However, Marcus and Siders have pointed out[22] that the rate decrease in the inverted region will be largely smoothed out by diffusion. Thus, inverted behavior would be best observed in a diffusion-free medium, as in the present case. Clearly, further studies at $\Delta E > 0.8$ V are necessary and are in progress.

In summary, the data show that electron transfer between ruthenium polypyridyl homologues and MV^{2+} occurs over rather limited distances on the microsecond time scale. The present report is inconsistent with suggestions of 30-Å electron-transfer distances in vesicles.[9a] However, the accessible distance can be strongly modulated by ΔE, in quantitative agreement with modern theories of electron transfer. Our results are largely consistent with analogous studies by Miller et al.,[10] who observed reaction distances of up to 15 Å (center–center) by monitoring luminescence quenching of organic dyes. Interestingly, in their system, Miller et al. observe somewhat faster rates at equivalent distances and ΔE values. Finally, we note the intriguing possibility in such experiments of observing reactions in the inverted region. Present experiments are focused on this possibility.

Acknowledgment. We are grateful to John Miller for helpful discussion and criticism, and particularly for pointing out the method of analysis in ref 17 and 18a. J. Beitz, E. Buhks, R. Marcus, and P. Siders provided helpful comments, and E. Buhks provided a critical reading of the manuscript. George McLendon gratefully acknowledges the support of a Sloan Fellowship and Dreyfus Teacher–Scholar Award. Thomas Guarr is a Huntington Hooker Fellowship and Sherman Clarke Fellowship recipient of the University of Rochester.

Registry No. I, 47860-47-9; II, 15158-62-0; III, 32881-03-1; IV, 64894-64-0; V, 58452-44-1; MV^{2+}, 4685-14-7.

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Thermal Fragmentation of Silacyclobutane. Formation of Silylene, Methylsilylene, and Silene

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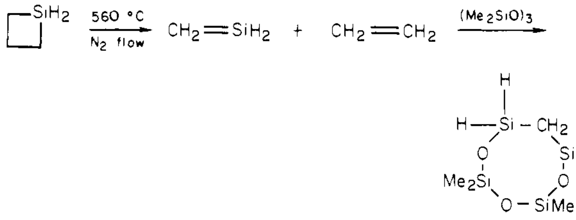
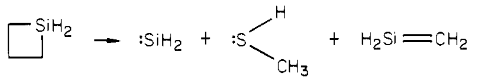
Received August 24, 1982

Although the thermal decomposition of the unsubstituted silacyclobutane has been studied by several groups,[1-5] only in the original work of Sommer and co-workers was a silicon-containing product identified. Evidence for the parent silene, anticipated from the 2 + 2 fragmentation of silacyclobutane, was based on the isolation of a product from addition of a silicon–oxygen σ bond across the silicon–carbon π bond (eq 1). We report here that thermal decomposition leads not only to silene as previously suggested but predominantly to methylsilylene ($SiHCH_3$) and also the parent silylene (SiH_2; eq 2).

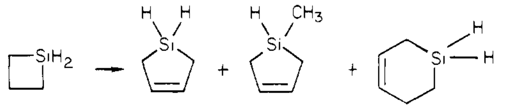


(1)



(2)

Table I. Temperature Dependence of Product Formation



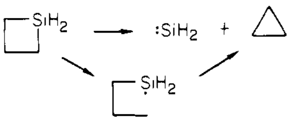
1 2 3

T, °C	decomp,[a] %	yield,[a] % 1	2	3	product ratios 1:(2 + 3)	2:3
556	16	1.9	5.9	5.1	0.17	1.2
600	34	4.8	14.1	7.6	0.22	1.9
650	67	9.9	29.9	13.1	0.23	2.1
697	97	13.7	49.1	9.7	0.23	5.1

[a] Percent decomposition and percent yield were measured relative to hexane as an inert internal standard and based on the amount of silacyclobutane decomposed.

Pyrolyses were carried out with a 10-fold excess of 1,3-butadiene in a high-vacuum flow system[6] to optimize efficiency of trapping the primary fragments from silacyclobutane. Over the temperature range 556–697 °C, three silicon-containing products were formed from reactions with butadiene as shown in Table I. Both silacyclopent-3-ene[7] (**1**) and 1-methyl-1-silacyclopent-3-ene[7] (**2**) are products previously observed from reactions of the respective silylene and methylsilylene with butadiene. The third product, silacyclohex-3-ene[8] (**3**), is the 2 + 4 adduct expected from silene and butadiene.

At 556 °C the elimination of silylene from silacyclobutane was accompanied by an equivalent amount of cyclopropane, which isomerized to propylene at the higher temperature range. Two possible pathways for this extrusion are a cheleotropic elimination requiring concurrent cleavage of both silicon–carbon bonds or a stepwise process initiated by homolysis of a silicon–carbon bond followed by cleavage of the other one within the biradical (eq 3).



(3)

The variation of product ratios with reaction temperature (Table I) permits comment on these mechanisms. As the decomposition temperature was raised from 556 to 697 °C, the amount of SiH_2 product **1** increased, albeit slightly, relative to the combined yields of $SiCH_4$ products **2** and **3**. Since the stepwise elimination of SiH_2 is expected to have higher activation parameters than a concerted pathway, the enhanced yields of **1** at higher temperature support the radical mechanism.

Especially intriguing and somewhat controversial[9] is the mechanism of formation of the methylsilylene adduct to butadiene.

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(6) All pyrolyses were carried in a seasoned hot zone consisting of a 10-mm i.d. × 30-cm quartz tube. Residence times in the hot zone were on the order of tenths of seconds, and pressures in the hot zone were 1–3 torr. Both residence time and pressure were controlled by a 0.8-mm aperture placed at the end of the pyrolysis chamber.

(7) Jenkins, R. L.; Kedrowski, R. A.; Eliot, L. E.; Tappen, D. C.; Schlyer, D. J.; Ring, M. A. *J. Organomet. Chem.* **1975**, *86*, 347. Previously unreported ^{13}C NMR (neat) for **1** δ 11.2 (t, CH_2Si), 130.4 (d, =CH—); for **2** δ −5.6 (q, CH_3Si), 14.9 (t, CH_2Si), 130.2 (d, =CH—).

(8) ^1H NMR (neat) δ 0.54 (2 H, approx sept), 1.02 (2 H, br. s), 1.82 (2 H, br s), 3.59 (2 H, approx q), 5.21 (2 H, br s); ^{13}C NMR (neat) δ 2.9 (t, CH_2Si), 4.9 (t, CH_2Si), 22.0 (t, CH_2), 124.7 (d, —CH=), 130.1 (d, —CH=); *m/e* (relative intensity) 98 (50), 97 (86), 96 (11), 83 (32) 70 (100), 69 (19), 67 (30), 55 (49), 53 (28).

(9) Yoshioka, Y.; Schaefer, H. F. *J. am. Chem. Soc.* **1981**, *103*, 7366. These authors have calculated a barrier of 41 kcal/mol for this isomerization.

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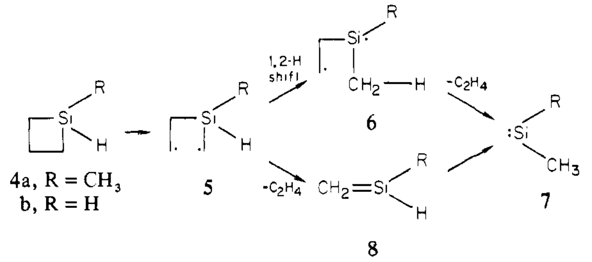
As pyrolysis temperatures were raised from 556 to 697 °C, the ratio of methylsilylene to silene products, **2**:**3**, increased from 1.2 to 5.1. While the decrease in silene products and increase in methylsilylene products might be attributed to isomerization of silene to methylsilylene,[10] it is also possible that the change in product ratios may originate from a branching step prior to silene formation (vide infra).

It is of interest to consider these results in light of the recent work of Barton and co-workers,[11] who demonstrated that 1-methylsilene, generated thermally at 450 °C from a methylsilabicyclooctadiene, adds to dienes in the typical Diels–Alder fashion. These authors suggested that formation of a methyl-substituted silylene from a hydridosilacyclobutane might be accommodated by the following sequence (eq 4): ring opening of **4** via C–C bond cleavage affords the 1,4-biradical **5**, which isomerizes to the 1,3-biradical **6**. Homolysis of another Si–C bond in **6** can account for a methylsilylene (**7**) and ethylene. The key step, a 1,2-hydrogen shift from silicon to carbon (**5** → **6**), is expected to be exothermic by roughly 8 kcal/mol.[12] If the barrier height for this hydrogen shift were less than the barrier for cleavage of the opposing silicon–carbon bond, a methylsilylene could be formed without intervention of a silene.



(4)

Although both reaction sequences **5** → **6** → **7** and **5** → **8** → **7** are reasonable pathways leading to methylsilylene, an analysis of the temperature dependence of methylsilylene to silene products ratios, **2**:**3**, permits a distinction. The major decomposition pathway of **4** likely involves the 1,4-biradical **5**. Subsequent isomerization to give the 1,3-biradical **6** or fragmentation to give the silene **8** would be expected to proceed with low and comparable activation energies.[13] However, the activation entropy for the 1,2-H shift from **5** to **6** is likely to be significantly lower than the entropy of fragmentation to **8**. Therefore, over the relatively large temperature range 556–697 °C, the change in relative rates of fragmentation to isomerization should be determined by entropy and favor the silene pathway. We observe the opposite, a considerable decrease in silene products and an increase in methylsilylene products. Consistent with our observation is the isomerization of silene to methylsilylene in the high-temperature range.

It is important to point out that the kinetic arguments presented here for rapid isomerization of silene to methylsilylene at these temperatures are not in conflict with the theoretical studies of Schaefer[14] nor the experimental contributions of Barton.[11] Currently our efforts are directed toward elucidating the reversible reaction pathway between hydridosilenes and hydridosilacyclobutanes and measuring the activation barrier for the isomerization.[15]

Acknowledgment. We gratefully acknowledge the Robert A. Welch Foundation, the North Texas State Faculty Research Fund, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Registry No. 1, 7049-25-4; **2**, 55544-25-7; **3**, 84057-67-0; silacyclobutane, 287-29-6; 1,3-butadiene, 106-99-0.

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(10) Conlin, R. T.; Wood, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 1943. In our initial report on the thermal decomposition of 1-methylsilacyclobutane, all pyrolyses were conducted at 650 °C, where only dimethylsilylene products were detected. At lower temperature, 556 °C, adducts from methylsilene and methylsilylene to butadiene are formed. The product ratios from both methylsilacyclobutane and silacyclobutane are approximately the same at 556 °C. Furthermore, control experiments indicate that products are stable during the reaction conditions.

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(13) Differences as large as 10 kcal/mol for these pathways do not affect the argument.

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(15) Subsequent to the submission of this paper, we have observed the isomerization of methylsilene, generated from methylsilabicyclo[2.2.2]octadiene at high temperature. Conlin, R. T.; Kwak Y. W., manuscript in preparation.

Partial Synthesis of (20*R*)-25-Hydroxycholesterol Involving a Nickel(II)-Promoted Dienol Rearrangement

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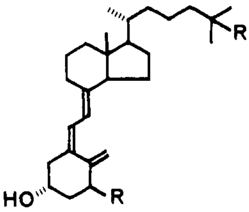
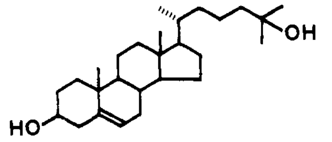
The recognition that 25-hydroxycholecalciferol (**2**) and 1α,25-dihydroxycholecalciferol (**3**) exhibit increased calcium transport, bone mineral mobilization, and calcification relative to vitamin D_3 (**1**) has generated interest in the synthesis of 25-hydroxy-substituted cholestanes. Considerable synthetic activity has focused on the partial synthesis[1] of (20*R*)-25-hydroxycholesterol (**4**), which as served as a progenitor of **2**[2] and **3**.[3] We report a new partial synthesis of **4** from pregnenolone (**5**) that employs a new approach for assembling steroid side chains and relies on an intriguing dienol rearrangement to transform a C-20 hydroxy steroid to a C-25 hydroxy steroid.



1, R = R′ = H
2, R = H, R′ = OH
3, R = R′ = OH



4

We have investigated an approach to the cholestane side chain based on the sequential construction of the C-20,22 and C-24,25 bonds as summarized in Scheme I. Metalation of 1-(methylthio)-1-(trimethylsilyl)-2-propene[4] (**6**) using *sec*-butyllithium (1.3

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(4) Compound **6** was prepared from allyl methyl thioether according to Kyler and Watt (Kyler, K. S.; Watt, D. S. *J. Org. Chem.* **1981**, *46*, 5182).

(5) All new compounds had satisfactory IR, NMR, and mass spectral and C, H combustion (or high-resolution mass spectral) data.

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