positions with respect to the allyl fragments. To lengthen these contacts, the methylene groups move out of the allyl planes away from the Zr atom. This means that the hybridization of C(4) and C(7) changes from sp^2 to sp^3 with consequential change from π to σ Zr–C(4) and Zr–C(7) bonding. Indeed these bond lengths lie in the range of other σ Zr–C bonds.[9]

The prediction[2] of the type of Zr–allyl asymmetry in II is particularly important. The distortions could be caused by the repulsions just described for the case in III if the C_8 chain also has C_2 symmetry. This conformation is of particular interest since it brings a bridging methylene group of one butadiene fragment into the proximity of the terminal methylene group of the other. Upon displacement of the dimer from the complex, H transfer occurs from the former to the latter group forming octa-1,3,6-triene.[2] Correspondingly, the product mixture obtained by catalytically oligomerizing piperylene with I contains deca-2,4,7-triene; therefore, III appears to be a true intermediate.[3]

As C(2) and C(9) are far from the zirconium atom, coplanarity of the methyl carbon atoms with the respective allyl fragments might mean that C(2) and C(9) do not interact with the zirconium atom. However, H(2) and H(9) are not coplanar with the allyl moieties and thus indicate stereochemically significant Zr–C(2) and Zr–C(9) bonding. A possible explanation for these contradictory observations is as follows. A normal Zr–allyl interaction is accompanied by C–H(syn) and C–H(meso) bonds inclining out of the allyl plane toward the Zr atom while C–H(anti) bonds bend in the opposite direction.[4] These departures from planarity, which probably signalize the mixing of carbon σ and π orbitals, tend to lengthen the nonbonded contacts Zr–H(anti) while Zr–H(syn) and Zr–H(meso) tend to shorten. Therefore exactly opposite to the above-described case of anti substitution by a methylene group, syn substitution by the sterically larger methyl group should oppose nonplanarity and the subsequent increase in Zr–CH_3 nonbonded repulsions.

Registry No. III, 79681-74-6.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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Communications

Thermochemistry of Di- and Trisilanyl Radicals. Observations and Comments on Silene-to-Silylene Rearrangements

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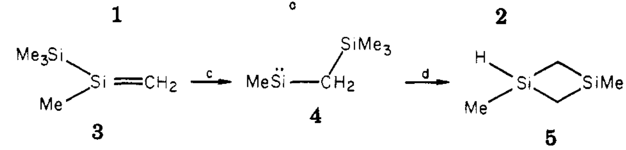
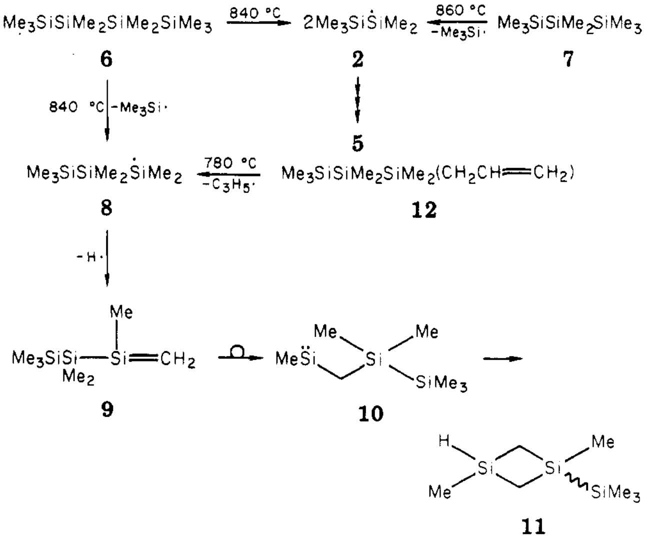
Summary: Di- and trisilanyl radicals are shown to undergo a thermal sequence of disproportionation to silenes, rearrangement to silylenes via 1,2-silyl migration, and cyclization via γ-C–H insertion.

Recently we reported[1] that flash vacuum pyrolysis of allylpentamethyldisilane (1) gave rise to 1,1,3-trimethyl-1,3-disilacyclobutane (5) as the major volatile product. Our proposed mechanism consisted of four steps: (a) Si–C bond homolysis to form pentamethyldisilanyl radical (2); (b) disproportionation of 2 to form silylsilene 3; (c) rearrangement of 3, via 1,2 migration of Me_3Si–, to β-silylsilylene 4; and (d) γ-CH insertion by 4 to form 5. Although steps a,[2] b,[3] and d[4] have literature precedents, step c had never before been observed or postulated.



One of the experimental necessities to establish the disproportionation of 2 to 3 was to explain the absence of decamethyltetrasilane (6), the expected radical combination product of 2. Thus, we conducted the flash vacuum pyrolysis of 6 under the conditions employed for 1 (840 °C, 10^{-4} torr; horizontal quartz-packed tube). Indeed the major volatile product of this pyrolysis is 5 (21%), which



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[1] Barton, T. J.; Jacobi, S. A. *J. Am. Chem. Soc.* **1980**, *102*, 7979.

[2] Davidson, I. M. T.; Wood, I. T. *J. Organometal. Chem.* **1980**, *202*, C65.

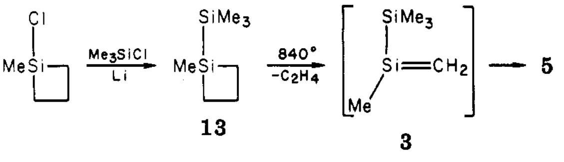
[3] Davidson, I. M. T.; Howard, A. V. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 69, and references therein.

[4] Wulff, W. D.; Goure, W. F.; Barton, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 6236.

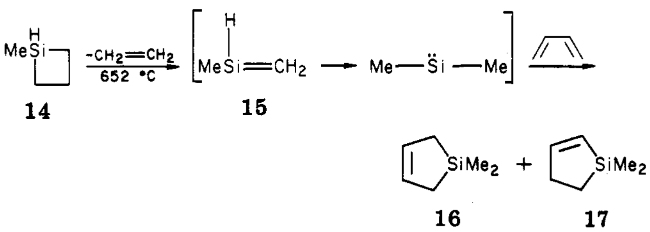
0276-7333/82/2301-0210$01.25/0

is almost certainly formed via initial Si_2–Si_3 homolysis to afford disilanyl radical **2**. Equally clean was the pyrolysis of octamethyltrisilane (**7**) (860 °C, 10^{-3} torr) which gave rise to **5** (20%) as almost the exclusive volatile product. Also formed (5%) in the pyrolysis of **6** was a mixture of *cis*- and *trans*-1,3-dimethyl-1-(trimethylsilyl)-1,3-disilacyclobutane (**11**). It could be demonstrated that **11** arose from heptamethyltrisilanyl radical **8** by obtaining **11** as the only major volatile product (23%) from the pyrolysis (780 °C, 10^{-3} torr) of 1-allylheptamethyltrisilane (**12**). Thus, the same process of disproportionation (**8** → **9**), silene rearrangement (**9** → **10**), and cyclization (**10** → **11**) appears to be operative for trisilanyl radical **8** as for disilanyl radical **2**.

In order to gain further evidence for the rearrangement of silylsilenes to silylenes (**3** → **4**) it was desirable to generate silene **3** by an alternate route. Thus we synthesized 1-methyl-1-(trimethylsilyl)-1-silacyclobutane (**13**) and conducted its flash vacuum pyrolysis (840 °C, 10^{-4} torr) to obtain **5** in a remarkable 98% yield. Since silacyclobutanes are well-known to produce silenes upon thermal decomposition,[5] this result would seem to confirm the rearrangement of **3** to **4**.



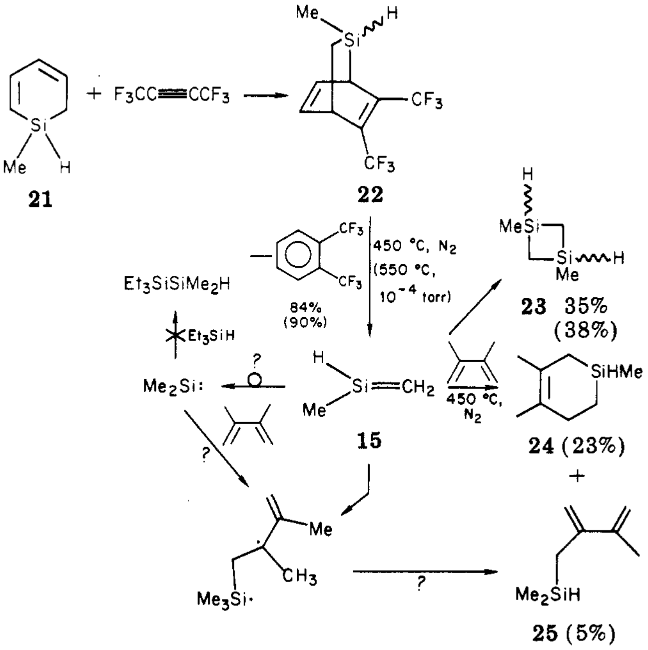
Quite recently Conlin[6] has elegantly demonstrated that the pyrolysis of 1-methyl-1-silacyclobutane (**14**) affords dimethylsilylene, which could be trapped in excellent yield. For example, copyrolysis of **14** and 1,3-butadiene gave the usual products of silylene trapping, dimethylsilacyclopentenes **16** and **17**, in a combined yield of 64%.

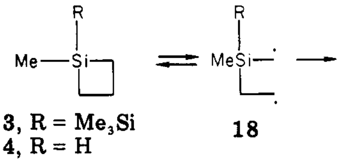


Thus it was reasonably concluded that initially formed 2-silapropene (**15**) underwent 1,2-hydrogen migration to produce Me_2Si:. Indeed this interpretation received considerable support in the accompanying report by Michl and West,[7] who presented evidence that photochemically generated **15** thermally isomerizes to Me_2Si: at 100 K!

We would introduce a note of caution in the interpretation of silene rearrangement results from silacyclobutane pyrolyses. While we have no doubt that appropriately substituted silenes will undergo thermal rearrangement to silylenes, this route is not demanded for the formation of silylenes from the thermolysis of silacyclobutanes. There is considerable evidence in the literature[8] that silacyclobutanes undergo thermal decomposition largely through initial C–C rather than Si–C ring-bond homolysis. Therefore, neither our results for **13** nor Conlin's results for **14** allow one to disregard the possibility that migration from silicon is occurring at the diradical (**18**) stage and that a final Si–C bond homolysis is the actual process leading to the silylene. Alternatively diradical **19** could close to silacyclopropane **20**, which would be expected to extrude the silylene.

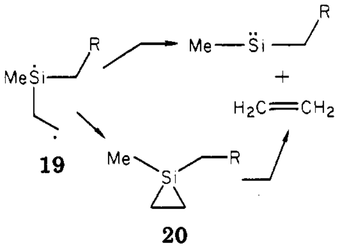
Scheme I





13, R = Me_3Si
14, R = H

18



19

20

In an effort to probe this mechanistic dichotomy, we sought to generate silene **15** from a precursor other than a silacyclobutane. As the thermal decomposition of silabicyclo[2.2.2]octadienes has been reported to proceed via a retrograde Diels–Alder extrusion of the bridging silene,[9] we synthesized **22** from the Diels–Alder reaction of 5-methyl-5-silacyclohexa-1,3-diene (**21**) (see Scheme I). Pyrolysis of **22** in a vertical tube (450 °C) with nitrogen flow afforded *o*-bis(trifluoromethyl)benzene in 84% yield and 1,3-dimethyl-1,3-disilacyclobutane (**23**) in 35% yield. Flash vacuum pyrolysis of **22** (550 °C, ~10^{-4} torr) produced the same two products in respective yields of 90% and 38%. Since **23** is known to be a major product resulting from the gas-phase dimerization of dimethylsilylene,[10] these results alone do not allow the assumption that **23** originates from dimerization of silene **15**. However, the inevitable coproduct from Me_2Si: dimerization, 1,1-dimethyl-1,3-disilacyclobutane, is not a product from the pyrolyses of **22**. More conclusive evidence that pyrolysis of **22** yields silene **15** is found in the copyrolysis (450 °C, N_2 flow) of bicyclic generator **22** and 2,3-dimethyl-1,3-

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[5] Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529.

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[9] Barton, T. J.; Kline, E. *J. Organometal. Chem.* **1972**, *42*, C21.

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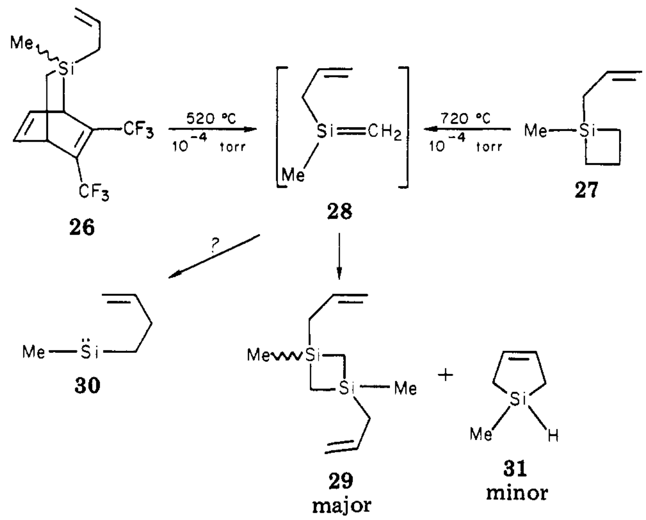
Scheme II



butadiene. After the hexafluoroxylene (74%), the major volatile product is silacyclohexene **24** (23%), the expected product of cycloaddition of **15** and the 1,3-diene. This result stands in stark contrast with the reported[6] copyrolysis of silacyclobutane **14** and 1,3-butadiene (vide supra). The flow pyrolysis of **22** also affords a small amount (5%) of 2-methyl-3-(dimethylsilyl)methyl-1,3-butadiene (**25**). Although we have previously observed this type of linear adduct from the reactions of silenes and butadienes,[11] it was conceivable that **26** arose from a stepwise radical addition of dimethylsilylene to dimethylbutadiene followed by hydrogen migration from carbon to silicon. This interpretation is rendered highly unlikely since pyrolysis of **22** in an excess of triethylsilane produced no 2,2-dimethyl-1,1,1-triethyldisilane, the normal product of silylene trapping by the Si–H bond.

Thus, as the evidence seems strong that pyrolysis of **22** does produce silene **15**, the case for generation and rearrangement of **15** from silacyclobutane **14** is at best weakened. However, the picture is confused by the recent report of isomerization of **15** to Me_2Si: at 100 K.[7] This amazingly facile hydrogen migration is consistent neither with our results for **22** nor with the recent calculations of Schaefer[12] which predict that the activation energy for the essentially thermoneutral rearrangement $H_2Si{=}CH_2 \rightarrow H{-}\ddot{Si}{-}CH_3$ is about 40 kcal/mol.

In the hopes of finding a silene particularly predisposed to rearrange to a silylene, we have generated allylmethylsilene **28**. This was accomplished by the flash vacuum pyrolyses (10^{-4} torr) of both silabicyclo[2.2.2]octadiene **26** and 1-allyl-1-methyl-1-silacyclobutane (**27**) (Scheme II). Pyrolysis of **26** (520 °C) was extremely clean, affording only hexafluoroxylene (83%) and 1,3-diallyl-1,3-dimethyl-1,3-disilacyclobutane (**28**, 85%). Pyrolysis of **27** required ~200 °C more than for **26**, but still produced **29** in 27% yield. Thus, although silene **28** seemed an excellent candidate for rearrangement to silylene **30** through a cyclic six-electron process, it appears that this does not happen, as **28** simply dimerizes in the normal head-to-tail fashion. However, in the pyrolysis of **27** there is a small amount (2.3%) of 4-methyl-4-silacyclopentene (**31**) formed which may well arise from the cyclization of silylene **30** followed by transannular hydrogen migration. This interpretation is not demanded as it is also possible to imagine **31** arising from **28** through a di-π-methane sequence.

The many syntheses and structural proofs involved in this report will be incorporated with current work and complete details from ref 1 in a full paper.

Acknowledgment is made to the National Science Foundation and to Dow Corning Corporation for support of this work. We thank Procter and Gamble Co. for a fellowship to G.T.B. during this period. We are grateful to Professor Rob Conlin for sending us his report on the pyrolysis of **14** prior to publication.

Registry No. 2, 23290-58-6; **3**, 76410-87-2; **5**, 25261-26-1; **6**, 865-76-9; **7**, 3704-44-7; **8**, 78697-99-1; **11** isomer 1, 78698-00-7; **11** isomer 2, 78698-01-8; **12**, 78698-02-9; **13**, 78698-03-0; **15**, 38063-40-0; **21**, 78698-04-1; **22**, 78715-28-3; **23**, 1628-01-9; **24**, 78698-05-2; **26**, 78698-06-3; **27**, 3944-06-7; **28**, 78698-07-4; **29**, 78698-08-5; 2,3-dimethyl-1,3-butadiene, 513-81-5; $F_3CC{\equiv}CCF_3$, 692-50-2.

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Rational Syntheses of Mixed Dialkylhaloboranes (R^AR^BBX) and Mixed Trialkylboranes ($R^AR^BR^CB$) via Stepwise Hydridation–Hydroboration of Alkyldihaloboranes

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Summary: **The stepwise hydridation of $R^ABBr_2 \cdot SMe_2$ with $LiAlH_4$, followed by stepwise hydroboration of two different alkenes, provides a convenient route to the mixed organoboranes, $R^AR^BR^CB$, and to the products into which such mixed organoboranes can be transformed.**

A rational synthesis of mixed dialkylhaloboranes (R^AR^BBX, **1**) and trialkylboranes ($R^AR^BR^CB$, **2**) has long eluded chemists. A convenient synthetic approach to such derivatives would greatly expand applications for the versatile organoboranes. We now wish to report the preparation of such mixed organoborane derivatives (**1**, **2**) via the controlled hydridation of alkyldihaloboranes ($R^ABX_2 \cdot SMe_2$, **3**), followed by sequential hydroboration (eq 1).

$$\underset{\substack{3A,\ X = Cl\\ 3B,\ X = Br}}{R^ABX_2 \cdot SMe_2} \rightarrow \underset{1}{R^AR^BBX \cdot SMe_2} \rightarrow \underset{2}{R^AR^BR^CB} \qquad (1)$$

The increasing importance of organoboranes[1] as synthetic intermediates reveals a need for mixed dialkylhaloboranes and mixed trialkylboranes. Partially mixed trialkylboranes, $R^A_2R^BB$ (**4**), have been prepared by various methods.[2-6] Most of the earlier approaches involved use of the stable R^A_2BH or R^BBH_2 reagents.[1,5] Recently, more general methods have been reported (eq 2).[4,6]

$$R^A_2BX \xrightarrow{MH} [R^A_2BH] \xrightarrow{\text{alkene B}} \underset{4}{R^A_2R^BB} \qquad (2)$$

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