12**)

2. Kinetic Results. Kinetic measurements were made by the stirred-flow (SFR) technique.[11,12] Products formed under SFR conditions were identified by pyrolyses in a similar apparatus with analysis by GC/mass spectrometry.[12] Compound **3** was too involatile for kinetic studies, but compounds **1**, **2**, and **4** gave the following results.

Compound **1**, pyrolyzed between 421 and 563 °C, gave as main products: recovered **1**, propene, and 1-methylsilole (**5**). To the best of our knowledge, this is the first observation of the simple silole **5** and our mass spectrum for it is the only available spectroscopic criterion for identifying a silole unsubstituted at carbon with a Si–H bond.[13] Minor products were five isomers of **1** (**1a–e**) which were not otherwise identified and which totaled ca. 20% of **1** transformed.[14] The kinetics of formation of propene and silole **5** were measured; the resulting first-order rate constants and Arrhenius parameters derived from them are in Table I, Figure 1, and Figure 2.

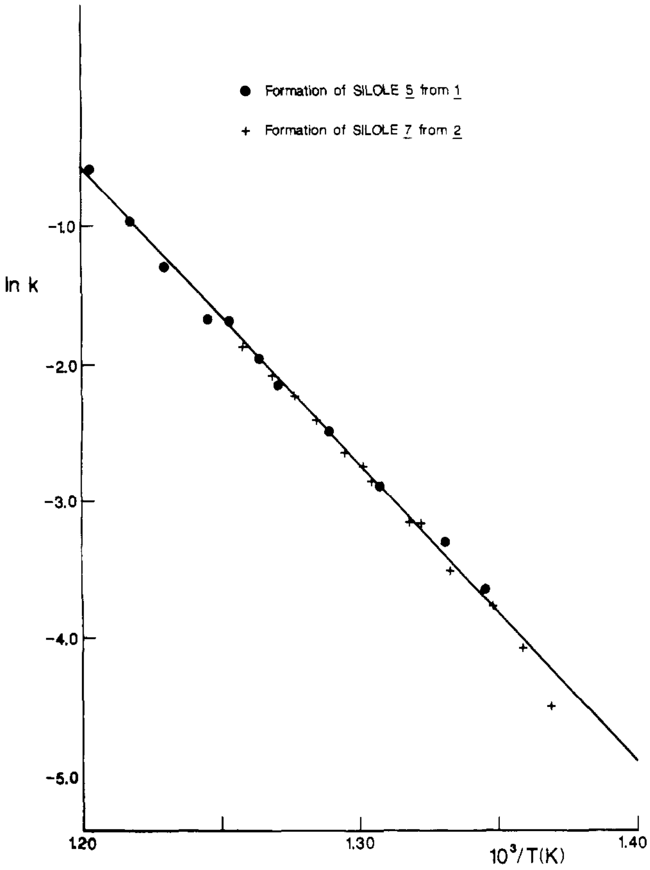


Figure 1. Pyrolysis of **1** and **2**: Arrhenius plot for formation of siloles.

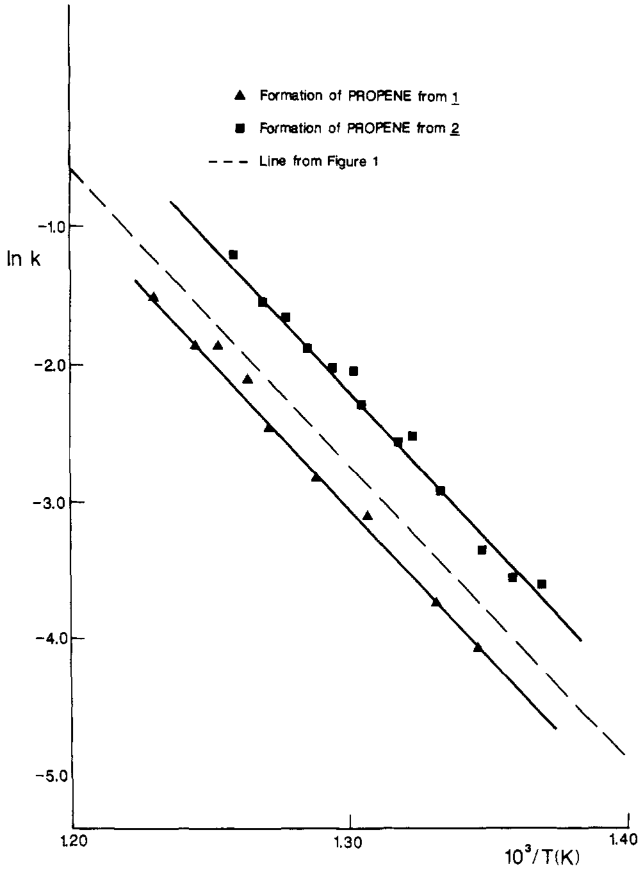


Figure 2. Pyrolysis of **1** and **2**: formation of propene.

The products expected[1] from compound **2** were propene, the silole **7**, and a small amount of its isomer **8**. In fact,

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(6) (a) Burns, G. T.; Colomer, E.; Corriu, R. J. P. *Organometallics* **1983**, *2*, 1901. (b) Ananias de Carvalho, L. C.; Dartiguenave, M.; Dahan, F.; Dartiguenave, Y.; Dubac, J.; Laporterie, A.; Manuel, G.; Iloughmane, H. *Ibid.* **1986**, *5*, 2205. (c) Burns, G. T.; Colomer, E.; Corriu, R. J. P.; Lheureux, M.; Dubac, J.; Laporterie, A.; Iloughmane, H. *Ibid.* **1987**, *6*, 1398.

(7) (a) Atwell, W. H.; Weyenberg, D. R.; Gilman, H. *J. Org. Chem.* **1967**, *32*, 885. (b) Carré, F.; Colomer, E.; Corey, J. Y.; Corriu, R. J. P.; Guérin, C.; Henner, B. J. L.; Kolani, B.; Wong Chi Man, W. W. W. *Organometallics* **1986**, *5*, 910 and references therein.

(8) (a) Hwang, R. J.; Gaspar, P. P. *J. Am. Chem. Soc.* **1978**, *100*, 6626. (b) Siefert, E. E.; Loh, K. L.; Ferrieri, R. A.; Tang, Y. N. *Ibid.* **1980**, *102*, 2285. (c) Gaspar, P. P.; Chen, Y.; Helfer, A. P.; Konieczny, S.; Ching-Lin Ma, E.; Mo, S. *Ibid.* **1981**, *103*, 7344. (d) The dimer of the silole would be formed during the thermolysis of 1,1,1,3,3,3-hexamethyltrisilane in presence of butadiene in low yield (2%): Boo, B. H.; Gaspar, P. P. *Organometallics* **1986**, *5*, 698.

(9) (a) Davidson, I. M. T.; Wood, I. T. *J. Organomet. Chem.* **1980**, *202*, C65. (b) Barton, T. J.; Burns, S. A.; Davidson, I. M. T.; Ijadi-Maghsoodi, S.; Wood, I. T. *J. Am. Chem. Soc.* **1984**, *106*, 6367. (c) Auner, N.; Davidson, I. M. T.; Ijadi-Maghsoodi, S. *Organometallics* **1985**, *4*, 2210.

(10) Maleic anhydride reacts easily at room temperature with various C-unsubstituted or C-methylated siloles. This type of adduct has probably the endo configuration.[2b,d] The *a* isomer (**11**, **12**) in which the (Si)–H atom is shielding by the ethylenic C(5)–C(6) bond is probably the *syn*-SiR^1 isomer (90% with the large Si–Ph substituent).

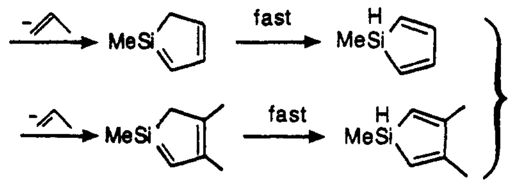
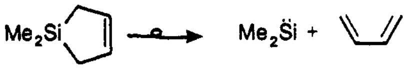
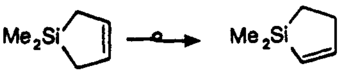
(11) Baldwin, A. C.; Davidson, I. M. T.; Howard, A. V. *J. Chem. Soc., Faraday Trans 1* **1975**, *71*, 972.

(12) Davidson, I. M. T.; Eaton, G.; Hughes, K. J. *J. Organomet. Chem.* **1988**, *347*, 17.

(13) The mass spectrum of silole **5** (see Experimental Section) is entirely consistent with that of a hydrogenosilole (cf. the mass spectra of the known compounds **7** and **9**); there were three peaks of strong intensity retaining the ring structure, at m/e 96 (M^+), 95 ($[M - H]^+$), and 81 ($[M - Me]^+$). The fragmentation of the dienic ring of C-methylated siloles[3] involves loss of propyne from M^+, $[M - H]^+$, and $[M - Me]^+$ ions. The fragmentation of the dienic ring of silole **5** likewise seems to involve loss of acetylene from ring fragments (peaks at m/e 68–70 and 53–55); the ions formed would be derivatives of silirene (silacyclopropene).

(14) **1a** appears to have a free allyl group, like **1** itself; **1b** and **1c** have almost identical mass spectra with loss of propene and methyl as prominent processes; loss of propene and ethene are important in the mass spectrum of **1d** and loss of propyl and ethene in **1e**.

Table I. Arrhenius Parameters and Rate Constants

reaction	log *A*	*E*, kJ mol^{-1}	$k_{500°C}$, s^{-1}	ref
1 2 	11.0 ± 0.1	179 ± 2	8.01 × 10^{-2}	
4 → 4b (trans-isomer)	11.6 ± 0.3	176 ± 4	5.09 × 10^{-1}	
4 → 4c (cis-isomer)	11.3 ± 0.2	173 ± 3	4.07 × 10^{-1}	
	12.3 ± 0.1	200 ± 1	6.09 × 10^{-2}	28
	11.2 ± 0.1	199 ± 2	5.65 × 10^{-3}	9c
	11.6 ± 0.5	230 ± 8	1.14 × 10^{-4}	9b
	15.6 ± 0.5	307 ± 8	7.15 × 10^{-6}	9b
	11.9 × 0.2	230 ± 4	2.28 × 10^{-4}	23
	12.3 ± 0.6	251 ± 9	2.18 × 10^{-5}	23

under the conditions used for kinetic experiments between 452 and 521 °C, the only GC peaks observed were recovered 2, propene, and silole 7, with the isomer 8 as a small unresolved feature on the tail of that peak. In contrast to compound 1, no isomers of 2 were formed.

The presence of 8 under SFR conditions was established in separate experiments at higher temperatures (528–557 °C) using a high-resolution capillary column in the GC/mass spectrometer. Two clearly separated peaks corresponding to 7 and 8 were observed; the ratio of 7:8 was 7.69:1 at 528 °C, decreasing to 3.01:1 at 557 °C.

Kinetic data for the formation of propene and of (7 + 8) are in Table I. First-order rate constants for the formation of silole 5 from 1 agreed very well with those for the formation of (7 + 8) from 2, as shown in the combined Arrhenius plot, Figure 1. The best straight line through the points in Figure 1 gave log *A* (s^{-1}) = 11.0 ± 0.1; *E*/kJ mol^{-1} = 179 ± 2. Rate constants for the formation of propene were rather more scattered and were higher in the pyrolysis of 2 than in the pyrolysis of 1, but both sets of points gave Arrhenius lines parallel to that in Figure 1, as shown in Figure 2. There may have been some heterogeneous elimination of propene as a minor process, especially in the pyrolysis of compound 2.

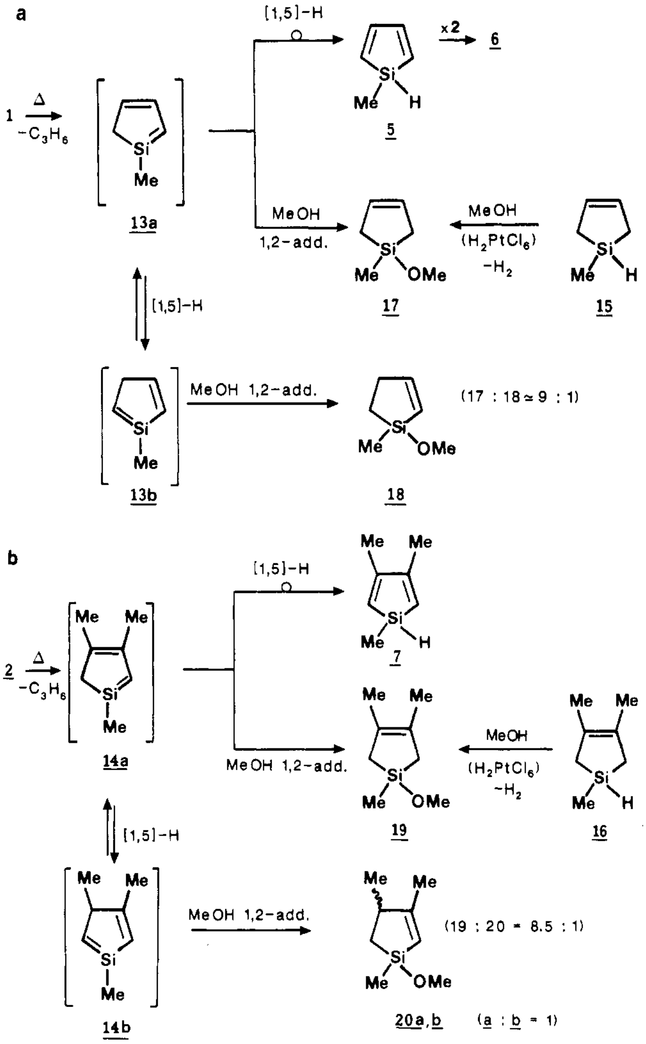
Compound 4 was pyrolyzed between 431 and 507 °C. The main products were butene, silole 7 (and probably also 8 unresolved under these conditions, as with 2), and the isomers 4a–c observed and identified in the FVP experiments. Other isomers analogous to those formed from 1 were not observed. The isomerization products **4b** and **4c** were formed in slightly greater amount than the products butene and silole 7. Kinetic data were obtained for all of these products; Arrhenius plots for formation of butene and silole 7 were curved, indicating kinetic complexity, but good Arrhenius lines were obtained for the formation of the isomers **4b** and **4c** (Arrhenius parameters are in Table I), corresponding to a **4b**:**4c** ratio of 1.19:1 at 427 °C, rising to 1.26:1 at 507 °C.

The most likely explanation for the curved Arrhenius plots for the formation of butene and silole 7 is that at least one of the isomers **4b** and **4c** also decomposes to butene and silole 7 at a similar rate to 4 itself. This possibility will be pursued in the Discussion.

3. Identification of intermediates (2*H*-Siloles) by Trapping with Methanol. It is clear from the relative size of the rate constants for retroene eliminations in Table I that exocyclic loss of propene (analogous to that in allyltrimethylsilane) is unimportant in the pyrolysis of 1, 2, and 4 under the conditions used in this work; only endocyclic eliminations need be considered. The nature of the intermediates formed in these eliminations was investigated by trapping with methanol.

Compound 1 was pyrolyzed in the SFR at 544 °C with a 20-fold excess of methanol. The products, besides propene and recovered or isomerized 1, were the methylsilole 5 and two new products 17 and 18 (17:18 ≃ 9:1). These two products, which have similar mass spectra and the same molecular mass (M$^+$ = 128), are two isomers

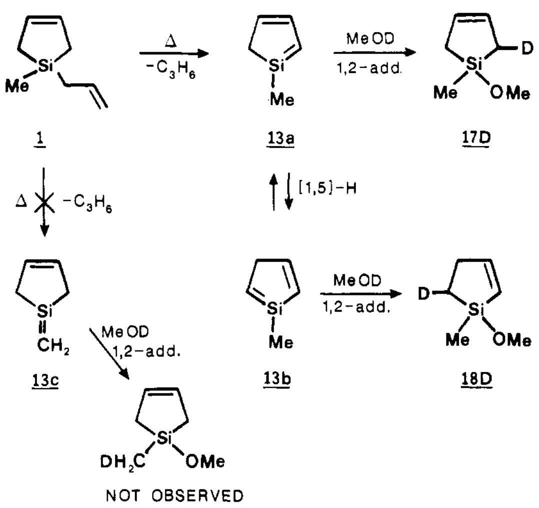
Scheme IV



corresponding to the addition of methanol to silole intermediates with a silicon–carbon π-bond in the ring. As we felt that mass spectra alone were insufficient to identify these new methoxysilacyclopentenes **17** and **18**, we attempted to prepare them by FVP of **1**. This was unsuccessful, even in the presence of a substantial excess of methanol, presumably because isomerization of cyclic silenes to **5** by a 1,5-H shift was very rapid (the methanol adducts were observed under SFR conditions either because of the different time scale or because isomerization to **5** may be surface-catalyzed; surface reactions are favored under FVP conditions but suppressed in the SFR because of the high pressure of carrier gas[11,12]). However, we successfully prepared 1-methoxy-1-methylsilacyclopent-3-ene directly from 1-methylsilacyclopent-3-ene (**15**) (Scheme IVa) and found that its mass spectrum was identical with that of product **17**. As the differences in the mass spectra of **17** and **18** were those to be expected between silacyclopent-3-enes and silacyclopent-2-enes[17a] and as **18** was the minor product, we are confident that it is the methoxysilacyclopent-2-ene.

It is believed that methanol undergoes both 1,2- and 1,4-addition to conjugated silenes, with the former being preferred,[15,16] but the foregoing results could be explained simply in terms of 1,2-addition to a 2*H*- and 3*H*-silole, respectively, the latter being formed from the former by a 1,5-H shift, as shown in Scheme IVa.

Scheme V



Similar experiments in the SFR with compound **2** and methanol were thwarted by the substantial difference in volatility between the two compounds, but we succeeded with trapping experiments in a sealed tube at 460 °C, again with a 20-fold excess of methanol. Although there were many products under these conditions, there were three GC peaks, one of which was the most intense in the chromatogram, with mass spectra consistent with the expected methoxysilacyclopentenes **19** and **20** (Scheme IVb). The most abundant product (**19**:**20** = 8.5:1) was identified with 1-methoxy-1,3,4-trimethylsilacyclopent-3-ene, prepared as shown in Scheme IVb from 1,3,4-trimethylsilacyclopent-3-ene (**16**). The two other minor products were probably the cis and trans isomers of the silacyclopentene **20**.[17b]

To confirm the kinetic argument against exocyclic elimination, we undertook some trapping experiments with MeOD, which should give different adducts from each intermediate, as shown in Scheme V. Copyrolysis of **1** and MeOD (99% isotopic purity in 10-fold excess) at 559 °C gave two adducts, just as in the experiment with MeOH. The main adduct had a more complex mass spectrum than we had expected probably because of some deuterium exchange reactions in the apparatus, but it was clear that the 74^+:75^+ intensity ratio was the same as in the nondeuteriated adduct **17**; as 74^+ is $[MeSiOMe]^+$ resulting from loss of butadiene, that confirms that the adducts are **17D** and **18D** from **13a** and **13b**; an adduct from **13c** would have deuterium incorporated in a methyl group. It should also be noted that 1,4-addition of MeOD to **13b** would give an adduct that is still a silene and would therefore be expected rapidly to add another molecule of MeOD; our nonobservance of such an adduct may be additional evidence that 1,2-addition is of much greater importance than 1,4-addition.

Discussion

1. Considerations on the Stability of the Siloles 5, 7, and 9. The dilute gas-phase conditions of our SFR

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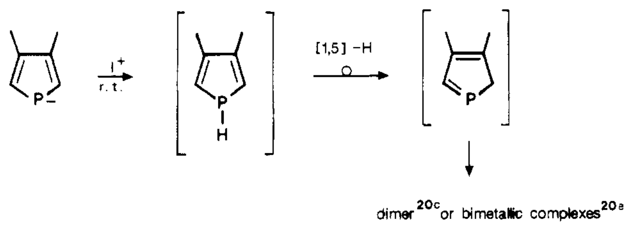
(15) Barton, T. J.; Wulff, W. D.; Arnold, E. V.; Clardy, J. *J. Am. Chem. Soc.* **1979**, *101*, 2733.

(16) (a) Ando, W.; Hamada, Y.; Sekiguchi, A. *J. Chem. Soc., Chem. Commun.* **1982**, 787. (b) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419 and references therein.

(17) (a) The silacyclopent-2-enes give a higher peak ratio of $[M - Me]^+$:M^+ than the silacyclopent-3-enes, with less intense $[M - C_4H_6]^+$ and $[M - HCl]^+$ (for 1-chlorosilacyclopentenes) or $[M - MeOH]^+$ (for 1-methoxysilacyclopentenes). (b) The mass spectra of **20a** and **20b** are almost identical, with a base peak at *m/e* 59 ($[SiOMe]^+$) like **19**, but with two important differences: a higher peak ratio $[M - Me]^+$:M^+ for **20** than for **19**, but a less intense $[M - MeOH]^+$.

Scheme VI



experiments sufficiently impeded dimerization of silole **5** for it to be observed entirely as the monomer; dimerization is known to be rapid in the condensed phase.[2a] The siloles **7** and **9** are stabilized in the monomeric state compared to the 1-methylsilole **5** by the double C-methylation on carbon atoms 3 and 4.[18] It appears from previous work[2e,19] that transoid species such as **8** and **10** are the thermodynamic isomers of 3,4-dimethylsiloles, while siloles **7** and **9** are the kinetic products in the pyrolysis reactions studied in this work. In our SFR experiments to confirm the presence of **8** in the pyrolysis of **2**, the ratio of **8** to **7** increased with increasing temperature, consistent with isomerization to the transoid form in the SFR reactor.

It is interesting to consider the relative stability of 1*H*- and 2*H*-siloles and of 1*H*- and 2*H*-phospholes.[20] 2*H*-Siloles, having a Si=C double bond, are unstable intermediates. In 1979, Barton et al.[15] trapped a 2*H*-silole obtained by isomerization of 1-methyl-1-trimethylsilyl-2,5-diphenylsilole, which underwent a sigmatropic 1,5-trimethylsilyl migration below 100 °C (trimethylsilyl migration occurs more readily than hydrogen migration[21]).

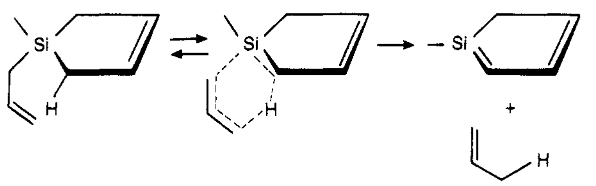
1*H*-Siloles (including the previously undetected simple silole **5**) were the ultimate products in our SFR experiments, but we also chemically identified adducts resulting from the trapping of 2*H*-siloles by methanol, thus indicating that the 1*H*-siloles were formed by 1,5-H migration from 2*H*-siloles. On the other hand, Mathey et al.[20] have observed that 1*H*-phospholes isomerize to 2*H*-phospholes, which dimerize spontaneously but may be trapped by complexation (Scheme VI).

Consequently, the relative stability of the two isomeric forms of heteroles, 1*H* and 2*H*, is reversed on passing from phosphorus to silicon. This result is understandable when one compares the relative stability of ω-bonds in silanes and phosphines (Si > P) and of π-bonds in silenes and phosphenes (Si < P).[22]

2. Kinetic Results. Our kinetic results are in Table I, together with those for some related pyrolyses. Since the rate constants for pyrolysis of 1,1-dimethyl-1-silacyclopent-3-ene[23] are so much lower than those for the reactions of **1**, **2**, and **4**, it is obvious that the silacyclopentene ring is thermally stable under the conditions of this work.

There were two competing primary processes in the pyrolysis of allyltrimethylsilane, viz., radical-forming homolysis of the silicon–allyl bond, and a concerted retroene elimination of propene.[9a,b] In the pyrolysis of diallyldimethylsilane, the retroene reaction was considerably facilitated by weakening of a carbon–hydrogen bond by the second allyl group; homolysis was therefore unimportant by comparison, but three isomers of diallyldimethylsilane were observed as minor products.[9c] The kinetic results for the retroene reactions of allyltrimethylsilane and diallyldimethylsilane were entirely consistent with those for the well-established analogous reactions in other allylic organic compounds.[24-26] As **1** and **2** are diallyl compounds, they might be expected to undergo retroene elimination of propene with similar Arrhenius parameters to those for diallyldimethylsilane; the *A* factors are indeed similar, but the activation energy is 20 kJ mol^{-1} lower, making the retroene reactions of **1** and **2** ca. 14 times faster than in diallyldimethylsilane at 500 °C. We believe that this reduction in activation energy is a conformational effect; in silacyclopent-3-enes, which are planar rings,[27] the allylic carbon–hydrogen bond in the ring is more easily accessible to the allyl group attached to silicon for forming the six-center transition state than in diallyldimethylsilane, as shown in Scheme VII.

Scheme VII



Formation of the isomers **4b** and **4c** from compound **4** had very similar Arrhenius parameters. These reactions are likely to be sigmatropic 1,3-silyl shifts, exactly analogous to those observed by Kwart and Slutsky.[28] Relative to the trimethylsilyl compound studied by these authors, isomerization of **4** requires an activation energy that is lower by some 25 kJ mol^{-1} but with a tighter transition state (indicated by the lower A factor), giving a 14-fold rate enhancement at 500 °C (Table I). This may also be a conformational effect resulting from increased accessibility of silicon in the cyclic compound **4**.

With regard to the formation of butene and silole **7** in the pyrolysis of compound **4**, it is likely that the retroene reaction forming these products would have very similar Arrhenius parameters for the original compound **4** and for the isomer **4b** [1-(*trans*-crotyl)-1,3,4-trimethylsilacyclopent-3-ene] but that the retroene reaction from isomer **4c** [1-(*cis*-crotyl)-1,3,4-trimethylsilacyclopent-3-ene] would have a significantly higher activation energy because the cis methyl group would interfere with the formation of the transition state.

The foregoing conformational suggestions were confirmed by molecular graphics using CHEM-X.[29] Calculations on compounds **1** and **4** showed that the lowest energy conformers had angles between the methyl and allyl groups attached to silicon that were larger than the tetrahedral angle (112° for compound **1** and 115° for compound **4**) because of the reduced ring angle at silicon (ca.

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[18] For a discussion of the stability of siloles toward the [4 + 2] dimerization reaction, see ref 2d.

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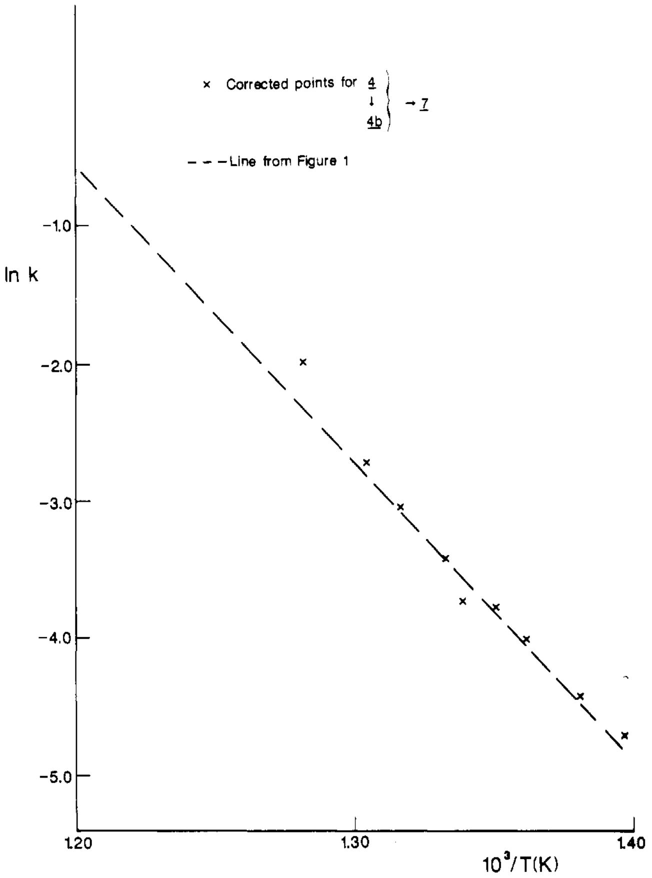

Figure 3. Pyrolysis of 4: corrected rate constants for formation of silole 7.

98°), thus making the transition state for the retroene reaction more accessible than in diallyldimethylsilane. Also, bond rotation to adopt the conformation for the retroene reaction required a smaller repulsion energy barrier to be overcome in compounds 1 and 4 than in diallyldimethylsilane. The most stable conformer of compound 4 is very close to that required for the 1,3-silyl shift, in keeping with the observed reduction in activation energy compared to acyclic systems.[28] For the retroene reaction, the repulsion energy in the cis isomer **4c** was indeed considerably higher than in **4b** or **4** itself.

Kinetic data were therefore recalculated for the formation of **7** in the SFR pyrolysis of **4**, on the assumption that both **4** and **4b**, but not **4c**, underwent the retroene reaction forming **7** with the same rate constant; that rate constant could be calculated at each experimental temperature from the measured rate constants for the total formation of **7** and for the isomerization of **4** to **4b**, as explained in the Appendix. These calculated rate constants lay close to the combined Arrhenius line of Figure 1, as shown in Figure 3. This result depends on silole **7** being formed only from **4** and **4b**; the linearity of the points and the agreement with the original line break down if the calculation is extended to include formation of **7** from the isomer 4c.

We conclude that the foregoing assumptions are reasonable and that retroene formation of an alkene and a silole has about the same Arrhenius parameters for compounds **1**, **2**, **4**, and **4b**. It should be noted that the sigmatropic 1,3-silyl shift in compound **4** is ca. 5 times faster than the retroene reaction; consequently, this silyl shift is in principle an important reaction of allylsilanes, although of course it gives no new product if the allyl group is unsubstituted. On the other hand, compounds with two unsubstituted allyl groups attached to silicon (compound **1** and diallyldimethylsilane) give multiple isomers as minor pyrolysis products; formation of these isomers does not occur if one of the allyl groups is substituted (compounds **2** and **4**).

Experimental Section

1. **General Data.** Flash Vacuum Pyrolysis (FVP) experiments were carried out by introducing the pure silacyclopentene in argon carrier gas into a 40-cm quartz tube (9-mm diameter) packed with quartz chips and heated in a tube furnace. The exit pressure was 0.05 mmHg. The inlet of the quartz tube was preheated electrically. The crude product, collected in a trap cooled in liquid nitrogen, was warmed to room temperature, analyzed by GC (20 ft, 20% SE-30/Chromosorb W and 150 ft capillary columns were used), and distilled.

Kinetic measurements were made by the SFR technique with analysis by gas chromatography; products were identified by pyrolysis in a similar SFR apparatus with analysis by GC/mass spectrometry (HP 5995C). Both techniques have been fully described elsewhere.[11,12] The GC was calibrated in the normal way for propene, butene, and compounds **1**, **2**, **4**, **7**, and **9**. Direct calibration for silole **5** was, of course, not possible; 1-methylsilacyclopent-3-ene (**15**) was used instead because the sensitivity of the flame ionization detector depends mainly on the carbon skeleton of the molecule. Kinetics of the isomerization of **4** to **4b** and **4c** were based on the assumption that these three compounds had the same sensitivity.

Proton, carbon-13, and silicon-29 NMR spectra were recorded on a Bruker AM 300 WB spectrometer.

2. **Preparation and Identification of Compounds.** The starting silacyclopentenes **1**–**4** were prepared by the use of highly reactive magnesium.[30]

1-Allyl-1-methylsilacyclopent-3-ene (1). To a suspension of highly reactive magnesium in THF (500 mL) prepared from dibromoethane (94 g, 0.50 mol), magnesium (14 g, 0.57 mol), and sodium (19 g, 0.83 mol)[31] was added butadiene (80 mL, ≈1 mol), and the mixture was stirred at room temperature for 3 h (methanol reflux condenser at -20 °C). Then allylmethyldichlorosilane (65.14 g, 0.42 mol) in THF (300 mL) was slowly added, the stirring continued at room temperature for 4 h, and the THF refluxed for 4 h. After hydrolysis at low temperature, ether extractions and sodium sulfate drying, the organic phase was concentrated. Distillation gave 1 (35.42 g) in 61% yield; bp 66 °C (40 mmHg) [lit.[2a] 55 °C (23 mmHg)]. NMR: Tables II and IV. GC/MS: *m/e* (≥5%) 138 (M^+, 2), 110 (7), 98 (11), *97* ($[M - C_3H_5]^+$, 100%), 96 ($[M - C_3H_6]^+$, 73), 95 (44), 81 (6), 71 (15), 69 (21), 67 (7), 58 (8), 55 (18), 54 (5), 53 (11), 45 (13), 44 (6), 43 (54), 42 (7), 39 (8), 29 (6), 28 (5), 27 (5).

1-Allyl-1,3,4-trimethylsilacyclopent-3-ene (2). The synthesis of this silacyclopentene (68% yield), by the same method as for 1, has been described.[30] Note that the contact time between highly reactive magnesium and 2,3-dimethylbutadiene (12 h) was much more than with butadiene (compound 1) at room temperature. NMR: Tables II and IV. GC/MS: *m/e* (≥5%) 166 (M^+, 4), 126 (12), 125 ($[M - C_3H_5]^+$, 87), *124* ($[M - C_3H_6]^+$, 100%), 123 (42), 110 (9), 109 (21), 97 (13), 95 (8), 85 (20), 83 (18), 81 (5), 69 (13), 67 (11), 59 (79), 55 (16), 53 (10), 45 (13), 44 (5), 43 (48), 42 (5), 41 (8), 39 (9), 29 (6), 28 (6).

1-Allyl-1-phenyl-3,4-dimethylsilacyclopent-3-ene (3). 3 (63.31 g) was obtained in 66% yield by the same method from allylphenyldichlorosilane (91.21 g, 0.42 mol) and 2,3-dimethylbutadiene (54 g, 0.66 mol); bp 104 °C (0.2 mmHg). NMR: Tables II and IV. GC/MS: *m/e* (≥5%) 228 (M^+, 2), 188 (21), *187* ($[M - C_3H_5]^+$, 100%), 186 ($[M - C_3H_6]^+$, 93), 185 (18), 172 (17), 159 (9), 145 (25), 131 (7), 121 (13), 110 (8), 109 (63), 107 (13), 105 (58), 81 (6), 79 (9), 69 (8), 67 (8), 59 (9), 53 (12). Anal. Calcd for $C_{15}H_{20}Si$: C, 78.87; H, 8.82. Found: C, 78.92; H, 8.78.

1-(1-Methyl-2-propenyl)-1,3,4-trimethylsilacyclopent-3-ene (4). 4 (16.41 g) was obtained in 65% yield by the same method from (1-methyl-2-propenyl)methyldichlorosilane (23.68 g, 0.14

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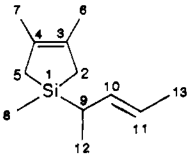
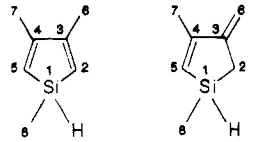
Table II. ^{1}H and ^{13}C NMR Spectra of Silacyclopentenes[a]



		2,5	3,4	6,7	8	9	10	11	12 or 13
1	^{1}H	1.18 (d)[b] 1.33 (d)	5.93 (s)		0.05 (s)	1.50 (d)	5.72 (m)	4.89 (m)	
	^{13}C	16.18	131.07		−4.21	22.50	134.51	113.45	
2	^{1}H	1.23 (d)[b] 1.41 (d)		1.72 (s)	0.09 (s)	1.53 (d)	5.78 (m)	4.93 (m)	
	^{13}C	23.80	130.58	19.37	−4.03	22.75	134.82	113.45	
3	^{1}H	1.59 (s)		1.78 (s)	*c*	1.82 (d)	5.77 (m)	4.92 (m)	
	^{13}C	23.12	129.52	19.42	*c*	21.27	134.33	114.03	
4 (4**a**)	^{1}H	1.22 (d)[b] 1.43 (d)		1.71 (s)	0.07 (s)	1.64 (m)	5.89 (m)	4.92 (m)	1.07 (d)
	^{13}C	22.67 22.82	130.66	19.36	−5.68	26.47	141.19	110.56	13.27
4b[e]	^{1}H	1.29 (d)[b] 1.43 (d)		1.72 (s)	0.11 (s)	1.50 (d)	5.40 (m)	5.27 (m)	1.61 (d)
	^{13}C	24.15 24.32	130.57	19.40	−3.93	20.82	126.93	123.61	18.16
4c[e]	^{1}H	1.29 (d)[b] 1.43 (d)		1.72 (s)	0.11 (s)	1.56 (d)	5.45 (m)	5.35 (m)	1.53 (d)
	^{13}C	24.15 24.32	130.57	19.40	−3.75	16.16	126.16	121.69	12.76
17	^{1}H	1.16 (d)[b] 1.36 (d)	5.92 (s)		0.19 (s)		3.23 (s)[d]		
	^{13}C	15.59	131.14		−5.02		50.47[d]		
19	^{1}H	1.17 (d)[b] 1.48 (d)		1.69 (s)	0.21 (s)		3.27 (s)		
	^{13}C	23.03	130.72	19.26	−4.76		50.40[d]		

[a] Chemical shifts in ppm from TMS; ^{1}H, ν_0 = 300 MHz; ^{13}C, ν_0 = 75.47 MHz; solvent C_6D_6. [b] CH_2: AB system. [c] Ph(^{1}H): 7.50 and 7.20 ppm; Ph(^{13}C), 128.15, 130.78, 134.19, 137.17 ppm. [d] OMe. [e] The attribution of signals of the two isomers **4b** and **4c** has been carried out from ^{13}C spectrum (gate decoupling), 2D ^{1}H/^{13}C NMR Shift correlation, and from a homonuclear (^{1}H) irradiation. The coupling constants CH=CH were determined: ^3J (*cis*-**4c**) = 10.6 Hz, ^3J (trans-**4b**) = 15 Hz.

Table III. ^{1}H and ^{13}C NMR Spectra of Siloles and Their Transoid Isomers[a]



		1	2,5	3,4	6,7	8
7	^{1}H	4.55 (m)	5.71 (b s)		1.82 (b s)	0.15 (d) ^3J = 4.1 Hz
	^{13}C		123.87	159.03	20.78	−7.74
8	^{1}H	4.55 (m)	1.60 (m) 5.86 (b s)		1.71 (b s) 5.13, 5.04 (m)	0.07 (d) ^3J = 3.5 Hz
9	^{1}H	5.10 (b s)	5.79 (b s)		1.82 (b s)	*b*
	^{13}C		125.92	160.14	20.57	*b*
10	^{1}H	5.10 (b s)	1.59 (m) 5.92 (b s)		1.71 (b s) 5.07, 5.19 (m)	*c*

[a] Chemical shifts, ν_0, and solvent, see Table II. [b] Ph(^{1}H), 7.20 and 7.59 ppm; Ph(^{13}C), 127.9, 128.1, 130.5, 135.3 ppm. [c] Ph(^{1}H): 7.14 and 7.51 ppm.

Table IV. ^{29}Si NMR Spectra of Siloles and Silacyclopentenes

	1	2	3	4	7	8
δ[a]	16.98	10.51	5.47	13.73	−20.63	−10.95
	9	**10**	**15**	**16**	**17**	**19**
δ[a]	−21.62	−11.68	−2.37	−9.45	21.63	26.21

[a] Chemical shifts in ppm from TMS; ν_0 = 59.63 MHz; solvent C_6D_6.

mol), prepared in 45% yield from methyltrichlorosilane and Grignard of the 3-chloro-1-butene in Et_2O, bp 59–61 °C (15 mmHg), and 2,3-dimethylbutadiene (18 g, 0.22 mol), bp 88 °C (15 mmHg). NMR: Tables II and IV. GC/MS: *m/e* (≥5%) 180 (M^+, 5), 126 (14), *125* ($[M - C_4H_7]^+$, 100%), 124 ($[M - C_4H_8]^+$, 78), 123 (33), 109 (17), 97 (28), 95 (10), 85 (21), 83 (27), 81 (8), 73 (7), 71 (9), 69 (15), 67 (11), 60 (7), 59 (88), 55 (20), 53 (11), 45 (19), 44 (7), 43 (54), 41 (8), 39 (9), 29 (10), 28 (14), 27 (8). Anal. Calcd for $C_{11}H_{20}Si$: C, 73.25; H, 11.18. Found: C, 73.27; H, 11.16.

1-Methylsilole (5). The FVP of the silacyclopentene 1 has been previously described;[2a] we only studied this pyrolysis kinetically in the SFR. Nevertheless, use of a SFR apparatus with GC/mass spectrometry enabled us to obtain the mass spectrum of the 1-methylsilole **5**, which dimerizes rapidly in the condensed phase.[2a] GC/MS: *m/e* (≥5%) 97 (12), *96* (M^+, 100), 95 ($[M - H]^+$, 52), 93 (7), 81 ($[M - CH_3]^+$, 37), 80 (8), 77 (5), 70 (33), 69 (23), 68 (32), 67 (15), 66 (8), 65 (6), 56 (6), 55 (60), 54 (20), 53 (57), 44 (8), 43 (47), 42 (16), 41 (5), 39 (5), 29 (13), 28 (18), 27 (6).

1,3,4-Trimethylsilole (7) and 7-Methyl-7-sila[2.2.1]bicyclo-5-heptene-2,3-dicarboxylic Anhydride (11). FVP of 1-Allyl-1,3,4-trimethylsilacyclopent-3-ene (2). Silacyclopentene **2** (16.53 g, 0.1 mol) were treated in three experiments, each of 5.54 g (1 h × 3), with cleaning of the quartz tube between experiments. Distillation, after propene elimination, gave two fractions. The first one (5.47 g), bp 60–63 °C (45 mmHg), contained the 1,3,4-trimethylsilole (**7**) together with its transoid isomer **8** (GC and NMR, **7**:**8** = 6.14:1). The second fraction (7.48 g), bp 76 °C (15 mmHg), corresponded to the starting silacyclopentene **2**. With respect to consumed **2**, the yield of **7** and **8** was 80%. NMR: Tables III and IV. IR: 2120 (Si–H), 1520 cm^{-1} (C=C siloles).[2d] GC/MS: *m/e* (≥5%) 124 (M^+, 41), 123 (20), 110 (12), *109* ($[M - Me]^+$, 100%), 107 (6), 97 (6), 95 (12), 84 (7), 83 (36), 82 (6), 81 (23), 69 (26), 68 (7), 67 (28), 66 (11), 59 (7), 58 (8), 55 (13), 53 (18), 45 (7), 44 (6), 43 (42), 42 (7), 39 (8), 29 (5), 28 (9). Anal. Calcd for $C_7H_{12}Si$: C, 67.66; H, 9.73. Found: C, 67.69; H, 9.68.

The maleic anhydride (0.30 g, 3.12 mmol) adduct of silole **7** (**7** + **8**, 0.46 g, 3.71 mmol) was prepared in CCl_4 at room temperature. The crude product was heated under reduced pressure to eliminate **8**. **11** (0.57 g, viscous oil) was obtained in 83% yield with respect to silole **7**. Two isomers appeared in the ^1H NMR spectrum (300 MHz, C_6D_6): δ -0.30 (d, J = 3 Hz, SiMe, isomer **a**), -0.21 (d, J = 2.6 Hz, SiMe, isomer **b**), 1.48 (s, CMe, **b**), 1.53 (s, CMe, **a**), 2.00 (m, SiCH, **a** + **b**), 2.85 (m, O=CCH, **a**), 3.07 (m, O=CCH, **b**), 3.60 (m, SiH, **a**), 4.24 (m, SiH, **b**), SiMe {SiH, **a**} 0.30 (s), SiMe {SiH, **b**} -0.21 (s); **11a**:**11b** = 1.22:1.[10] Anal. Calcd for $C_{11}H_{14}O_3Si$: C, 59.42; H, 6.34. Found: C, 59.35; H, 6.40.

FVP of 1-(1-Methyl-2-propenyl)-1,3,4-trimethylsilacyclopent-3-ene (4). The pure silacyclopentene **4** (9 g, 0.05 mol) was pyrolyzed by the same method as **2**. The silole **7** (1.40 g) was obtained in 69% yield with respect to consumed **4**, but 6.08 g (75% of the crude product) of silacyclopentene **4** was recovered. GC/MS analysis showed that the recovered **4** was a mixture of three isomers, **4a**:**4b**:**4c** = 1:1.48:1.22. These isomers were identified by NMR (Table II). **4a**, with the shortest GC retention time, is the starting silacyclopentene **4**, **4b** the 1-(*trans*-crotyl)-1,3,4-trimethylsilacyclopent-3-ene, and **4c**, with the longest retention time, the *cis*-crotyl isomer.

1-Phenyl-3,4-dimethylsilole (9) and 7-Phenyl-7-sila-[2.2.1]bicyclo-5-heptene-2,3-dicarboxylic Anhydride (12). FVP of silacyclopentene **3** (11.4 g, 0.05 mol) was carried out as for **2**. Distillation of crude product gave recovered **3** (3.43 g) and silole **9** in presence of a little of its transoid isomer **10** (2.79 g; GC and NMR, **9**:**10** = 9:1). The yield (40%) was lower than in the FVP of **2**, bp 70–72 °C (0.1 mmHg). NMR: Tables III and IV. IR: 2130 (Si–H), 1520 cm^{-1} (C=C siloles).[2d] GC/MS: m/e (≥5%) 187 (18), *186* (M^+, 100%), 185 (14), 172 (10), 171 (66), 146 (6), 145 (23), 143 (9), 142 (7), 141 (6), 131 (13), 108 (22), 107 (23), 106 (8), 105 (51), 79 (11), 67 (13), 53 (18). Anal. Calcd for $C_{12}H_{14}Si$: C, 77.35; H, 7.57. Found: C, 77.45; H, 7.50.

As for **11**, the adduct **12** to maleic anhydride was prepared from **3** in CCl_4. Two isomers appeared in the ^1H NMR spectrum of the crude product (300 MHz, C_6D_6): δ 1.49 (s, CMe, **b**), 1.58 (s, CMe, **a**), 2.20 (m, SiCH, **b**), 2.22 (m, SiCH, **a**), 2.80 (m, O=CCH, *a*), 3.04 (m, O=CCH, **b**), 4.07 (m, SiH, **a**), 4.67 (m, SiCH, **b**), 7.2 (b m, SiPh); **12a**:**12b** = 1:9. Addition of pentane gave a white solid precipitate (isomer **b**) in 60% yield; mp 100–102 °C. Anal. Calcd for $C_{16}H_{16}O_3Si$: C, 67.59; H, 8.39. Found: C, 67.56; H, 8.40.

1-Methoxy-1-methylsilacyclopent-3-ene (17). To a stirred solution of 1-methylsilacyclopent-3-ene (**15**)[32] (0.98 g, 0.01 mol) in 5 mL of Et_2O were added three drops of H_2PtCl_6 solution in THF (1 g/100 mL) and methanol (0.32 g, 0.01 mol). The reaction, followed by GC, was quantitative in 2 h at room temperature. After concentration under reduced pressure (100 mmHg), the residue consisted of pure silacyclopentene **17**. NMR: Tables II and IV. GC/MS: m/e (≥5%) 128 (M^+, 18), 113 ($[M - Me]^+$, 23), 96 ($[M - MeOH]^+$, 19), 75 (6), 74 ($[M - C_4H_6]^+$, 24), 61 (5), 60 (7), *59* ($SiOMe^+$, 100%), 53 (5), 43 (10), 28 (5). Anal. Calcd for $C_6H_{12}OSi$: C, 56.19; H, 9.43. Found: C, 56.22; H, 9.40.

1-Methoxy-1,3,4-trimethylsilacyclopent-3-ene (19). By the same method, from 1,3,4-trimethylsilacyclopent-3-ene (**16**)[33] (1.8 g, 0.014 mol), compound **19** was obtained (2.05 g) in 92% yield; bp 78 °C (30 mmHg). NMR: Tables II and IV. GC/MS: m/e (≥5%) 157 (8), 156 (M^+, 55), 142 (7), 141 ($[M - Me]^+$, 46), 126 (5), 125 (15), 124 ($[M - MeOH]^+$, 86), 113 (7), 111 (13), 110 (6), 109 (32), 101 (5), 99 (7), 83 (5), 75 (16), 74 (10), 69 (5), 67 (8), 61 (6), 60 (7), *59* ($SiOMe^+$, 100%), 63 (5), 45 (17), 43 (16), 41 (10), 39 (12). Anal. Calcd for $C_8H_{16}OSi$: C, 61.47; H, 10.32. Found: C, 61.50; H, 10.30.

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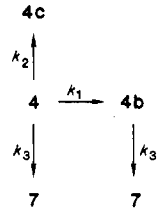
Appendix. Derivation of Rate Expression for the Formation of Silole 7 from 4 and 4b

Rate expressions for pyrolyses in the SFR are derived from mass balances.[11,12] Thus, for a simple reaction, A → B, with rate constant k, mass balance for B is $kv(A) - u(B) = 0$, where v = reactor volume and u = volumetric flow rate; hence, $k = (B)u/(A)v = (B)/(A)\tau$, where $\tau = v/u$. In the pyrolysis of **4**, formation of silole **7** was treated as a simple reaction, giving apparent rate constants

$$k = (\mathbf{7})/(\mathbf{4})\tau \qquad \text{(i)}$$

If silole **7** was also formed from isomer **4b**, with the same rate constant as from **4**, but was not formed from isomer **4c**, the reaction scheme is



mass balance for **4b**: $k_1v(\mathbf{4}) - k_3v(\mathbf{4b}) - u(\mathbf{4b}) = 0$ (ii)

mass balance for **7** : $k_3v(\mathbf{4}) + k_3v(\mathbf{4b}) - u(\mathbf{7}) = 0$ (iii)

from (ii): $(\mathbf{4b}) = k_1(\mathbf{4})/(k_3 + 1/\tau)$

substitute in (iii): $k_3v(\mathbf{4}) + k_1k_3v(\mathbf{4})/(k_3 + 1/\tau) - u(\mathbf{7}) = 0$

hence: $(k_3 + k_1k_3/\{k_3 + 1/\tau\}) = (\mathbf{7})/(\mathbf{4})\tau = k$, from (i)

hence: $k_3^2 + (1/\tau + k_1 - k)k_3 - k(1/\tau) = 0$ (iv)

Values of k_3 were calculated from the solutions to the quadratic equation iv, using the measured values of k and k_1. The resulting points are plotted in Figure 3.

Registry No. **1**, 66806-78-8; **2**, 102725-46-2; **3**, 102725-47-3; **4**, 119820-48-3; **4b**, 119820-54-1; **4c**, 119820-55-2; **5**, 72132-51-5; **6**, 72132-52-6; **7**, 102725-49-5; **8**, 102725-50-8; **9**, 102725-52-0; **10**, 102725-53-1; **11a**, 119905-63-4; **11b**, 119905-64-5; **12a**, 119820-49-4; **12b**, 119905-65-6; **15**, 55544-25-7; **16**, 92386-04-4; **17**, 119820-51-8; **18**, 119820-52-9; **19**, 24429-72-9; **20a**, 119820-53-0; **20b**, 119820-50-7; butadiene, 106-99-0; allylmethyldichlorosilane, 1873-92-3; allylphenyldichlorosilane, 7719-03-1; 2,3-dimethylbutadiene, 513-81-5; (1-methyl-2-propenyl)methyldichlorosilane, 64473-00-3; methyltrichlorosilane, 75-79-6; 3-chloro-1-butene, 563-52-0; maleic anhydride, 108-31-6.

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[33] Maier, G.; Mihm, G.; Reisenauer, H. P.; Littman, D. *Chem. Ber.* **1984**, *117*, 2369.