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PYROLYSIS OF 1,1,2-TRIMETHYL-1-SILACYCLOBUTANE. SITE OF INITIAL RING CLEAVAGE

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Summary

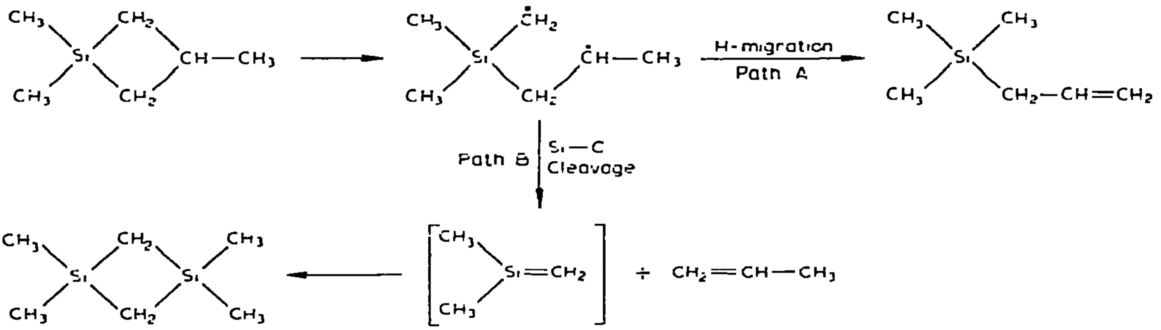
The gas-phase, flow pyrolysis of 1,1,2-trimethyl-1-silacyclobutane (I) is described. A total of six products, containing two silicon atoms, have been analyzed with respect to relative yields (at 520°, 570°, 620° and 680°) and mechanistic origin. It is concluded that thermolysis of I occurs with predominant initial cleavage of the carbon—carbon bond rather than the silicon—carbon bond and that further cleavage affords a silaalkene, $Me_2Si{=}CHCH_3$. The pyrolysis of 1,1,3,3-tetramethyl-1,3-disilacyclobutane at 700° leads to silaalkene production as shown through trapping with benzaldehyde.

Introduction

The gas-phase thermal decomposition of monosilacyclobutanes, first reported in 1966 [1], has been rather conclusively established to proceed through the intermediacy of a species which at least behaves as if it contained a silicon—carbon (p—p) π double bond. Evidence for the transient silaalkene has come from kinetic studies [2] and a variety of trapping reactions [3]. As a result of the kinetic studies it was concluded [2] that decomposition occurred through initial homolytic fission of one bond but the site of initial cleavage, whether a silicon—carbon or carbon—carbon bond, was immediately questioned [4].

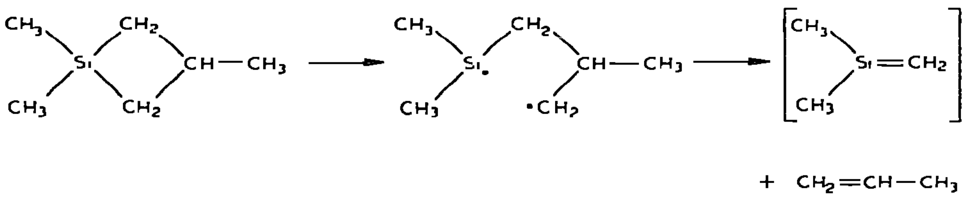
In 1970 Nametkin [5] reported that 1,1,3-trimethyl-1-silacyclobutane thermally decomposed in a gas flow system at 562° to afford propene, allyltrimethylsilane and the usual product of silaalkene dimerization, 1,1,3,3-tetramethyl-1,3-disilacyclobutane. The assumed mechanism involved initial homolytic scission of a C—C bond [6] (Scheme 1). However, it should be noted that only the product allyltrimethylsilane appears to demand the diradical formed from initial C—C bond fission and that the products from Path B, the route involving formation of the silaalkene, predominated by a

SCHEME 1



factor of ten. It is entirely possible to account for the formation of propene and 1,1,3,3-tetramethyl-1,3-disilacyclobutane utilizing initial Si—C bond rupture (Scheme 2). Thus the question of the site of initial cleavage is still very much open.

SCHEME 2



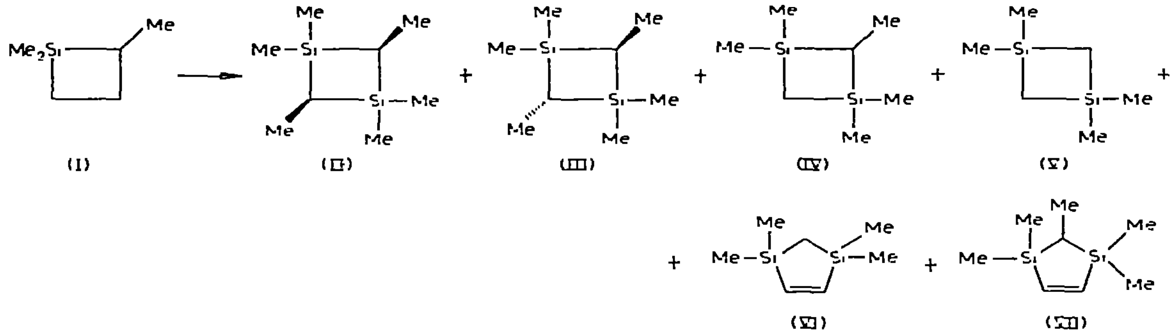
As it would be desirable to examine the behavior of a less symmetrical silacyclobutane, we undertook the study of the pyrolysis of 1,1,2-trimethyl-1-silacyclobutane.

Results

Pyrolysis of 1,1,2-trimethyl-1-silacyclobutane (I) was conducted in a vertical tube packed with Vycor chips with continuous nitrogen flow.

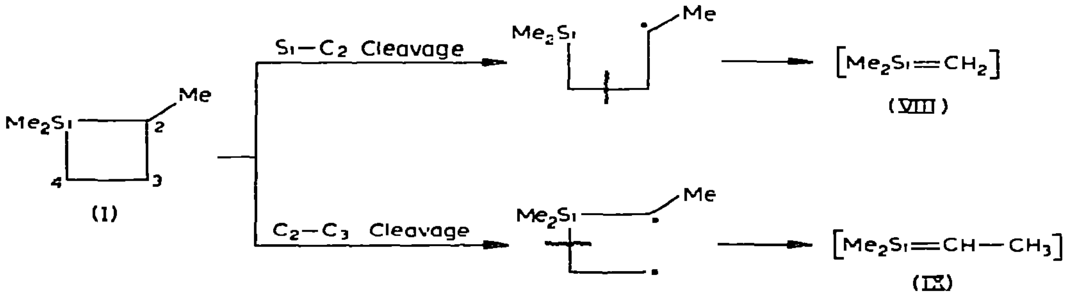
Product analysis was initially performed by a combination of gas chromatography (GC) and mass spectroscopy. Mass recovery was normally above 70% but above 600° much of the pyrolysate was not GC-analyzable and was assumed to be oligomeric. GC analysis of the product mixture from runs varying in temperature from 520 to 680° revealed *cis*-1,1,2,3,3,4-hexamethyl-1,3-disilacyclobutane (II), *trans*-1,1,2,3,3,4-hexamethyl-1,3-disilacyclobutane (III), 1,1,2,3,3-pentamethyl-1,3-disilacyclobutane (IV), 1,1,3,3-tetramethyl-1,3-disilacyclobutane (V), 1,1,3,3-tetramethyl-1,3-disilacyclopent-4-ene (VI) and 1,1,2,3,3-pentamethyl-1,3-disilacyclopent-4-ene (VII) (Scheme 3). Only in the 520° run was a significant amount of unreacted I (ca. 10%) observed.

An analysis of the possible modes of cleavage of I leads one to the conclusion that if a Si—C bond were first ruptured, it would be the bond connecting Si and C_2 as this would yield a secondary carbon radical as opposed to the primary radical generated from Si—C_4 cleavage. By the same rationale, initial C—C bond cleavage should be favored between C_2 and C_3. Consequently, SCHEME 3



initial Si—C bond rupture would lead to 2-methyl-2-silapropene (VIII), while initial C—C bond rupture would lead to formation of 2-methyl-2-silabut-2-ene (IX) (Scheme 4). Of course an equilibrium can exist between I and any diradical formed from a single cleavage but in the absence of any stereochemical information we can know nothing about such processes and can only direct our attention toward routes which continue on to the reaction products.

SCHEME 4



Products II and III are clearly formed by dimerization of IX, product IV from one molecule each of VIII and IX, and V from a dimerization of VIII. Relative yields for a spread of four pyrolysis temperatures are presented in graphical form in Fig. 1. It is clear that below 600° the major route involves the intermediacy of silaalkene (IX) and therefore an initial cleavage of the C_2—C_3 bond. The origin of the disilacyclopentenes (VI and VII) is not obvious. Two different mechanistic possibilities present themselves (Scheme 5). Path A involves the initial formation of IX, loss of a hydrogen atom to form an allylic type radical which could add across the silicon—carbon double bond of VIII to form the cyclopentyl radical (X) followed by hydrogen atom expulsion to afford VI. Product VII would be formed by addition across IX rather than VIII. Path B would involve conversion of a disilacyclobutane through homolytic opening, hydrogen atom expulsion and intramolecular attack by silyl radical on the generated π-bond and formation of VI (or VII if starting with II or III) through a final hydrogen loss.

From Fig. 1 it can be seen that with increasing pyrolysis temperatures the relative yields of II, III and IV, products which result from the interme-

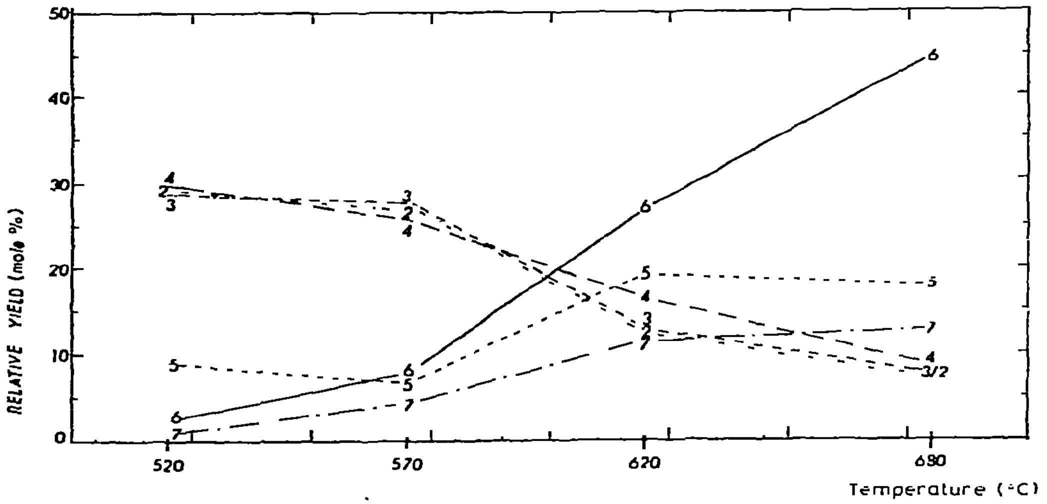
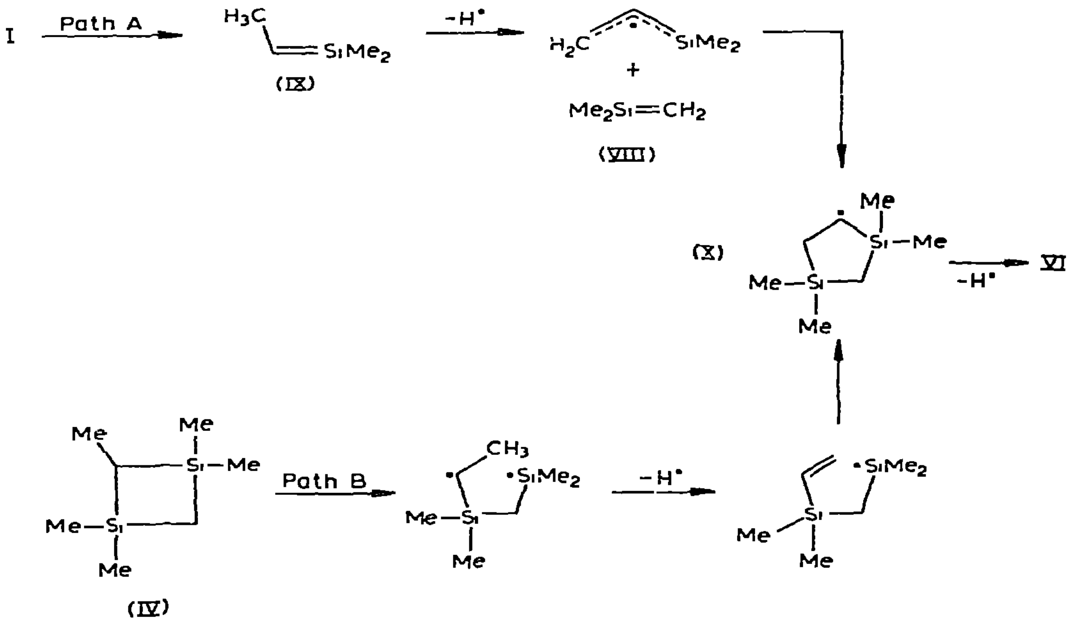


Fig. 1. Relative yields of pyrolysis products containing two silicon atoms.

SCHEME 5



diacy of silaalkene IX, fall with respect to the relative yields of VI and VII. This pattern is consistent with both paths A and B (Scheme 5). However, we favor Path B since a separate pyrolysis of IV at 630° yielded VI as the only detectable product (GC) along with unreacted IV. If IV were cleaving to molecules of VIII and IX, we would certainly expect to find significant amounts of dimers II, III and V in the product mixture.

Regardless of the complete mechanistic routes to the disilacyclopentenes (VI and VII), it is clear that at some stage the formation of VI requires one

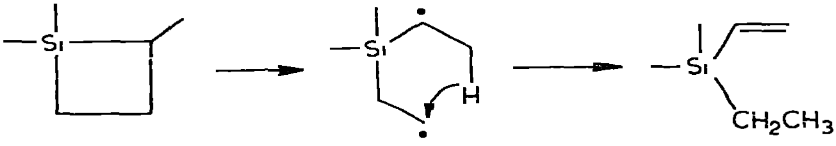
TABLE 1

Pyrolysis temp. (°C)	Products resulting from initial [a] Si—C cleavage	C—C cleavage
520	24.8	75.2
570	24.5	75.5
620	41.4	58.6
680	44.9	55.1

[a] Mole % of total disilane products.

molecule each of VIII and IX while VII requires two molecules of IX. Therefore, we are now in a position to analyze the total silicon-containing products with respect to their silaalkene origin. Products II, III and VII result solely from IX, IV and VI from one molecule each of VIII and IX, and only V comes solely from VIII. The results are tabulated in Table 1 for all of the products containing two silicon atoms. From these results it seems that products resulting from initial C—C bond cleavage predominate by ca. three to one below 600° but at higher temperatures sufficient energy is available to make the two processes competitive. In fact the results listed for 520° carry an unfair bias for Si—C cleavage as a significant amount (7%) of dimethylethylvinylsilane (XI), which clearly arises from initial C—C bond rupture, is formed (Scheme 6).

SCHEME 6



(XI)

We assume that this preference for initial C—C bond cleavage is in some part due to stabilization of the β-radical by silicon both through σ—π conjugation and interaction of the empty *d*-orbitals with the radical center [7, 8].

The apparent pyrolytic rearrangement of IV to VI still leaves the question of possible formation of two silaalkenes from the pyrolysis of a single molecule of 1,3-disilacyclobutane. Previous work on the pyrolysis of 1,1,3,3-tetramethyl-1,3-disilacyclobutane (V) had been concerned with polymer production at relatively low temperatures in static systems [9-13]. A single report of attempted trapping of silaalkene (VIII) with water in the gas phase thermolysis of V revealed a very complex mixture of products, some of which could well have arisen from silaalkene intermediacy [14].

Previous success in our laboratory with benzaldehyde as an extremely efficient trap for VIII [15] suggested its use in determining whether V yielded VIII upon pyrolysis*. Gas-phase flow co-pyrolysis (N_2) of (V) and

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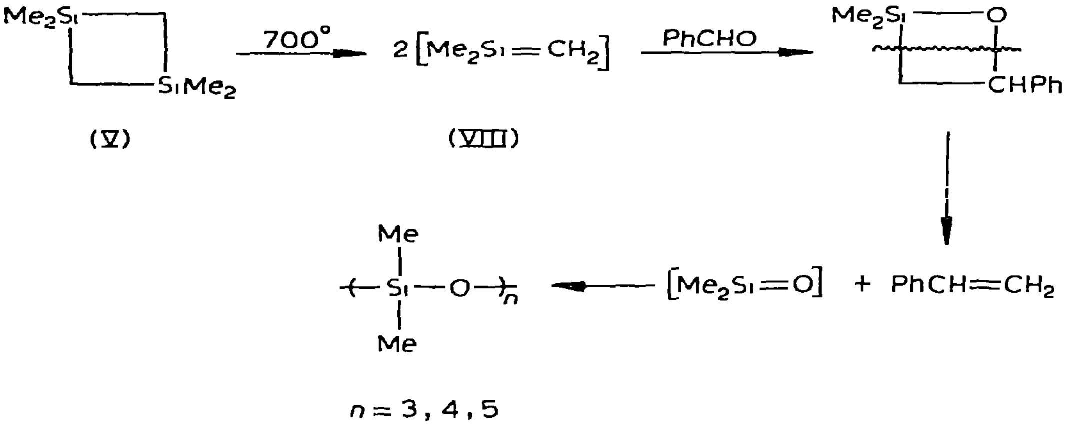
* For a more comprehensive discussion of the reactions of ketones and aldehydes with silaalkenes see [16].

a three-fold excess of benzaldehyde produced no reaction below 700° when styrene (25%), hexamethylcyclotrisiloxane (1.4%), octamethylcyclotetrasiloxane (4.1%) and decamethylcyclopentasiloxane were isolated. These products support the intermediacy of 2-methyl-2-silapropene (VIII) as in the mechanism shown in Scheme 7.

SCHEME 7



Our inability to gain evidence for VIII below ca. 700° supports the essential irreversibility of the dimerization reaction at temperatures normally used for silaalkene generation. This is in agreement with the kinetic studies of Gusel'nikov and Flowers [2]. At higher temperatures the dimerization is indeed reversible. However, the extreme temperatures required make this method of generation of no synthetic value.

Experimental

60 MHz NMR spectra were recorded on a Perkin—Elmer Model R-20B spectrometer and a Varian Model A-60 spectrometer. NMR spectra of compound III were also obtained on Varian HA-100 spectrometer and a Varian 220 MHz spectrometer. All NMR spectra were obtained using carbon tetrachloride solutions with tetramethylsilane as an internal reference. Routine mass spectra were recorded on an Atlas CH-4 mass spectrometer and exact mass measurements were carried out on a AEI MS 902 high resolution instrument. Analytical and preparative gas chromatography was performed with a Varian Aerograph Model 1700 using 16' × 1/4" copper columns packed with 6% QF-1 + 4% SE30 on Chromosorb W 60/80. A helium flow of 30 ml/min was used with a temperature program of 50°-200° at 2°/min. Gas chromatographic/mass spectral (GCMS) analyses were performed on a Perkin—Elmer Model 270 mass spectrometer using a 6' × 3mm glass column packed with 6% QF-1 + 4% SE30 on Chromosorb P 80/100.

The following compounds were synthesized by the referenced procedures: 1,1,2-trimethyl-1-silacyclobutane (I) [17], 1,1,2,3,3-pentamethyl-1,3-disilacyclobutane (IV) [12], 1,1,3,3-tetramethyl-1,3-disilacyclobutane (V) [18], dimethylethylvinylsilane (XI) [19].

Pyrolysis of 1,1,2-trimethyl-1-silacyclobutane (I)

A vertical Vycor tube (12 mm × 30 cm) packed with Vycor chips was heated to the desired temperature in a tube furnace. A controlled downward air stream was directed through the furnace to obtain a more constant temperature throughout the furnace. The upper end of the tybe was equipped with a rubber septum, for syringe introduction of the sample, and a gas inlet. The nitrogen flow rate was 5 ml/min and sample (neat) introduction time was ca. 0.1 ml/8 min. The collection trap was cooled with liquid nitrogen. Typically 70-80% volume recovery was experienced regardless of the pyrolysis temperature. No attempt was made to trap and identify the volatile hydrocarbon products. For relative yield analysis the thermal conductivity factors of V (1.23) and I (1.05) were determined using benzene as a reference standard. Insufficient amounts of the other products were obtained in pure state for accurate thermal conductivity factors to be determined thus the factor for V, 1.23, was used for those products containing two silicon atoms.

Dimethylethylvinylsilane (XI). Retention time 14.8 min. Positive identification was obtained from spectral comparison with an authentic sample. This product was only observed in the pyrolysate from the 520° run to the extent of ca. 7%. Increasing temperature resulted in a decrease in XI (570°, 3%; 620° and 680°, not detectable by GC). Separate pyrolysis of XI at 620° revealed that it is not a thermal precursor of any of the compounds II-VII (Table 2).

1,1,3,3-Tetramethyl-1,3-disilacyclobutane (V) Retention time 24 min. Positive identification was obtained by NMR and mass spectral (MS) comparison with an authentic sample.

1,1,3,3-Tetramethyl-1,3-disilacyclopent-4-ene (VI). Rentention time 29 min.: the NMR spectrum was the same as reported by Fritz [20]; high resolution MS, parent ion *m/e* 156.0790 ± 0.0008. $C_7H_{16}Si_2$ calcd.: 156.0791.

1,1,2,3,3-Pentamethyl-1,3-disilacyclobutane (IV). Retention time 31 min; NMR (δ, ppm) 0.17 (s, 6H, $SiCH_3$), 0.20 (s, 6H, $SiCH_3$), —0.08 (s, 2H, CH_2), 1.00 (d, *J*=8 Hz, 3H, CH_3), the methine hydrogen was too diffuse to observe in this very dilute solution; MS *m/e* 158 (52%, parent ion), 143 (26%, P—CH_3), 129 (64%), 115 (100%). Positive identification was made from comparison of the NMR, MS and GC retention time with an authentic sample.

1,1,2,3,3-Pentamethyl-1,3-disilacyclopent-4-ene (VII). Retention time 37.5 min; NMR (δ, ppm) 0.07 (s, 6H, SiMe), 0.11 (s, 6H, SiMe), 1.05 (d, *J*= 7.5 Hz, 3H, CH_3), 6.93 (s, 2H, vinyl), dilution too great to observe the me-

TABLE 2

RELATIVE YIELDS OF SILAALKENE DERIVED PRODUCTS (%)

Product	Pyrolysis temperatures (°C) 520	570	620	680
II	29.4	26.1	12.3	7.5
III	29.3	27.2	12.3	7.5
IV	29.6	17.6	16.6	8.7
V	9.2	6.9	19.5	18.0
VI	2.3	7.8	27.2	45.0
VII	0.9	4.5	12.0	13.0

thine quartet; MS *m/e* 170 (45%, parent ion), 155 (100%, P—CH_3); high resolution MS *m/e* 170.0944 (±0.0009), $C_8H_{18}Si_2$ calcd.: 170.0947.

cis-1,1,2,3,3,4-Hexamethyl-1,3-disilacyclobutane (II). Retention time 38 min; NMR (δ, ppm) 0.10 (s, 6H, $SiCH_3$), 0.17 (s, 6H, $SiCH_3$), 1.00 (d, 6H, CH_3, J=8 Hz), the sample was too dilute to identify the two methine hydrogens; MS *m/e* 172 (100%, parent ion), 157 (40%, P—CH_3), 143 (45%), 129 (63%), 97 (27%), 85 (20%), 73 (31%); high resolution MS *m/e* 172.1103 ± 0.0009, $C_8H_{20}Si_2$ calcd.: 172.1104.

trans-1,1,2,3,3,4-Hexamethyl-1,3-disilacyclobutane (III). Retention time 39.5 min; NMR (100 MHz) (δ, ppm) 0.15 (s, 12H, SiMe), 1.03 (d, 6H, CH_3), 0.35 (q, 2H, methine C—H), decoupling was performed on a 220 MHz instrument where irradiation at 0.35 ppm caused collapse of the methyl doublet and irradiation at 1.03 ppm produced collapse of the methine quartet; the mass spectrum was identical to that of II; high resolution MS *m/e* 172.1102 ± 0.0009, $C_8H_{20}Si_2$ calcd.: 172.1104.

Pyrolysis of 1,1,3,3-tetramethyl-1,3-disilacyclobutane (V) with benzaldehyde

A solution of V (1.075 g, 7.4 mmol) and benzaldehyde (4.77 g, 45 mmol) was introduced (0.2 ml/min with N_2 flow) into the pyrolysis tube held at 700°. Pyrolysate analysis and isolation by GC revealed styrene (25.4%), hexamethylcyclotrisiloxane (1.4%), octamethylcyclotetrasiloxane (4.1%) and decamethylcyclopentasiloxane (1.5%). All products were identified by GC, NMR, IR and MS comparison to authentic samples. Co-pyrolysis of V and benzaldehyde at 500° and 600° failed to shown any reaction of V.

Acknowledgements

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