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REACTION OF SILYLENES AND GERMYLENE WITH 1,3-BUTADIENE

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Summary

Sila-3-cyclopentenes were obtained from reaction of 1,3-butadiene with SiH_2, ClSiH and CH_3SiH generated from disilane pyrolyses. 1-Silylsila-3-cyclopentene and 1,2-disila-4-cyclohexene were obtained in near equal quantities from the reaction of 1,3-butadiene with Si_2H_4 (H_3SiSiH or $H_2Si{=}SiH_2$) generated from the pyrolysis of Si_3H_8. Competitive reactions of SiH_2 with 1,3-butadiene and Si_2H_6 and of GeH_2 with 1,3-butadiene and digermane have demonstrated that while SiH_2 addition to 1,3-butadiene can compete favorably with insertion into Si_2H_6, GeH_2 addition to 1,3-butadiene cannot compete with insertion into Ge_2H_6.

Introduction

The addition of $(CH_3)_2Si$ and $(CH_3O)_2Si$, generated from the pyrolysis of methoxymethyldisilanes, to 2,3-dimethyl-1,3-butadiene has produced the corresponding sila-3-cyclopentenes [1]. The addition of SiH_2, generated from the $^{31}P(n,p)$—^{31}Si nuclear transformation of PH_3 or from the pyrolysis of Si_2H_6, to 1,3-C_4H_6 forming sila-3-cyclopentene has also been reported [2,3].

We have demonstrated that Si_2H_6 [4], Ge_2H_6 [4], $ClSi_2H_5$ [5], $CH_3Si_2H_5$ [6] and Si_3H_8 [7] decompose thermally by 1,2-hydrogen shifts forming SiH_2 and GeH_2 from Si_2H_6 and Ge_2H_6 and forming SiH_2 along with ClSiH, CH_3SiH and SiH_3SiH from $ClSi_2H_5$, $CH_3Si_2H_5$ and Si_3H_8 respectively. We have proposed that the Si_2H_4 reactive intermediate is SiH_3SiH [7], while Strausz et al. have suggested that Si_2H_4 exists as $H_2Si{=}SiH_2$ [8].

In this paper, we report our results on the reactions of the silylenes, GeH_2 and Si_2H_4 mentioned above with 1,3-butadiene.

Results and discussion

The following reactions were carried out in a recirculating flow system containing a thermal zone and a low temperature cold trap which removed products less volatile than the reagents.

Addition of silylenes to 1,3-butadiene

The volatile products from the flow pyrolysis of Si_2H_6 and 1,3-C_4H_6 at 385° were SiH_4, sila-3-cyclopentene (C_4H_8Si), Si_3H_8 and 4-vinylcyclohexene produced in the neat pyrolysis of 1,3-C_4H_6. Disilane [4] decomposes into SiH_4 and SiH_2 which then reacts with Si_2H_6 or 1,3-C_4H_6:

$$Si_2H_6 \rightarrow SiH_2 + SiH_4 \qquad (1)$$

$$SiH_2 + Si_2H_6 \rightarrow Si_3H_8 \qquad (2)$$

$$SiH_2 + 1{,}3\text{-}C_4H_6 \rightarrow C_4H_8Si \qquad (3)$$

The gas phase ratio of 1,3-C_4H_6/Si_2H_6 was 1.2 while the Si_3H_8/C_4H_8Si product ratio was 3.6. If one assumes that both SiH_2 trapping products are removed before any significant decomposition, the relative rate of SiH_2 addition to Si_2H_6 compared to 1,3-C_4H_6 is 4.2/1 on a molecular basis. We have previously demonstrated that Si_3H_8 is essentially quantitatively removed by our cold traps in these systems [7]. The thermal stability of C_4H_8Si appears similar to that of Si_3H_8 so that it should also be essentially quantitatively removed by our cold trap.

The products from the flow pyrolysis of $CH_3Si_2H_5$ and 1,3-C_4H_6 were SiH_4, CH_3SiH_3, C_4H_8Si, 1-methylsila-3-cyclopentene ($C_4H_7SiCH_3$) and 4-vinylcyclohexene. Due to complications in the flow pyrolysis of $CH_3Si_2H_5$ [9], the ratio of SiH_2 to CH_3SiH formed is not known so that we cannot accurately compare the relative addition rate of SiH_2 and CH_3SiH to 1,3-C_4H_6.

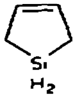
The products from the flow pyrolysis of $ClSi_2H_5$ and 1,3-C_4H_6 were SiH_4, $ClSiH_3$, C_4H_8Si and 1-chlorosila-3-cyclopentene (C_4H_7SiCl) in a ratio of 9/7/4/5. We have suggested that the $SiH_4/ClSiH_3$ ratio is a measure of the yields of ClSiH compared to SiH_2 from reactions 4 and 5 [5]:

$$ClSi_2H_5 \rightarrow ClSiH + SiH_4 \qquad (4)$$

$$ClSi_2H_5 \rightarrow SiH_2 + ClSiH_3 \qquad (5)$$

However, the lifetime of ClSiH may be significantly greater than that of SiH_2, so we cannot obtain relative addition rates of SiH_2 and ClSiH to 1,3-C_4H_6. We can note that the formation of the ClSiH and SiH_2 adducts with 1,3-C_4H_6 were obtained in similar ratios to the apparent formation yields of the two silylenes.

It has been previously observed that for $(CH_3)_2Si$, the relative reactivities for trapping are [1]: saturated hydrocarbons < benzene < ethylene < dimethoxytetramethyldisilane < dienes. Our results demonstrate that on a molecular basis, the insertion of SiH_2 into Si_2H_6 (eqn. 2) is about 4 times faster than the addition of SiH_2 to 1,3-C_4H_6 forming III (eqn. 3).



(III)

In the neat pyrolysis of $CH_3Si_2H_5$, the SiH_2 and CH_3SiH insertion products ($CH_3Si_3H_7$ and $(CH_3)_2Si_3H_6$) were obtained in significant quantities [6]. However, these products were not observed when $CH_3Si_2H_5$ was pyrolysed in the presence of a 20/1 excess of 1,3-C_4H_6 while both sila-3-cyclopentenes were produced. Thus, it appears that CH_3SiH addition to 1,3-C_4H_6 can also compete reasonably with insertion into silicon—hydrogen bonds. The addition of $ClSiH$ to 1,3-C_4H_6 appears to occur with a rate similar to that of SiH_2 addition.

Thermal reaction of trisilane with 1,3-butadiene

Si_3H_8 [7,9] decomposes to generate the reactive intermediates SiH_2 and Si_2H_4 (eqns. 6 and 7):

$$Si_3H_8 \rightarrow SiH_2 + Si_2H_6 \qquad (6)$$

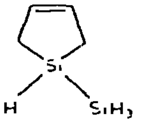
$$Si_3H_8 \rightarrow H_3SiSiH + SiH_4 \qquad (7)$$

The neat pyrolysis of Si_3H_8 [7] produces both tetrasilanes and n- and i-pentasilane from the reactions of SiH_2 and Si_2H_4 with Si_3H_8:

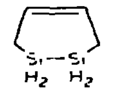
$$SiH_2 + Si_3H_8 \rightarrow Si_4H_{10}\ (\text{n and i}) \qquad (8)$$

$$Si_2H_4 + Si_3H_8 \rightarrow Si_5H_{12}\ (\text{n and i}) \qquad (9)$$

We have examined the thermal reaction of Si_3H_8 with 1,3-C_4H_6. The products obtained in addition to those from the neat pyrolysis and 4-vinylcyclohexene (obtained in the neat pyrolysis of 1,3-C_4H_6) were sila-3-cyclopentene, 1-silylsila-3-cyclopentene (I), and 1,2-disila-4-cyclohexene (II). The ratio of I and II was about 1/1. The last three products are undoubtedly from reaction of SiH_2 and Si_2H_4 with 1,3-C_4H_6.



(I)



(II)

In an effort to determine the possibility of interconversion of I to II (or II to I) under our reaction conditions, we examined the flow pyrolyses of I and II at low pressure (0.8 mm) with an inert propane carrier at 35 mm Hg. At 450°, the only observed product from the pyrolysis of I was sila-3-cyclopentene while no product was observed from the pyrolysis of II. At most, only a few percent of I or II decomposed under these conditions. Thus there was no interconversion of I and II in our trisilane—butadiene thermal reaction. Since I is a substituted disilane, it is not surprising that it decomposes by a 1,2-hydrogen shift forming sila-3-cyclopentene and SiH_2 [4].

The nature of the reactive intermediate, Si_2H_4, is unresolved. It is presumed that when formed in the pyrolysis of Si_3H_8, Si_2H_4 can be represented as SiH_3SiH [7,9]. However, the species that reacts with 1,3-C_4H_6 could be represented as SiH_3SiH, $H_2\dot{S}i\dot{S}iH_2$ or $H_2Si{=}SiH_2$.

We examined the copyrolysis of a 1/1 mixture of Si_3H_8 and Si_3D_8 and the only disilanes produced were Si_2H_6 and Si_2D_6. If Si_2D_4 existed as $D_2\dot{S}i\dot{S}iD_2$, it should have extracted H atoms from Si_3H_8 forming the disilanes Si_2D_5H and $Si_2D_4H_2$. Since these were not observed, it would appear that the chemistry observed in the pyrolysis of trisilane is not due to biradical species such as $H_2\dot{S}i\dot{S}iH_2$.

It appears that the reaction of SiH_2 and Si_2H_4 with Si_2H_6 and Si_3H_8 occur with very low activation energies [7,9,10] (possibly as low as 1 kcal/mol). Since it is difficult to envision a low activation route for the reaction of $H_2Si{=}SiH_2$

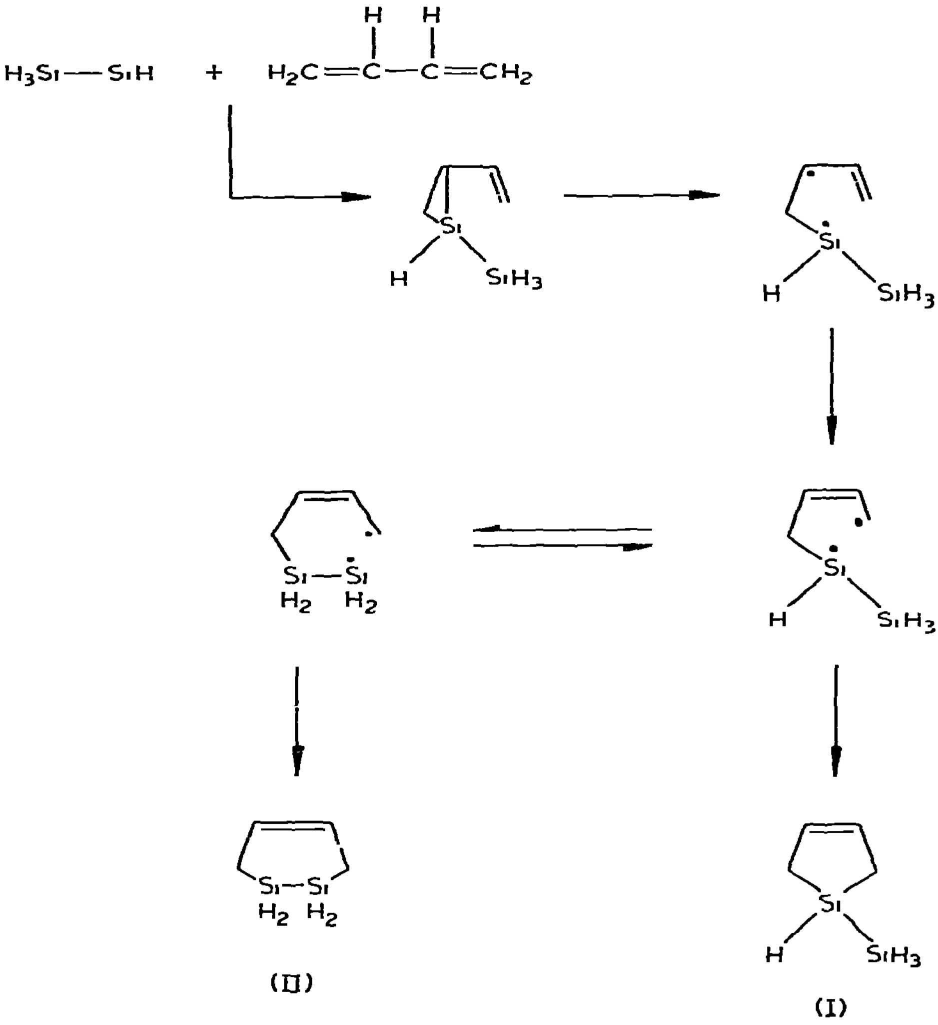


Fig. 1. Reaction of silylsilylene with 1,3-butadiene.

with Si_2H_6 or Si_3H_8 to form tetra- and penta-silanes it would appear that the Si_2H_4 species that reacts with Si_3H_8 to form the pentasilanes is SiH_3SiH. Thus a significant fraction of the reactive intermediate, Si_2H_4 appears to react as SiH_3SiH.

The addition of SiH_2 to *trans*-2-, *trans*-4-hexadiene does not occur by a concerted 1,4-cycloaddition [11]. We assume the addition of SiH_3SiH to 1,3-C_4H_6 would be similar. The addition of SiH_3SiH to 1,3-C_4H_6 could produce both products I and II by a nonconcerted 1,4-cycloaddition as described in Fig. 1. If $H_2Si{=}SiH_2$ were present, it would add to 1,3-C_4H_6 to form II.

Unfortunately our results do not allow for an identification of Si_2H_4, but do suggest that Si_2H_4 does, to some extent, react as SiH_3SiH.

Reaction of germylene with 1,3-butadiene

The products from the flow pyrolysis of Ge_2H_6 and 1,3-C_4H_6 were GeH_4,

Ge_3H_8 and germa-3-pentene ($C_4H_{10}Ge$). The expected GeH_2 addition product with 1,3-C_4H_6, germa-3-cyclopentene was not observed. The product ratio, $Ge_3H_8/C_4H_{10}Ge$, was very dependent on the diameter of the thermal zone. In a small diameter thermal zone (short residence time), the Ge_3H_8 yield was at least 70% and the $Ge_3H_8/C_4H_{10}Ge$ ratio was very large. In a large diameter thermal zone (long residence time) the yield of Ge_3H_8 was low and the product ratio, $Ge_3H_8/C_4H_{10}Ge$, was near unity. These results are consistent with the following eqns. 13-19. We are unsure of the source of GeH_3 radicals. A logical choice appeared to be from secondary GeH_4 decompositions. However, control experiments with GeH_4 and 1,3-C_4H_6 under our reaction conditions demonstrated that the GeH_3 radicals for eqn. 18 were not generated from GeH_4.

(i) For short residence time:

$Ge_2H_6 \rightarrow GeH_2 + GeH_4$ (13)

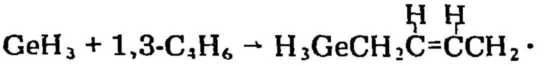
$GeH_2 + Ge_2H_6 \rightarrow Ge_3H_8$ (14)

(ii) For long residence times:

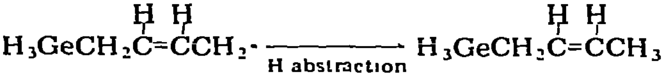
$Ge_2H_6 \rightarrow GeH_2 + GeH_4$ (15)

$GeH_2 + Ge_2H_6 \rightleftharpoons Ge_3H_8$ (16)

$Ge_3H_8 \rightarrow H_3GeGeH + GeH_4$ (17)



$GeH_3 + 1,3\text{-}C_4H_6 \rightarrow H_3GeCH_2\overset{H}{C}=\overset{H}{C}CH_2\cdot$ (18)



$H_3GeCH_2\overset{H}{C}=\overset{H}{C}CH_2\cdot \xrightarrow[\text{H abstraction}]{} H_3GeCH_2\overset{H}{C}=\overset{H}{C}CH_3$ (19)

The fact that germa-3-cyclopentene was not obtained by reaction of GeH_2 with 1,3-C_4H_6 could be due to its formation followed by complete decomposition prior to removal by the cold trap or by the GeH_2 insertion rate into Ge_2H_6 being much greater than addition to 1,3-C_4H_6. It would appear that the latter is much more likely.

In acetone, $GeBr_2$ readily adds to 1,3-C_4H_6 forming 1,1-dibromo-1-germa-3-cyclopentene [12]. Thus, germylenes do add to 1.3-C_4H_6 forming germa-3-cyclopentenes.

Experimental

Si_2H_6 and CH_3SiH_3 were prepared by the reduction of the corresponding chloride with $LiAlH_4$. Disilane-d_6 was prepared from the reaction of Si_2Cl_6 with $LiAlD_4$ while Si_3D_8 was prepared from the flow pyrolysis of Si_2D_6. $CH_3Si_2H_5$ [6] and $ClSi_2H_5$ [13] were prepared as previously described while GeH_4 was prepared by reduction of GeO_2 [14]. The purity of these reagents was checked by IR, mass and proton NMR spectral methods. Products such as SiH_4, $ClSiH_3$, CH_3SiH_3, GeH_4 and Ge_3H_8 were identified by their IR spectra.

Improved preparation of trisilane

A synthesis for Si_3H_8 has been developed by which Si_3H_8 can be obtained in 44% yields from Si_2H_6.

The apparatus consisted of a heated zone 7 cm long and 18 mm in diameter wrapped with a heating tape. A 500 cm^3 bulb next to the heated zone acted as a reactant container while three "U" traps after the heated zone acted as product traps. The pressure in the heated zone was controlled by a Teflon needle valve located between the heated zone and the product traps. The rate at which the reactants entered the heated zone was controlled by a Teflon needle valve located between the heated zone and reactant bulb.

In a typical experiment with the oven at 418—422°, Si_2H_6 (12.2 mmol) was allowed to flow through the heated zone. The product traps were immersed in liquid nitrogen and opened to a vacuum line so that hydrogen could be removed. The flow rate of Si_2H_6 was regulated at 1.7 mmol/min while the pressure in the heated zone was maintained between 35 and 40 mm Hg. The product fraction was separated by trap to trap distillations. The fraction condensed at —196° was SiH_4 (2.2 mmol) while the fraction condensed at —160° was Si_2H_6 (8.9 mmol). The product fraction condensed at —103° was Si_3H_8 (0.72 mmol). A polysilane mixture (0.26 mmol) which was mainly Si_4H_{10} was collected in the —78° trap.

Improved preparation of digermane

The preparation of Ge_2H_6 from the pyrolysis of GeH_4 was carried out in a flow system containing an automatic Toepler pump, a 50 mm diameter* 25 cm long thermal zone and a "U" trap. The thermal zone was heated by a very well insulated heating tape. The cold trap was maintained at —112° which set the GeH_4 pressure in the system at 240 mm provided that some GeH_4 was present condensed in the cold trap. The trap also removed Ge_2H_6 from the stream as it was produced. The pyrolyses were carried out at between 240-280°. The temperature required for reaction very slowly increased presumably due to polymer (or Ge mirror) deposition inside the reaction chamber. The effect of temperature on conversions and yields can be seen in Table 1.

Thermal reactions of 1,3-butadiene with disilane, methyldisilane, chlorodisilane and trisilane

The pyrolysis experiments with the polysilanes were carried out in a pyrex tube 9 mm in diameter and 15 to 20 cm long, which was wrapped with a heating tape and insulated with several layers of asbestos tape. The thermal zone was connected to a "U" cold trap and an automatic Toepler pump for cycling the

TABLE 1

PYROLYSES OF GeH_4 AT 240 mm Hg FOR 30 MIN IN OUR FLOW SYSTEM

Temp. (°C)	GeH_4 consumed (mmol)	Ge_2H_6 produced (mmol)	Yield (%)
280	2.86	0.47	32
270	2.46	0.42	34
260	1.80	0.40	44
251	1.11	0.38	66

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* In order to produce useful quantities (> 0.5 mmol/h) it was necessary to use the much wider diameter thermal zone which allowed more GeH_4 to be in the thermal zone at a given time and which also increased the residence time in the thermal zone (i.e., semi-stirred flow).

reactants. The cold trap removed any products less volatile than the reagents. The inner wall of the thermal zone was coated with a silicon mirror deposited from the pyrolysis of SiH_4 to prevent pyrex catalysis. The Ge_2H_6 experiments were carried out in a tube as described above which was coated with a germanium mirror formed from the pyrolysis of GeH_4.

The pyrolysis of disilane in the presence of 1,3-butadiene

In a typical experiment, Si_2H_6 (1.31 mmol) was pyrolysed in the presence of 1,3-C_4H_6 (2.62 mmol) for 10 h at 385° with the cold trap maintained at −83°. The gas phase ratio, 1,3-C_4H_6/Si_2H_6, was determined by GLPC to be 1.22. Very little H_2 was produced. The reaction mixture was separated by trap to trap distillations. The fraction passing the −160° trap was SiH_4 (0.54 mmol). The fraction (3.01 mmol) condensed at −160° which passed the −95° trap was a mixture of Si_2H_6 and 1,3-C_4H_6 as identified by an IR spectrum. The fraction (0.37 mmol) condensed at −95° which passed a −78° trap was a mixture of Si_3H_8 and sila-3-cyclopentene. The GLPC spectrum of this mixture consisted of two peaks with relative intensities of 4.2 (Si_3H_8) to 1 (C_4H_8Si). This assignment was based on the known retention time of Si_3H_8. From repeated GLPC separations we obtained a pure sample of C_4H_8Si.

The compound sila-3-cyclopentene was identified as follows: The proton NMR spectrum in $DCCl_3$ consisted of resonances at δ 1.35 (complex due to $-CH_2-$), 3.85 (triplet due to SiH_2) and 5.75 (complex due to $=CH-$) of relative intensities 2.2/1.1/1.0 (calcd. 2/1/1). This NMR spectrum was that of the entire mixture (Si_3H_8 and C_4H_8Si) and demonstrated that the ratio Si_3H_8/C_4H_8Si, was 3.6. The mass spectrum at 15 V contained the following envelope intensities: $C_4H_xSi^+$ (100), $C_3H_xSi^+$ (8), $C_2H_xSi^+$ (35) and CH_xSi^+ (4). The highest main peak was at *m/e* 84 as expected. No higher mass peaks were observed except those at 85 and 86 due to ^{29}Si and ^{30}Si. The gas phase IR spectrum consisted of the following bonds (cm^{-1}): 3030m, 2920m, 2160vs, 2150vs, 1610w, 1270m, 1110s, 965s, 955s, 870s, 675s, 660w.

The pyrolysis of methyldisilane in the presence of 1,3-butadiene

The flow pyrolysis of $CH_3Si_2H_5$ (0.50 mmol) was carried out for 10 h at 385° in the presence of 1,3-C_4H_6 (2.21 mmol) with the cold trap maintained −78°. The calculated gas phase ratio 1,3-$C_4H_6/CH_3Si_2H_5$ was about 20/1. The reaction mixture was separated by trap-to-trap distillations. The fraction condensed at −196° which passed a −160° trap was SiH_4 (0.04 mmol). The fraction condensed at −160° was CH_3SiH_3 (0.07 mmol). The fraction condensed at −130° which passed a −95° trap was a mixture of $CH_3Si_2H_5$ and 1,3-C_4H_6 (2.5 mmol). The fraction condensed at −95° (0.09 mmol) was determined to be a mixture of C_4H_8Si (0.07 mmol) and 1-methylsila-3-cyclopentene (0.02 mmol). The analysis of this mixture was based on GLPC and mass spectral data. The identification of 1-methylsila-3-cyclopentene was based solely on the mass spectrum which had the main large intensity peak at *m/e* 98 as expected. No larger peaks other than those due to ^{29}Si at ^{30}Si (*m/e* 99 and 100) were observed.

The pyrolysis of $ClSi_2H_5$ in the presence of 1,3-butadiene

The flow pyrolysis of $ClSi_2H_5$ (0.58 mmol) was carried out in the presence of 1,3-C_4H_6 (1.97 mmol) at 385° for 10 h with the cold trap maintained −63°. The calculated gas phase ratio of 1,3-$C_4H_6/ClSi_2H_5$ was 40/1. The product fraction passing a −160° trap condensed at −196° was SiH_4 (0.09 mmol) while the fraction condensed at −160° was $ClSiH_3$(0.07 mmol). The fraction condensed at −123° was 1,3-C_4H_6 with a little $ClSi_2H_5$. The fraction condensed at −95° (0.30 mmol) was a mixture of $ClSi_2H_5$ and sila-3-cyclopentene. The ratio in this fraction, $ClSi_2H_5/C_4H_8Si$, was 7/1 as determined by a proton NMR spectrum. The fraction condensed at −78° (0.05 mmol) was identified as 1-chlorosila-3-cyclopentene. This compound was identified as follows: The proton NMR spectrum in $DCCl_3$ consisted of resonances at δ 1.68 (CH_2), 5.21 (ClSiH) and 5.89 (=CH−) of relative intensities 3.8/1.0/1.8 (calcd. 4/1/2). The spectrum was not of high quality. The mass spectrum at 15 eV consisted of peaks due to the fragments of $C_4H_xSiCl^+$ (100), $C_2H_xSiCl^+$ (45), $C_4H_xSi^+$ (84), $C_3H_xSi^+$, $SiCl^+$ (22), $C_4H_x^+$ (50). The gas phase IR spectrum consisted of bands at (cm^{-1}): 3040m, 2930m, 2180s, 1630w, 1420w, 1210w, 1110s, 950m, 860s, 818w, 798w, 760s, 670m, 648s, 530s.

The pyrolysis of digermane in the presence of 1,3-butadiene

In a typical experiment Ge_2H_6 (1 mmol) was pyrolyzed in the presence of 1,3-C_4H_6 (2 mmol) at 240° for 1 h with the cold trap maintained at −78° in the flow system described earlier for the preparation of Ge_2H_6. The fraction condensed at −196° which passed a −130° trap was GeH_4 (0.55 mmol). The fraction condensed at −130° was Ge_2H_6. The fraction condensed at −78° (0.04 mmol) consisted of Ge_3H_8 and a second product in about equal quantities as estimated by a mass spectrum of this mixture. The molecular weight, with ^{74}Ge, of this second product as determined from the mass spectrum was 132 and not 130 (C_4H_8Ge). We were unable to separate these two compounds by low temperature column distillations. Therefore the mixture was pyrolyzed at 235° in our flow system without a cold trap to destroy the Ge_3H_8. After 1 h, all of the Ge_3H_8 had decomposed leaving what was presumably the other compound. The IR and mass spectra of this compound were identical to that of the original mixture minus those peaks due to Ge_3H_8. This compound was then prepared by the 1 h flow pyrolysis of Ge_2H_6 (0.8 mmol) in the presence of 8 mmol of 1,3-C_4H_6 at 230°. The desired product was obtained in about 6% yield (0.4 mmol). The proton NMR spectrum in $DCCl_3$ consisted of resonances at δ 1.65 (complex due to CH_3 and CH_2), 3.54 (triplet due to GeH_3) and 5.40 (complex due to =CH−) of relative intensities 5.2/3.0/1.98 (calcd. for $GeH_3CH_2CH{=}CCH_3$, 5/3/2. The gas phase IR spectrum of this compound consisted of absorptions at (cm^{-1}): 3015m, 2920s, 2850w, 2060vs, 1410m, 965m, 882s, 833vs, 698m, 622m, 570w, 500m.

The pyrolysis of digermane in the presence of 1,3-butadiene

This was also examined in a flow system containing a small diameter (8 mm) thermal zone, where the residence time in the thermal zone was short. These pyrolyses were carried out as in the preceding preparation at 240, 252 and 294°. The volatile products were GeH_4, Ge_3H_8 and only trace quantities of $GeH_3CH_2CH{=}CHCH_3$. The yields of Ge_3H_8 were in excess of 70% at 240 and 252°.

The pyrolysis of trisilane in the presence of 1,3-butadiene

The thermal reaction between Si_3H_8 and 1,3-C_4H_6 was carried out in a flow system with a −45° bath on the "U" trap. In a typical reaction Si_3H_8 (0.5 mmol) and 1,3-C_4H_6 (2.2 mmol) were pyrolysed for 6 h at 400°. The products which passed a −78° trap were separated by trap-to-trap distillations and the compounds identified by their IR spectra. The products and reactants so obtained are listed in Table 2. The products condensed in the −78° trap were analyzed by GLPC. These products are also listed in Table 2. The tetra- and penta-silanes were identified by their retention times. Mass spectra were obtained for i-Si_4H_{10} and i-Si_5H_{12}. The other products were identified as follows:

Sila-3-cyclopentene (III) was identified by its retention time compared to an authentic sample. The compound was also isolated by trap-to-trap distillations in other runs and its identity verified by an IR and a mass spectrum.

The new compound, silylsila-3-cyclopentene (I), was isolated relatively pure (~90%) by GLPC. The impurity was isopentasilane. The proton NMR spectrum consisted of a complex multiplet centered at 1.70 (CH_2), a doublet at 3.18 (SiH_3) and a poorly defined resonance at δ 3.76 (SiH) and a singlet at δ 5.92 (HC=CH). The relative intensities were 4.0/3.04/1.03/1.94 compared to expected ratios of 4/3/1/2. This spectrum is as expected since that of sila-3-cyclopentene has similar resonances at δ 1.35 (CH_2), δ 3.85 (SiH_2) and 5.75 (HC=CH). The proton resonance in Si_2H_6 [15] is at δ 3.26 while the SiH_3 resonance in Si_3H_8 [15] is at δ 3.36 compared to δ 3.18 in I.

The mass spectrum of I at 20 eV consisted of a parent peak at *m/e* 114, a P—CH_3 peak at *m/e* 99 and a P—SiH_3 peak at *m/e* 83. The mass spectrum at 70 eV consisted of the following heavy atom envelopes: $C_4Si_2H_x^+$ (28), $C_3Si_2H_x^+$ (13), $C_4SiH_x^+$ (100), $C_3SiH_x^+$ (12), $C_4H_x^+$ (33) and $C_3H_x^+$ (16). The major peaks were at *m/e* 114, 99, 83, 67, 55 and 43. The gas phase IR spectrum consisted of the following absorptions (cm^{-1}): 3030m, 2910m, 2150vs, 1620w, 1460w, 1200 1108m, 1000w, 935m, 890m, 840s, 730s, 650w.

The compound 4-vinylcyclohexene (IV) was prepared by the neat pyrolysis of 1,3-C_4H_6 under our reaction conditions and identified by its NMR and IR

TABLE 2

PRODUCTS FROM THE THERMAL REACTION OF Si_3H_8 (0.5 mmol) AND 1,3-C_4H_6 (2.2 mmol)

Products		Quantity (mmol)
	H_2	0.06
	Si_2H_6	0.04
	Si_3H_8	0.1
	1,3-C_4H_6	2.0
III	C_4H_8Si	0.04
	i-S_4H_{10}	0.01
	n-S_4H_{10}	0.01
	n-Si_5H_{12}	trace
	i-S_5H_{12}	trace
I	$C_4H_{10}Si_2$	0.018[a]
IV	C_8H_{12}	0.022[a]
II	$C_4H_{10}Si_2$	0.017[a]

[a] Relative ratios checked by NMR spectra and found consistent with GLPC data.

spectra [16, 17]. The product obtained during the reactions with Si_3H_8 had the same retention time and NMR spectrum.

The new compound, 1,2-disila-4-cyclohexene (II) was isolated along with 4-vinylcyclohexene by GLPC. The spectral data were obtained from mixtures of II with 4-vinylcyclohexene. The IR and mass spectrum sample was about 75% II while the NMR spectrum sample was about 30% II.

The NMR spectrum of II consisted of a multiplet at δ 1.70 ($-CH_2-$), a multiplet at δ 3.55 ($-H_2SiSiH_2-$) and one at δ 5.70 (HC=CH). The integrated intensities were 1.6/2.2/1.0 while the calculated values are 2/2/1. The mass spectrum was very similar to that of silylsila-3-cyclopentene (I) with major peaks at *m/e* 114, 99, and 83 which infer that II is an isomer of I. The infrared spectrum consisted of absorptions (cm^{-1}): 3030w, 2950w, 2880w, 2130vs, 1190m, 1140w, 940s, 840s, 760m, 710m, 680m, 630w, 590w.

The IR spectra and GLPC retention times of I and II clearly demonstrate the presence of two compounds with almost identical mass spectra (15 and 70 eV). The identification of I as silylsila-3-cyclopentene appears clear based on its NMR spectrum. While the NMR spectra obtained for II were not as definitive, it does appear that II is 1,2-disila-4-cyclohexene.

Copyrolysis of trisilane and deuterotrisilane

The copyrolysis of a 1/1 mixture of Si_3H_8 and Si_3D_8 (0.4 mmol total) was carried out at 350° in our flow system with the "U" trap cooled to $-63°$. The trisilanes used were purified by trap-to-trap distillation and condensed at $-95°$. The pyrolyses were stopped every 15 minutes and the silanes and disilanes produced were removed by distillation through a $-95°$ trap. After 4 pyrolyses, the disilane product fraction (0.002 mmol) which distilled through a $-112°$ trap, was analyzed by IR and mass spectra. These demonstrated that only Si_2D_6 [18] and Si_2H_6 [18] were present with a trace of Si_2D_5H [18] which resulted from the Si_3D_7H impurity in Si_3D_8.

Control reaction

The pyrolysis of Si_2H_6 (2 mmol) was carried out in the presence of 0.4 mmol of sila-3-cyclopentene in our flow system at 400° with a $-45°$ cold trap. The products were silane, trisilane, tetrasilanes and pentasilanes. Butadiene and silylsila-3-cyclopentene were not obtained.

The pyrolysis of 1-silylsila-3-cyclopentene (I) and 1,2-disila-4-cyclohexene (II) was carried out in the single pass flow reactor, described for the preparation of Si_3H_8. Approximately 0.1 mmol of the compound (I or II) was mixed with 4.5 mmol of C_3H_8 (as a carrier for thermal equilibrium). The mixture was allowed to flow through the thermal zone which was heated to 450°. The pressure in the thermal zone was maintained at 35 mm Hg. The flow rate was 1 mmol/min. After the reaction, the C_3H_8 was removed by trap-to-trap distillations using a $-95°$ cold trap. The initial reactants and products were analyzed by their relative GLPC retention times compared to authentic samples. Under these conditions, at most, only a few percent decomposition occurred. No products were obtained from the pyrolysis of 1,2-disila-4-cycloxene (II) while the only product from the pyrolysis of 1-silylsila-3-cyclopentene (I) was sila-3-cyclopentene.

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