Rearrangement Reactions in 1-Methyl-2-vinylsilacyclopropane

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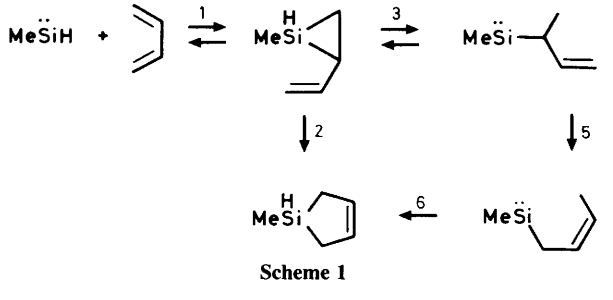
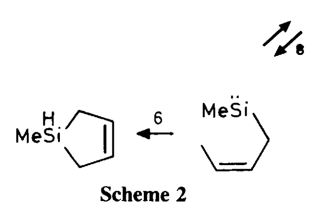
1-Methyl-2-vinylsilacyclopropane, formed by addition of methylsilanediyl (methylsilylene) to buta-1,3-diene, is shown by deuterium labelling to undergo rearrangements initiated by both a 1,2- and a 1,5-hydrogen shift; the former is more important, especially at lower temperature.

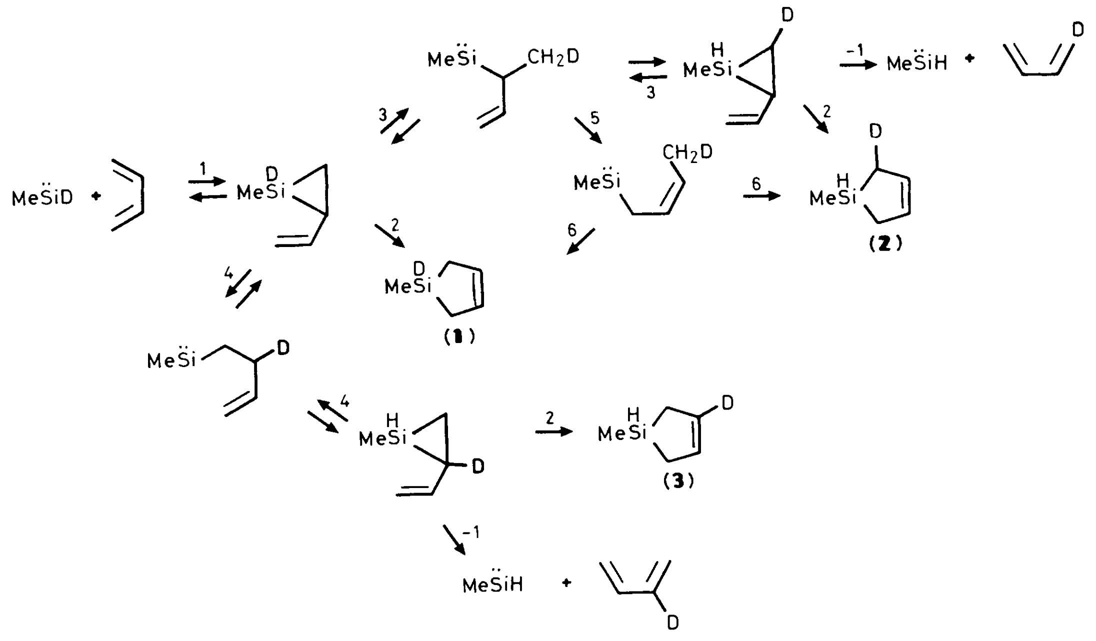
Gaspar and his co-workers[1—3] have shown that addition of silanediyls (silylenes) to 1,3-dienes proceeds by 1,2-addition to form a vinylsilacyclopropane, followed by rearrangement reactions; the nature of these reactions is of topical interest. The main products are usually a silacyclopent-3-ene and a silacyclopent-2-ene, and we have recently adduced evidence[4] that the silacyclopent-3-ene which is the major product is formed directly from the vinylsilacyclopropane by a 1,3-silyl shift.[5,6] The silacyclopent-2-ene undoubtedly results from C–C bond rupture.[1] However, silanediyls with a Si–H bond behave differently; addition of :SiMeH to buta-1,3-diene gives only one silacyclopentene, the silacyclopent-3-ene, which we explained[4] by the reactions in Scheme 1, all of which have precedents in silicon chemistry and would be faster than C–C bond rupture.



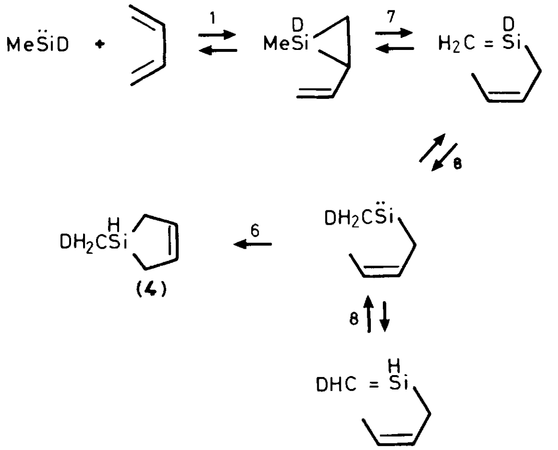
Scheme 1



Scheme 2



Scheme 3



Scheme 4

Reactions (3) and (4) are 1,2-H shifts, known to be important in the pyrolysis of hydridosilacyclobutanes;[7] reactions (2) and (5) are 1,3-silyl shifts.[5,6]

There is, however, another sequence of precedented reactions which could achieve the same result, as shown in Scheme 2.

Reaction (7) is a 1,5 sigmatropic H-shift, known to be an important rearrangement pathway in suitably substituted vinylsilacyclopropanes,[2] while reaction (8) is the well-established sila-alkene ⇌ silanediyl isomerisation.[8]

We now report experiments to establish the relative importance of the sequence in Schemes 1 and 2 by replacing :SiMeH by :SiMeD. The resulting counterparts to Schemes 1 and 2 are Schemes 3 and 4 respectively [to avoid undue confusion, not all possible examples of reactions (3) and (4) are included in Scheme 3].

The silacyclopent-3-enes (**1**)—(**3**) in Scheme 3 can be distinguished from the silacyclopent-3-ene (**4**) in Scheme 4 by mass spectrometry; the intense peak resulting from loss of methyl has *m/z* = 84^+ for (**1**)—(**3**), but *m/z* = 83^+ for (**4**).

:SiMeD was generated by pyrolysis of $Me_3SiSiMeD_2$, synthesised by reduction of $Me_3SiSiMeCl_2$ by $LiAlD_4$; its addition to buta-1,3-diene (diene : disilane = 10 : 1) was studied between 647 K and 817 K in a stirred-flow apparatus with analysis by g.c./mass spectrometry (HP 5995C). The deuteriated 1-methylsilacyclopent-3-enes which were formed were eluted as a single g.c. peak; in pyrolyses at 647 K, the mass spectrum of this g.c. peak had a 84^+ peak which was substantially more intense than 83^+, indicating that the reaction sequence originally suggested[4] (Schemes 1 and 3) is a more important route to the product than the sequence initiated by a 1,5-sigmatropic H-shift (Schemes 2 and 4). In the mass spectrum of undeuteriated 1-methylsilacyclopent-3-ene there is a small peak at 82^+; a minor correction factor calculated from that mass spectrum was applied to the 83^+ peak in the experiments with :SiMeD, giving $84^+ : 83^+$ = 5.0 : 1 at 647 K. This ratio decreased with increasing pyrolysis temperature to 2.1 : 1 at 817 K, corresponding to an activation energy for the formation of (**4**) which is 19 ± 3 kJ mol^{-1} greater than the activation energy for the formation of (**1**)—(**3**). Interpretation of this activation energy difference is not simple. Not only are Schemes 3 and 4 complex, but the stereochemistry of the vinylsilacyclopropane has to be considered; formation of the conventional six-centre transition state for the 1,5 sigmatropic H-shift [reaction (7)] would require the methyl and vinyl groups in the silacyclopropane to be in the *cis*-configuration, whereas the addition reaction (1) might be expected to form predominantly the *trans*-isomer. Thus, the increased formation of (**4**) at higher temperature might wholly or partly result from the increase in the rate of *trans* → *cis*-isomerisation with temperature. Nevertheless, it is clear that 1,2 H-migration followed by a 1,3-silyl shift (Schemes 1 and 3) is more important than the 1,5 H-shift

(Schemes 2 and 4), but that the latter does occur, becoming increasingly important at higher temperatures.

Small peaks were observed in the mass spectrum corresponding to 1-methylsilacyclopent-3-enes containing two atoms of deuterium. In Scheme 3, ring-closing and ring-opening reactions lead to scrambling of the deuterium label round the silacyclopropane ring, and hence to the formation of deuteriated butadiene when these rings extrude :SiMeH. Dideuteriated products would then be formed by addition of :SiMeD to that deuteriated butadiene. Similar results have recently been reported in the pyrolysis of a silacyclobutane deuteriated at silicon, also involving a silacyclopropane intermediate.[9]

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