Mechanism of Addition of Silanediyls (Silylenes) to Buta-1,3-diene

Michael P. Clarke and Iain M. T. Davidson*

Department of Chemistry, The University, Leicester LE1 7RH, U.K.

From experiments on the addition of :SiMeX (X = H, Cl, Me) to buta-1,3-diene, it is concluded that the main cyclic adduct in each case results from initial 1,2-addition to form a vinylsilacyclopropane followed by a 1,3-silyl shift, rather than Si–C bond rupture.

The mechanism of addition of silanediyls (silylenes) to dienes is of topical interest. From an ingenious series of studies of the addition of dimethylsilanediyl, $:SiMe_2$, to substituted dienes, Gaspar and his co-workers deduced from product composition, including the degree of stereospecificity, that the initial step is 1,2-addition to form a vinylsilacyclopropane which then rearranges to form products, as illustrated in Scheme 1 for hexa-2,4-dienes.[1,2] They envisaged the acyclic vinylpropenylsilane as being formed mainly by a 1,5 sigmatropic H-shift,[2] with C–C and Si–C bond rupture as the routes to the silacyclopent-2-ene and silacyclopent-3-ene, respectively; the former was the major cyclic product.[1]

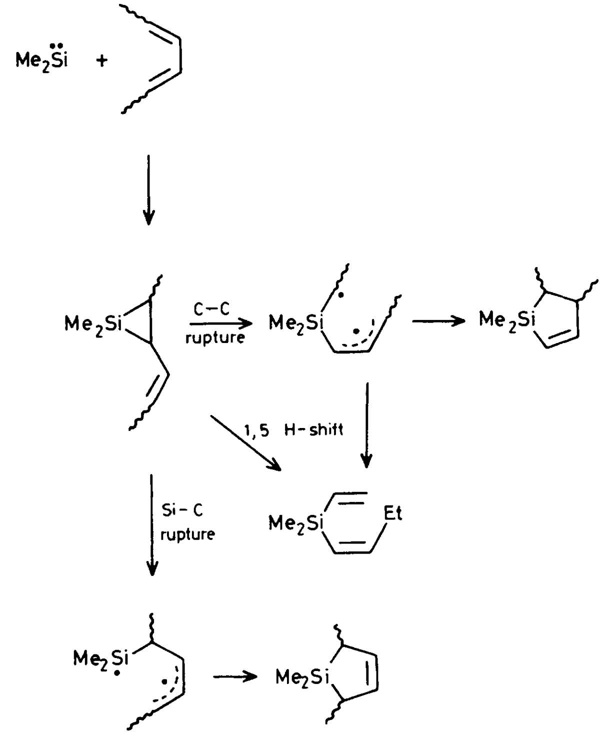
However, addition of $:SiMe_2$ to buta-1,3-diene gives mainly dimethylsilacyclopent-3-ene, with little of the silacyclopent-2-ene;[1] Gaspar and Lei have recently[3] obtained good evidence that the latter minor product results from C–C bond rupture in a vinylsilacyclopropane, as in Scheme 1, but the route to the silacyclopent-3-ene, the major product, is not obvious, especially as the evidence from acyclic compounds is that the Si–C bond would be *stronger* than C–C.[4,5] Whilst direct 1,4-addition cannot be ruled out, there are good indications that it is no more than a minor pathway.[1] We have sought to shed some light on this intriguing mechanistic question by studying the addition of $:SiMe_2$, $:SiMeCl$, and $:SiMeH$ to buta-1,3-diene.

The silanediyls were generated by pyrolysis of the appropriate disilane, $Me_3SiSiMe_2H$, $Me_3SiSiMeCl_2$, and $MeH_2SiSiMeH_2$, generally with a 10 : 1 excess of buta-1,3-diene, in a stirred-flow apparatus with analysis by g.c./mass spectrometry (HP 5995C). Under these conditions, $:SiMe_2$ gave dimethylsilacyclopent-3-ene and dimethylsilacyclopent-2-ene in the ratio of 9.5 : 1 at 436 °C, decreasing to 7.7 : 1 at 470 °C; the trisilane resulting from the competing insertion of $:SiMe_2$ into the disilane precursor amounted to less than 2% of the cyclic products. Reducing the ratio of butadiene to disilane from 10 : 1 to 1 : 1 increased the relative amount of trisilane, but did not affect the ratios quoted above for the two cyclic products. As these could not be distinguished from each other by mass spectrometry, structural assignment was based on separate sealed-tube pyrolyses analysed by 300 MHz ^1H n.m.r. spectroscopy.

In pyrolyses between 458 and 520 °C, $:SiMeCl$ likewise gave two isomeric cyclic products. G.c. traces were less clean, because of the presence of minor hydrolysis products, but the ratio of the two products was about 6 : 1, with little dependence on the butadiene : disilane ratio; the major product had the shorter retention time, the opposite of the $:SiMe_2$ result, but was nevertheless shown by 500 MHz ^1H n.m.r. spectroscopy still to be the symmetrical silacyclopent-3-ene.

Significantly different results were obtained with $:SiMeH$

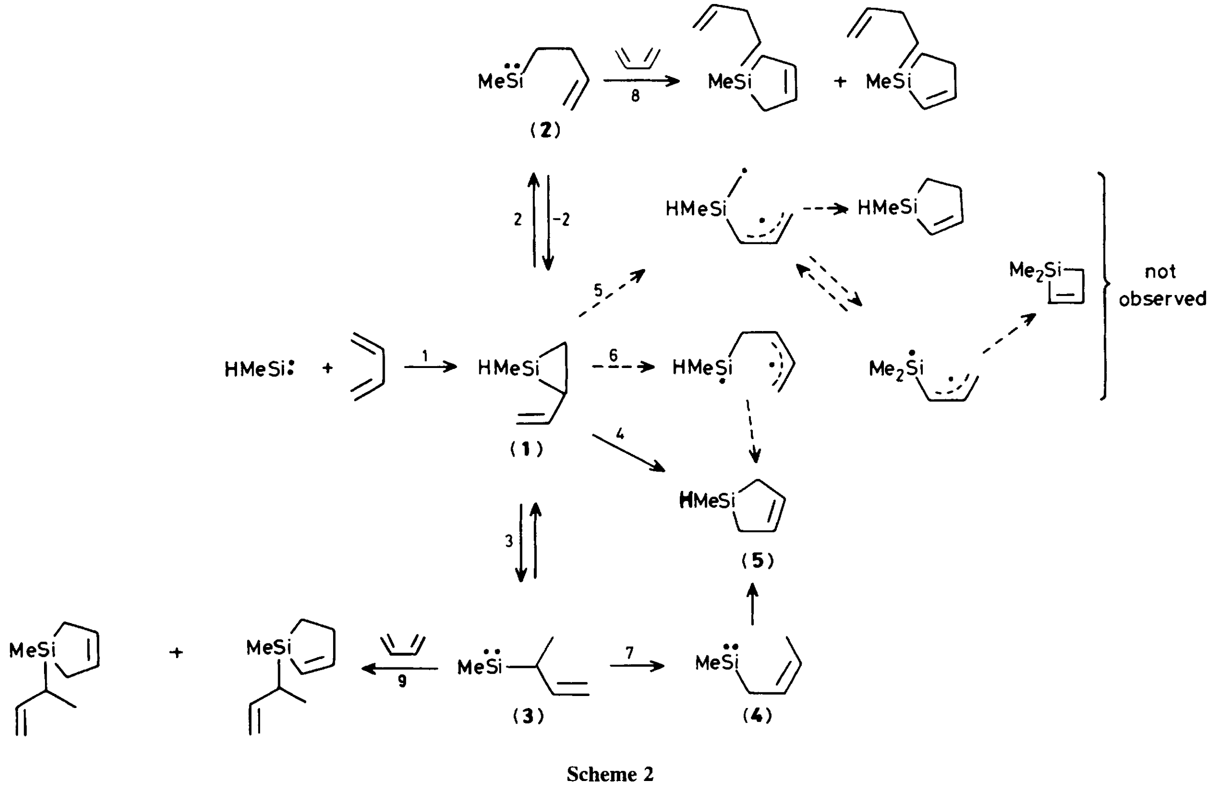
between 398 and 435 °C. With a 10 : 1 butadiene–disilane mixture, only one silacyclopentene was observed, shown by 300 MHz ^{1}H n.m.r. spectroscopy to be methylsilacyclopent-3-ene, but there were two other prominent products corresponding to the addition of one unit of :SiMeH to two of butadiene; each was preceded on the g.c. trace by a minor isomer. The trisilane product amounted to about 4% of the combined butadiene adducts. Reducing the butadiene : disilane ratio to 1 : 1 increased the complexity of the product composition; more trisilane was produced, as were two isomeric tetrasilanes, and there was a considerable increase in three other products, very minor in the 10 : 1 mixture, corresponding to addition of two units of :SiMeH to one of butadiene.



Scheme 1

We believe that these results are entirely consistent with initial 1,2-addition, as suggested by Gaspar, but with the silacyclopent-3-enes being formed by 1,3-silyl shifts rather than by Si–C bond rupture, the explanation previously favoured on balance.[1] 1,3-Silyl shifts have been invoked in two rearrangements in allylic systems related to this work, of allylsilanes[6] and of butenylsilylenes.[7] The significant difference between :SiMeH and the other two silanediyls is that it gives a vinylsilacyclopropane which can undergo silanediyl-forming ring-opening by a 1,2-hydrogen shift from silicon to carbon, known to be an important reaction of cyclic hydridosilanes,[8] and facilitated in this case by the high strain in the silacyclopropane ring. Our mechanism for the reactions of :SiMeH with excess of butadiene is shown in Scheme 2.

No products resulting from C–C bond rupture (reaction 5) were observed because that process was too slow to compete with the 1,2-hydrogen shifts[8] (reactions 2 and 3). Both of these reactions would be expected to occur more or less equally because the allylic bond-weakening effects are self-cancelling. If the Si–C bond is at least as strong as C–C,[4,5] it follows that reaction (6) was not an important route to the main product (5), which would be formed by one or both of the 1,3-silyl shifts, reactions (4) and (7). Reactions (−2) and (4) were suggested by Barton[7] to account for the exclusive formation of (5) from the butenylsilanediyl (2), while reaction (7) is analogous to the rearrangement of allylsilanes;[6] there is a precedent[7] for ring-closure of a silanediyl like (4) to form the product (5). In view of the reversibility of reactions (2) and



Scheme 2

(3), reactions (4) and (7) leading to the main product (**5**) are the only unimolecular sink reactions for either of the alkenylsilanediyls (**2**) and (**3**). Easier orbital overlap may favour reaction (7) over reaction (4).

With $:SiMe_2$ and :SiMeCl, where hydrogen-shifts corresponding to reactions (2) and (3) cannot occur, C–C bond breaking analogous to reaction (5) can compete, albeit as a minor process, with the 1,3-silyl shifts analogous to reaction (4). The alkenylsilanediyls (**2**) and (**3**) in Scheme 2 would behave similarly to $:SiMe_2$, each giving a silacyclopent-3-ene as the main product of reaction with butadiene with a silacyclopent-2-ene as minor product, giving a total of four products, two prominent and two minor, just as we found experimentally.

With the hexadienes in Scheme 1, we suggest that the silacyclopent-3-enes are likewise formed directly from vinyl silacyclopropanes by 1,3-silyl shifts, but silacyclopent-2-enes are now the main products because the C–C bond in the silacyclopropane is weakened by methyl-substitution, thus enhancing C–C bond breaking. In support of that explanation, we note that in the addition of $:SiMe_2$ to the *trans,trans*-hexa-2,4-diene at 460 °C, the ratio of silacyclopent-2-enes to silacyclopent-3-enes was[1] about 3 : 1; comparing that with the ratios found by us, and assuming that the rate constant for the 1,3-silyl shift was the same in each case, we calculate that the methyl substituent would have to lower the activation energy for C–C bond breaking by 13—19 kJ mol^{-1}, which is entirely reasonable.[5] Further evidence in support of the 1,3-silyl shift comes from the temperature-dependence of product yields in our own experiments with $:SiMe_2$. The change from 9.5 : 1 at 436 °C to 7.7 : 1 at 470 °C corresponds to an activation energy difference of 27 kJ mol^{-1}; the Si–C bond is unlikely to be 27 kJ mol^{-1} weaker than C–C, even if the ring strain is more acute at silicon than at carbon, whereas the 1,3-silyl shift could well have an activation energy that much lower than the C–C bond strength.

In the experiments with a 1 : 1 mixture of butadiene and the disilane precursor to :MeSiH, we cannot identify the new products corresponding to two units of :SiMeH and one of butadiene, but they were probably cyclic rearrangement products of disilenes resulting from the addition of :SiMeH to the $:SiMeC_4H_7$ silanediyls.[9]

We thank Dr. D. L. Turner (University of Leicester) for help with n.m.r. spectroscopy, Dr. R. S. Atkinson (University of Leicester), Professor P. P. Gaspar (Washington University, St Louis), and Dr. R. Walsh (University of Reading) for valuable discussions; and the S.E.R.C. and Dow Corning (Europe) for generous financial support.

Received, 23rd September 1987; Com. 1384

References

1 D. Lei, R.-J. Hwang, and P. P. Gaspar, *J. Organomet. Chem.*, 1984, **271**, 1.
2 D. Lei and P. P. Gaspar, *J. Chem. Soc., Chem. Commun.*, 1985, 1149.
3 P. P. Gaspar and D. Lei, reported at 8th International Symposium of Organosilicon Chemistry, St. Louis, U.S.A., 1987.
4 Si–C bond dissociation energies: R. Walsh, *J. Chem. Soc., Faraday Trans. 2*, 1986, **82**, 707; I. M. T. Davidson and C. E. Dean, *Organometallics*, 1987, **6**, 966.
5 C–C bond dissociation energies: D. F. McMillen and D. M. Golden, 'Hydrocarbon Bond Dissociation Energies,' in 'Annual Reviews of Physical Chemistry,' Annual Reviews Inc., Palo Alto, CA, 1982, p. 493; W. Tsang, *J. Am. Chem. Soc.*, 1985, **107**, 2872, and references therein.
6 H. Kwart and J. Slutsky, *J. Am. Chem. Soc.*, 1972, **94**, 2515; J. Slutsky and H. Kwart, *ibid.*, 1973, **95**, 8678.
7 T. J. Barton and G. T. Burns, *Organometallics*, 1983, **2**, 1.
8 I. M. T. Davidson, A. Fenton, S. Ijadi-Maghsoodi, R. J. Scampton, N. Auner, J. Grobe, T. J. Barton, and N. Tillman, *Organometallics*, 1984, **3**, 1593.
9 R. T. Conlin and P. P. Gaspar, *J. Am. Chem. Soc.*, 1976, **98**, 868.