nacarbonyl in the usual manner[7] provided 633 mg (47.2%) of an ca. 50:50 (by ^1H NMR) mixture of diastereomers **28**/**29** as a golden oil: $[\alpha]_D$ −3.93° (*c* 3.41, cyclohexane); ^1H NMR ($CDCl_3$) δ 8.05–7.80 (m, 12 H), 5.07 (dt, *J* = 8 and 2 Hz, 1 H), 3.10 (t, *J* = 6 Hz, 2 H), 2.75 (t, *J* = 3 Hz, 2 H), 1.10 (s, 3 H), 0.87 (2s, 3 H), 0.78 (2s, 3 H); IR ($CHCl_3$, cm^{-1}) 3045, 3030, 2945, 2910, 2840, 2030, 1940, 1585, 1500, 1455, 1445, 1422, 1365, 1315, 1280, 1260, 1250, 1180, 1135, 1115, 1100, 1010, 952, 945, 860, 815, 740, 660, 605, 590, 585, 575; *m*/*e*(calcd) 494.1000, *m*/*e*(obsd) 494.1020.

Acknowledgment. The research was made possible by the financial support of the National Science Foundation.

Kinetics and Mechanism of Pyrolysis of 1,1,3,3,4,4-Hexamethyl-1,3,4-trisilacyclopentane

Iain M. T. Davidson* and F. Timothy Lawrence

Department of Chemistry, The University, Leicester, Great Britian

Gerhard Fritz and Eberhard Matern

Institute of Inorganic Chemistry, The University, Karlsruhe, FRG

Received June 8, 1982

Pyrolysis of the title compound, which is known to give a ring expansion isomer at atmospheric pressure, proceeds differently at low pressure, the main product being 1,1,3,3-tetramethyl-1,3-disilacyclobutane formed in a first-order reaction with $\log_{10} A/s^{-1} = 16.1 \pm 0.6$ and $E/kJ\ mol^{-1} = 316 \pm 11$. A mechanism is suggested to rationalize the results at high and low pressure.

Introduction

Pyrolysis of 1,1,3,3,4,4-hexamethyl-1,3,4-trisilacyclopentane (HTSP) at 773 K and ca. 1 atm of pressure is known[1] to give the ring expansion isomer, 1,1,3,3,5-pentamethyl-1,3,5-trisilacyclohexane (PTSH), thus

Although reasonable suggestions as to mechanism have been made,[1] no detailed kinetic work had been done; we have now undertaken a gas kinetic investigation by low-pressure pyrolysis (LPP) with analysis by mass spectrometry,[2] to elucidate the mechanism of this interesting pyrolysis.

Results

HTSP was pyrolyzed at initial pressures of 0.1–0.2 mmHg (1 mmHg = 133.3 N m^{-2}) between 879 and 1036 K. The decomposition of HTSP was first order with the following Arrhenius parameters: $\log_{10} A/s^{-1} = 16.1 \pm 0.6$ and $E/kJ\ mol^{-1} = 316 \pm 11$. These parameters were derived from measurements between 939 and 992 K, the range within which the rate constants had optimum values for reliable measurement by LPP.[2]

In contrast to the original experiments at higher pressure[1] the ring expansion product PTSH was not observed, the main product being 1,1,3,3-tetramethyl-1,3-disilacyclobutane (TDSB) instead. TDSB accounted for 77% of the HTSP decomposed at 889 K, diminishing to ca. 16% at 924 K, partly because of secondary decomposition of TDSB (vide infra) and partly because of the tendency for loss of silicon from the gas phase, which is a feature of the pyrolysis of organosilicon compounds,[3] especially by LPP.[2]

Other products were methane (ca. 17% at 924 K) and some hydrogen. Both of these products arose from decomposition of polymer at the surface of the reaction vessel; but in separate experiments it was established that they also came from secondary decomposition of TDSB.[4] In keeping with this explanation the yields of methane and hydrogen increased with increasing temperature relative to the yield of TDSB.

It is not unusual in silicon chemistry for the product composition of a pyrolysis to be drastically affected by variation in pressure. For example, pyrolysis of hexamethyldisilane gives an isomer, $Me_3SiCH_2Si(H)Me_2$, as a principal product at relatively high pressure[5] but gives TDSB instead at low pressure.[6,7] Vinyltrimethylsilane is a major product of the pyrolysis of allyltrimethylsilane at high pressure,[8] but not at low.[9] In both cases the differences arise because of the effect of pressure on the rate of a bimolecular radical–molecule reaction relative to a competing unimolecular reaction. The likelihood that a similar explanation was responsible for the formation of TDSB at low pressure and PTSH at high pressure in the pyrolysis of HTSP was investigated in a LPP experiment at 689 K (well below the pyrolysis temperature for HTSP) in which methyl radicals were generated by pyrolysis of dimethylmercury in the presence of HTSP, thus giving a high concentration of radicals, even at low pressure. PTSH was indeed formed, with no TDSB.

---

(1) Fritz, G.; Grunert, B. *Z. Anorg. Allg. Chem.* **1976**, *419*, 249.

(2) Davidson, I. M. T.; Ring, M. A. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1520.

(3) Baldwin, A. C.; Davidson, I. M. T.; Reed, M. D. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 2171.

(4) Davidson, I. M. T.; Lawrence, F. T., to be published.

(5) Shiina, K.; Kumada, M. *J. Org. Chem.* **1958**, *23*, 139. Davidson, I. M. T.; Eaborn, C.; Simme, J. M. *J. Chem. Soc., Faraday Trans.* 1 **1974**, *70*, 249.

(6) Davidson, I. M. T.; Howard, A. V. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 69.

(7) Davidson, I. M. T.; Potzinger, P.; Reimann, B. *Ber. Bunsenges. Phys. Chem.* **1982**, *86*, 13.

(8) Sakurai, H.; Hosomi, A.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1970**, 767. Neider, S. M.; Chambers, G. R.; Jones, M., Jr. *Tetrahedron Lett.* **1979**, 3796.

(9) Davidson, I. M. T.; Wood, I. T. *J. Organomet. Chem.* **1980**, *202*, C65.

0276-7333/82/2301-1453$01.25/0

In the pyrolysis of HTSP, likely intermediates in the initial stages would be dimethylsilylene, $\mathrm{Me_2Si}$, and 2-methyl-2-silapropene, $\mathrm{Me_2Si{=}CH_2}$. The involvement of these intermediates was investigated in experiments with two trapping agents, each capable of giving distinctive products.

(i) Methyl Trimethylsilyl Ether. Expected trapping reactions were as follows: $\mathrm{Me_3SiOMe + Me_2Si \rightarrow Me_3SiSi(Me_2)OMe}$[10] and $\mathrm{Me_3SiOMe + Me_2Si{=}CH_2 \rightarrow Me_3SiCH_2Si(Me_2)OMe}$.[11] To test this trapping agent in the LPP apparatus, $\mathrm{Me_2Si}$ was generated by pyrolysis of pentamethylchlorodisilane[12] and $\mathrm{Me_2Si{=}CH_2}$ by pyrolysis of 1,1-dimethyl-1-silacyclobutane.[13] Pyrolysis of these precursors in the presence of methyl trimethylsilyl ether at 908 K gave the expected products, identified mass spectrometrically by their $(\mathrm{M - Me})^+$ ions. In the reaction with $\mathrm{Me_2Si{=}CH_2}$, $\mathrm{Me_3SiOMe}$ did not completely suppress the formation of TDSB.

In a trapping experiment with a 1.5:1 mixture of methyltrimethyl silyl ether and HTSP at 908 K both products were observed.

(ii) Hydrogen Chloride. Hydrogen chloride is known to react as follows in the LPP apparatus: $\mathrm{HCl + Me_2Si \rightarrow Me_2SiHCl}$[14] and $\mathrm{HCl + Me_2Si{=}CH_2 \rightarrow Me_3SiCl}$.[15] Both of these products were observed when a 4:1 mixture of hydrogen chloride and HTSP was pyrolyzed at 898 K. Unlike $\mathrm{Me_3SiOMe}$, hydrogen chloride traps $\mathrm{Me_2Si{=}CH_2}$ quantitatively under LPP conditions,[15] completely suppressing the formation of TDSB from $\mathrm{Me_2Si{=}CH_2}$.

Hence, both trapping agents give evidence for the presence of $\mathrm{Me_2Si}$ and $\mathrm{Me_2Si{=}CH_2}$. Another mechanistically significant point was that the formation of TDSB was still observed in the presence of hydrogen chloride; $\mathrm{Me_2Si{=}CH_2}$ could not, therefore, have been the main precursor to TDSB.

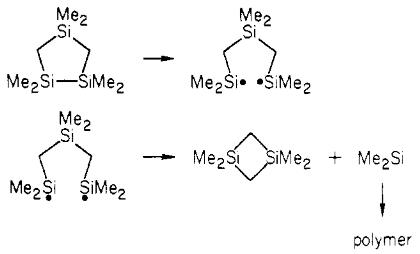
There is evidence[16] that the pyrolysis of TDSB involves formation of $\mathrm{Me_2Si{=}CH_2}$. TDSB was therefore pyrolyzed in the LPP apparatus. Over the same temperature range, it decomposed at ca. 10% of the rate of decomposition of HTSP, giving methane and hydrogen. Evidence for the presence of $\mathrm{Me_2Si{=}CH_2}$ came from trapping experiments with hydrogen chloride,[15] which gave $\mathrm{Me_3SiCl}$. A detailed account of the kinetics and mechanism of pyrolysis of TDSB will be published separately.[4]

Finally, as the original pyrolysis[1] of HTSP had been at lower temperature as well as higher pressure than the present work, a few experiments were done on the thermal stability of PTSH in the LPP apparatus between 847 and 1020 K. PTSH was not more thermally unstable than HTSP and gave no TDSB on pyrolysis.

Discussion

In the low-pressure pyrolysis of HTSP trapping experiments showed that $\mathrm{Me_2Si}$ and $\mathrm{Me_2Si{=}CH_2}$ were both present as intermediates. However, the $\mathrm{Me_2Si{=}CH_2}$ can be accounted for by secondary decomposition of the main product TDSB. The simplest conclusion from the trapping experiments is that only $\mathrm{Me_2Si}$ is directly produced in the LPP of HTSP and that the formation of TDSB is unaffected by trapping agents.

Scheme I



(1)

(2)

Table I

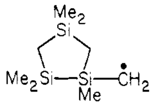
reactn	$\log_{10} A^a$	E/kJ mol^{-1}	ref
1	16.1	316	this work
3	10.4	75	7
4	12.3	90	7
5	10.4	75	7
6	8.8	0	7

[a] First-order A factors are in s^{-1} and second-order A factors in dm^3 mol^{-1} s^{-1}.

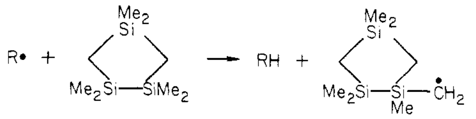
The silicon–methyl bond dissociation energy is at least[3,17] 355 kJ mol^{-1}, whereas the silicon–silicon bond dissociation energy in hexamethyldisilane[6] is only 337 kJ mol^{-1}. Hence the initial step in the pyrolysis of HTSP is rupture of the silicon–silicon bond.

In the light of the foregoing comments, the simplest mechanism to account for the formation of TDSB in the low-pressure pyrolysis of HTSP is shown in Scheme I. [Reaction 2 is not only the simplest route to TDSB, but the most energetically feasible, with a small endothermicity equal to the ring strain energy in TDSB (ca. 103 kJ mol^{-1}).[18] Such alternatives as the intermediacy of a 1,4 biradical would be endothermic by ca. 355 kJ mol^{-1}.] This sequence would be rate determined by reaction 1 with which the observed Arrhenius parameters can be identified. This is entirely plausible; the A factor of $10^{16.1\pm0.6}$ s^{-1} is reasonable for this type of reaction,[19] while the activation energy of 316 ± 11 kJ mol^{-1} implies a realistic ring strain energy of 21 ± 16 kJ mol^{-1}, since the silicon–silicon bond dissociation energy in hexamethyldisilane[6] is 337 ± 5 kJ mol^{-1}.

Our experiments with dimethylmercury that showed that PTSH was formed instead of TDSB in the presence of a radical source provide the key to understanding the different results of pyrolysis at low and high[1] pressure. The essential precursor to PTSH is evidently the radical



produced from HTSP by hydrogen abstraction (eq 3). A



(3)

similar radical containing the $\mathrm{Si{-}Si{-}\dot{C}H_2}$ skeleton is $\mathrm{Me_3SiSi(Me_2)\dot{C}H_2}$, which is known[7] to rearrange unimo-

---

(10) Atwell, W. H.; Weyenberg, D. R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 469.

(11) John, P.; Gowenlock, B. G.; Groome, P. *J. Chem. Soc., Chem. Commun.* **1981**, *806*. Davidson, I. M. T.; Wood, I. T. *Ibid.* **1982**, 550.

(12) Davidson, I. M. T.; Delf, M. E. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 1912.

(13) Flowers, M. C.; Gusel'nikov, L. E. *J. Chem. Soc. B* **1968**, 419.

(14) Davidson, I. M. T.; Lawrence, F. T.; Ostah, N. A. *J. Chem. Soc., Chem. Commun.* **1980**, 859.

(15) Davidson, I. M. T.; Dean, C. E.; Lawrence, F. T. *J. Chem. Soc., Chem. Commun.* **1981**, 52.

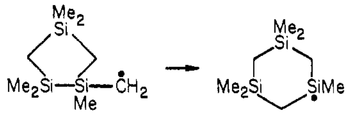
(16) Nametkin, N. S.; Gusel'nikov, L. E.; Volpina, E. A.; Vdovin, V. M. *Dokl. Akad. Nauk SSSR* **1975**, *220*, 386.

(17) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

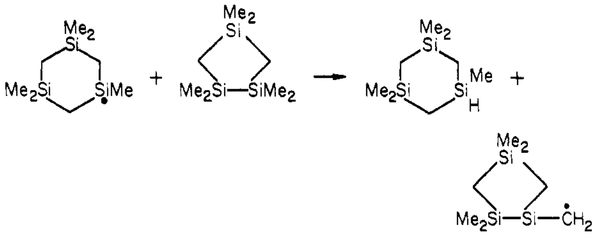
(18) O'Neal, H. E.; Ring, M. A. *J. Organomet. Chem.* **1981**, *213*, 419.

(19) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976; p 117.

lecularly to $Me_3SiCH_2SiMe_2$. The corresponding reaction in this case, followed by hydrogen abstraction, would give PTSH (eq 4 and 5). Reactions 4 and 5 constitute the propagation steps of a chain reaction converting HTSP to PTSH.



(4)



(5)

In the pyrolysis of HTSP at higher pressure,[1] the radical formed in reaction 1 would react mainly by reaction 3 instead of by reaction 2, thus initiating the chain leading to PTSH. Termination of the chain would probably be by self-combination of

reaction 6, giving three-halves-order kinetics,[6] with $k_{3/2} = (k_1k_5^2/2k_6)^{1/2}$. From the present work and by analogy with the isomerization of hexamethyldisilane,[7] Arrhenius parameters may be estimated for these reactions, as shown in the Table I. Hence, for $k_{3/2}$, $\log_{10} A = 13.9$ and $E/\mathrm{kJ\ mol^{-1}} = 233$.

For the isomerization of HTSP to PTSH, the chain length λ is given by $\lambda = k_{3/2}\,(\mathrm{HTSP})^{1/2}/k_1$. Under the original conditions,[1] the pressure was at least 1 atm and a typical temperature was 773 K. These conditions give a chain length of ca. 400, thus explaining the preponderant formation of PTSH. In contrast, the chain length under LPP conditions is only 0.4 at 939 K, diminishing to 0.2 at 1036 K. In fact, termination in the LPP apparatus is unlikely to be by the bimolecular reaction (6) but is more likely to be by unimolecular loss of the same radical to the walls of the reaction vessel. The formation of PTSH would then be second order, with even shorter chain lengths than those calculated above, resulting in the formation of TDSB by reaction 2 instead. Reactions 1–6 thus provide a satisfactory explanation for the different course of the pyrolysis of HTSP at high and low pressure.

The radical rearrangement (4) is exothermic by at least[17] 30 kJ mol^{-1}; from this work and from that on hexamethyldisilane[6] it appears to be rather a general reaction of alkyl silanes containing silicon–silicon bonds and is probably important in the pyrolytic formation of silicon-carbon fibers.

Experimental Section

HTSP and PTSH were prepared as previously described,[1] and TDSB was prepared by pyrolysis of 1,1-dimethyl-1-silacyclobutane[13] followed by purification by preparative GLC.

The LPP apparatus[2] was modified by addition of a dedicated microcomputer with real-time clock (RML 380Z), which received peak height measurements and times from an eight-channel peak selector, and was used for processing the kinetic results directly.

Acknowledgment. I.M.T.D. and F.T.L. thank the Science and Engineering Research Council for financial support.

Registry No. HTSP, 58679-67-7; PTSH, 17882-80-3; TDSB, 1627-98-1; Me_2Si, 6376-86-9; $Me_2Si{=}CH_2$, 4112-23-6; HCl, 7647-01-0; methyl trimethylsilyl ether, 1825-61-2; pentamethylchlorodisilane, 1560-28-7; 1,1-dimethyl-1-silacyclobutane, 2295-12-7; dimethylmercury, 593-74-8; methyl, 2229-07-4.

Pyrolytic Generation and Thermal Rearrangement of a 2-Silaindene

Thomas J. Barton* and Gary T. Burns

Department of Chemistry, Iowa State University, Ames, Iowa 50011

Received June 29, 1982

Flash vacuum pyrolysis of a 2-allyl-2-methyl-2-silaindan affords three products: a 3-silaindene, indene, and 2-sila-1,2-dihydronaphthalene. It is proposed that these arise from rearrangement of an initially formed 2-silaindene. Chemical trapping established the intermediacy of the 2-silaindene and an isobenzosilole.

Since 1942 when Alder[1] reported that isoindene (2) was trapped in a [4 + 2] cycloaddition when indene (1) was heated with maleic anhydride, the thermochemistry of indenes has been extensively investigated.[2] It is now firmly established that indene equilibrates with isoindene via 1,5-hydrogen shifts although the presence of pseudoindene (3) in this equilibrium mixture has never been demonstrated. Pseudoindenes have been prepared and thermally isomerized to isoindenes and indenes. One other fact of interest is that in addition to hydrogen migrations, 1,5 shifts of phenyl and methyl have also been documented.

Our recent discovery[3] that 1-methylsilole (5) is conveniently produced from the flash vacuum pyrolysis (FVP) of 4-allyl-4-methyl-4-silacyclopentene (4) suggested that we might be able to use this route to gain entry to silaindene–silaisoindene energy surface. Thus, we synthesized the desired precursor, 2-allyl-2-methyl-2-silaindan (8) in three steps in an overall yield of 28%. Coupling of benzylmagnesium chloride with (chloromethyl)methyldi-

---

(1) Alder, K.; Pascher, F.; Vagt, H. *Ber. Dtsch. Chem. Ges.* **1942**, *75*, 1501.

(2) For a current review see: Gajewski, J. J. "Hydrocarbon Thermal Isomerizations"; Academic Press: New York, 1981; pp 290–294.

(3) Burns, G. T.; Barton, T. J. *J. Organomet. Chem.* **1981**, *209*, C25.

0276-7333/82/2301-1455$01.25/0 © 1982 American Chemical Society