

SILYL AND SILYLMETHYL RADICALS, SILYLENES, SILA-ALKENES, AND SMALL RING SILACYCLES IN REACTIONS OF ORGANOCHLOROSILANES WITH ALKALI METAL VAPOURS *

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Summary

Dehalogenation of the organochlorosilanes Me_3SiCl (I), Me_2PrSiCl (II), $\text{Me}_3\text{-SiSiMe}_2\text{Cl}$ (III), $\text{Me}_3\text{SiCH}_2\text{SiMe}_2\text{Cl}$ (IV), $\text{ClCH}_2\text{SiMe}_3$ (V), $\text{ClCH}_2\text{SiMe}_2\text{SiMe}_3$ (VI), $\text{ClCH}_2\text{Me}_2\text{SiSiMe}_2\text{CH}_2\text{Cl}$ (VII), Me_2SiCl_2 (VIII), MePrSiCl_2 (IX), $\text{Me}_3\text{Si-CH}_2\text{SiMeCl}_2$ (X), $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{SiMeCl}_2$ (XI), $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{SiMeCl}_2$ (XII), $\text{ClCH}_2\text{Si(H)MeCl}$ (XIII), $\text{ClCH}_2\text{SiMe}_2\text{Cl}$ (XIV), $\text{ClMe}_2\text{SiSiMe}_2\text{Cl}$ (XV), $\text{ClCH}_2\text{-CH}_2\text{CH}_2\text{Si(H)MeCl}$ (XVI), $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{SiMe}_2\text{Cl}$ (XVII), $\text{ClCH}_2\text{-CH}_2\text{OSiMe}_2\text{Cl}$ (XVIII), $\text{ClMe}_2\text{SiCH}_2\text{SiMe}_2\text{Cl}$ (XIX), $\text{ClMe}_2\text{SiCH}_2\text{CH}_2\text{-SiMe}_2\text{Cl}$ (XX), and $\text{ClMe}_2\text{SiCH}_2\text{CH}_2\text{CH}_2\text{SiMe}_2\text{Cl}$ (XXI) with K/Na alloy vapours at 0.1–1 Torr and 300–320°C yields products derived from the reactions of short-lived intermediates, such as silyl and silylmethyl radicals, silylenes, and sila-alkenes. In addition, small-ring silacycles of low stability are formed as the intermediates in some of the dehalogenation reactions.

Combination and H-atom abstraction are the main reactions of silyl and silylmethyl radicals. These radicals are not prone to decomposition reactions when C–H, C–C, or Si–C bonds are at the β -position to the radical centre. The pentamethyldisilylmethyl radical decomposes at the $\beta(\text{Si-Si})$ bond with the formation of $\text{Me}_2\text{Si=CH}_2$ and the trimethylsilyl radical.

The generation of alkylmethylsilylenes is accompanied by their decomposition, with the formation of 1-alkene and methylsilane. A mechanism has been proposed for the decomposition process, which involves intramolecular β (C–H) insertion of alkylmethylsilylenes and $[3 \rightarrow 2 + 1]$ -thermocyclodecomposition of intermediate silacyclopropanes. The contribution of $\delta(\text{C-H})$ and $\epsilon(\text{C-H})$ insertion reactions is much less pronounced, and in the case of $\text{Me}_3\text{Si(CH}_2)_x\dot{\text{SiMe}}$ ($x = 2$ or 3), these insertion reactions result in the formation of five- or six-membered silacycles. We did not succeed in obtaining monosilacyclobutanes, as the intramolecular $\gamma(\text{C-H})$

* Dedicated to Professor Oleg A. Reutov on the occasion of his 65th birthday on 5 September 1985.

** Deceased.

insertion reaction is not typical for silylenes with alkyl substituents.

Dehalogenation of chloromethylchlorosilanes with alkali metal vapours yields sila-alkenes, and that of 1,2-dichlorodisilanes gives disilenes. 1-Methyl-1-silaethylene, obtained by this method, does not rearrange into dimethylsilene, but dimerizes to give 1,3-dimethyl-1,3-disilacyclobutane. The formation of 1,3,5-trisilacyclohexanes takes place due to subsequent radical addition at the silicon-carbon double bond and cyclization of 1,6-biradicals.

Dehalogenation of organochlorosilanes XVI, XVII, and XX opens up possibilities for the gas-phase synthesis of small organosilicon heterocycles: monosilacyclobutanes and 1,2-disilacyclobutanes. A new, low-stability heterocycle, i.e. 1,1,2,2-tetramethyl-1,2-disilacyclobutane, has been obtained, which enables a new, high polymer, polyethylenetetramethyldisilene, to be obtained. In the case of organochlorosilanes XVIII and XIX, cyclization is accompanied by secondary reactions of silacycles, rearrangements, dimerization, or decomposition.

Introduction

The reactions of organohalosilanes with alkali metal vapours are of great interest for the study of short-lived organosilicon intermediates in the gas phase. Compared to pyrolysis, this method enables radicals, silylenes, and other intermediates to be generated at much lower temperatures by using readily available organosilicon compounds as starting materials. The reactions are carried out in a flow reactor at low pressures, which contributes to the fast removal of products from the reaction zone. The fast removal of reaction products suppresses side reactions, which is of great importance in synthesizing low-stability and thermally labile compounds.

Since the earlier work of Skell and co-workers [1-5], almost no attention has been given to the reactions of organochlorosilanes with alkali metal vapours. Some time ago, we obtained, by this method, a previously unknown 1,1,2,2-tetramethyl-1,2-disilacyclobutane, a strained heterocycle with an Si-Si bond [6], and on the basis of this, polyethylenetetramethyldisilene, a new, high crystalline polymer with alternating dimethylene and disilene links in the main chain [7]. In this paper, we shall discuss the alkali metal vapour dehalogenation reactions of various mono- and dichloro-derivatives of organosilanes (I-XXI);

Me_3SiCl	(I)	$\text{Me}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{SiMeCl}_2$	(XII)
Me_2PrSiCl	(II)	$\text{ClCH}_2\text{Si(H)MeCl}$	(XIII)
$\text{Me}_3\text{SiSiMe}_2\text{Cl}$	(III)	$\text{ClCH}_2\text{SiMe}_2\text{Cl}$	(XIV)
$\text{Me}_3\text{SiCH}_2\text{SiMe}_2\text{Cl}$	(IV)	$\text{ClMe}_2\text{SiSiMe}_2\text{Cl}$	(XV)
$\text{ClCH}_2\text{SiMe}_3$	(V)	$\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Si(H)MeCl}$	(XVI)
$\text{ClCH}_2\text{SiMe}_2\text{SiMe}_3$	(VI)	$\text{ClCH}_2\text{CH}_2\text{CH}_2\text{SiMe}_2\text{Cl}$	(XVII)
$\text{ClCH}_2\text{Me}_2\text{SiSiMe}_2\text{CH}_2\text{Cl}$	(VII)	$\text{ClCH}_2\text{CH}_2\text{OSiMe}_2\text{Cl}$	(XVIII)
Me_2SiCl_2	(VIII)	$\text{ClMe}_2\text{SiCH}_2\text{SiMe}_2\text{Cl}$	(XIX)
MePrSiCl_2	(IX)	$\text{ClMe}_2\text{SiCH}_2\text{CH}_2\text{SiMe}_2\text{Cl}$	(XX)
$\text{Me}_3\text{SiCH}_2\text{SiMeCl}_2$	(X)	$\text{ClMe}_2\text{SiCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SiMe}_2\text{Cl}$	(XXI)
$\text{Me}_3\text{SiCH}_2\text{CH}_2\text{SiMeCl}_2$	(XI)		

which proceed with the formation of unstable species and molecules of a four-valent silicon atom bonded with two, three, or four ligands as intermediates [6-20]. Attention will be focused on radical decomposition reactions, intramolecular re-

arrangements of silylenes, generation and reactions of sila-alkenes, and cyclization to prepare mono- and disilacyclobutane ring systems.

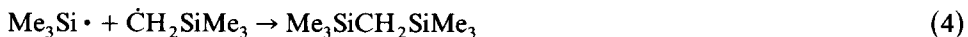
Results and discussion

According to Skell et al. [3], the reaction of trimethylchlorosilane (I) with K/Na vapours yields a trimethylsilyl radical which combines to form hexamethyldisilane. We studied the gas-phase dehalogenation of organochlorosilanes I–IV and found that this combination was the main reaction for other silyl radicals too. Less pronounced, but also significant, is the H-atom abstraction by silyl radicals. The combination and H-abstraction products were found to be in a ratio of about 10.



(R = Me, n-Pr, Me₃Si, Me₃SiCH₂)

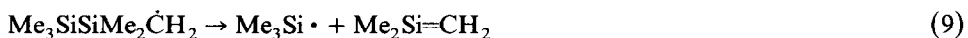
Unlike alkylhalides [21], triorganochlorosilanes, under our experimental conditions, did not produce any organosilicon products from the decomposition of the silyl radicals, although the reaction proceeded with pyrolytic generation of the radicals [22,23]. The dehalogenation of a mixture of I and V yields mainly bis(trimethylsilyl)methane, which is a cross-combination product of trimethylsilyl and trimethylsilylmethyl radicals:



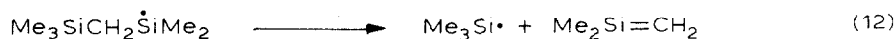
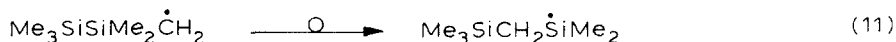
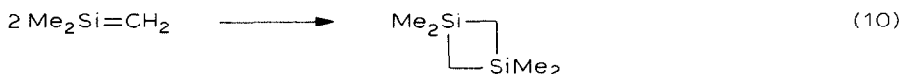
that is, the cross-combination reactions predominate over the radical combination reactions. Chloromethyltrimethylsilane alone yields 1,2-bis(trimethylsilyl)ethane and tetramethylsilane. This means that combination and H-atom abstraction reactions are the only reactions of the trimethylsilylmethyl radical:



Unlike V, dehalogenation of chloromethylpentamethyldisilane (VI) proceeds with decomposition of the pentamethyldisilanylmethyl radical at the β(Si–Si) bond, with the result that 1,1-dimethyl-1-silaethylene is generated and its dimer, 1,1,3,3-tetramethyl-1,3-disilacyclobutane, is formed [19]:



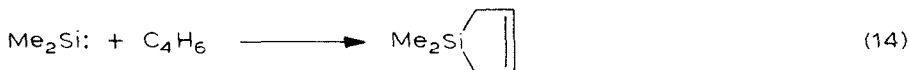
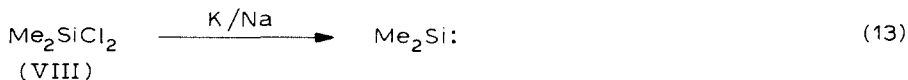
An alternative mechanism [24] for the production of dimethylsilaethylene by pyrolysis, involving isomerization of the initial radical and decomposition of the



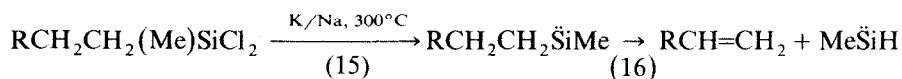
iso-radical (eq. 11, 12) was rejected, because under our experimental conditions, as shown earlier, the iso-radical generated from IV via reaction 1 does not decompose, but yields products via reactions 2 and 3.

Thus, β -decomposition reactions are not characteristic of silyl and silylmethyl radicals. An exception to this is pentamethyldisilanylmethyl radical, which has a Si-Si bond at the β -position to the radical centre.

We were also interested in studying the reactions of silylenes generated by vapour-phase dehalogenation of various organodichlorosilanes. It is known that polysilane oligomers are formed when dimethylsilylene is generated by this method [5,25]. In the presence of trimethylsilane, dimethylsilylene inserts into the Si-H bond, while in the presence of ethylene, it adds to the C=C double bond [1,25]. We have found that Me_2Si , generated by this method in a high yield, gives 1,1-dimethyl-1-silacyclopent-3-ene [15] in the presence of butadiene.

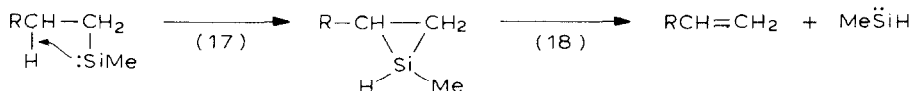


The direction of the transformations of organomethylsilylenes depends to a great extent on the nature and length of the organic substituent. Thus, unlike dimethylsilylene, the generation of organomethylsilylenes is followed by their decomposition, with the result that gaseous or low-boiling-point products are formed, 1-alkene being the main product conforming in composition to the organic substituent. For example, the generation of methylpropylsilylene was followed by the formation of gaseous products, of which more than 90% was propylene. Dehalogenation of XI and XII proceeded in the same way and led to the formation of vinyltrimethylsilane and allyltrimethylsilane, respectively [11]. Although this looks like a simple decomposition of silylenes (eq. 15, 16), we believe that a stepwise process involving (a)



(R = CH₃, Me₃Si, Me₃SiCH₂)

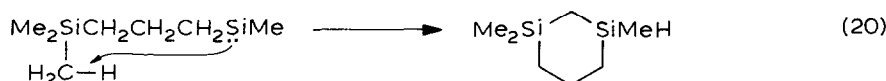
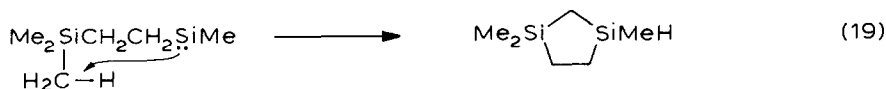
intramolecular β (C-H) insertion, which results in the silirane intermediate (reaction 17), and (b) [3 $\rightarrow$ 2 + 1]-cyclodecomposition of silirane to methylsilylene and alkene (reaction 18) provides a more adequate explanation:



Recently, a similar explanation was given by Barton and Burns [26] for the decomposition of thermally generated methylbutylsilylene.

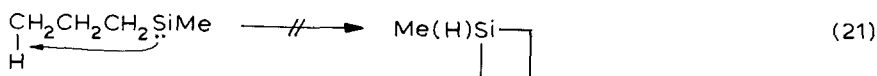
The mechanism proposed by us for intramolecular transformations of silylenes is based on the fact that $[3 \rightarrow 2 + 1]$ -thermocyclodecomposition of siliranes proceeds easily, even when the temperature is as low as 70°C [27]. Note that this mechanism is inconsistent with the data [2] on the isomerization of dimethylsilirane into vinyl dimethylsilane.

Among other reaction products whose formation is associated with intramolecular C–H insertion reactions, we must mention 1,1,3-trimethyl-1,3-disilacyclopentane ($\delta(\text{C–H})$ insertion) and 1,1,3-trimethyl-1,3-disilacyclohexane ($\epsilon(\text{C–H})$ insertion) derived in the dehalogenation of XI and XII (eq. 19, 20). Their content in the reaction



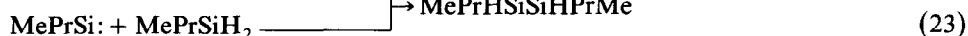
mixture is not more than 10% of the corresponding alkenylsilanes, i.e. the contribution of these processes is an order of magnitude less than that of $\beta(\text{C–H})$ insertion.

1,4-Migration of the H atom from C to Si was not observed, although we specifically tried to obtain 1-methyl-1-silacyclobutane via $\gamma(\text{C–H})$ insertion [18]:



No success was attained even when a diethyl ether quencher was used in the reactions of methylpropyldichlorosilane with K/Na vapours, that is the use of diethyl ether quencher does not enable 1-methyl-1-silacyclobutane to be synthesized via reaction 21, as reported in ref. 28.

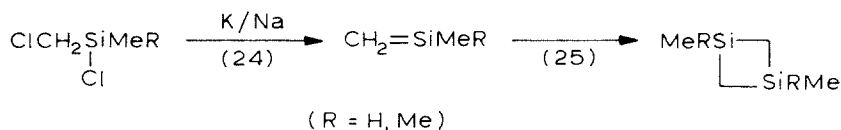
Besides intramolecular $\beta(\text{C–H})$ insertion reactions, dimerization and polymerization of silylenes take place when organomethyldichlorosilanes are dehalogenated. Thus, a small amount of 1,2-dimethyl-1,2-dipropyldisilane was detected in the case of IX; this can be regarded either as the hydrogenation product of 1,2-dimethyl-1,2-dipropyldisilene (reaction 22) or as the insertion product of silylene into the Si–H bond of hydrosilane (reaction 23).



Hydrosilanes are always formed when organohalosilanes are treated with K/Na vapours. For instance, methylpropylsilane is the main reaction product of IX.

Furthermore, we were interested in generating sila-alkenes. Thus, in the reactions of chloromethylchlorosilanes of XIII and XIV with K/Na alloy vapours, we isolated 1,3-disilacyclobutane [4,17] formed by cyclodimerization of the intermediate

silaethylenes (eq. 24, 25):



It is interesting, in particular, that with R = H we did not detect any products indicative of isomerization of methylsilaethylene into dimethylsilylene:

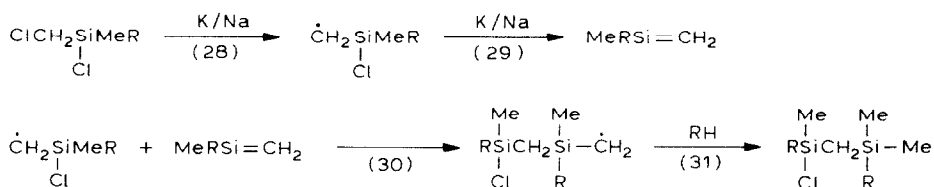


Reaction 26 was reported in refs. 29–32. However, it has been made questionable by both the theoretical calculation [33,34] and the experimental results [23], the recent study [31] shows that reaction 26 does occur, but only at significantly high temperatures.

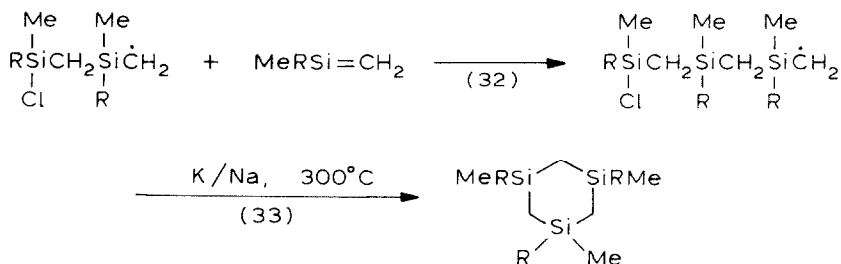
The participation of 1,1-dimethyl-1-silaethylene was proved by the isolation of 1,1-dimethyl-1-silacyclohex-3-ene from reaction 24 carried out with excess buta-1,3-diene:



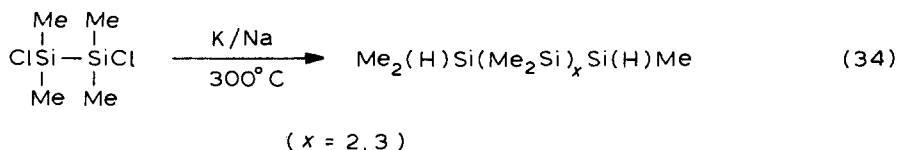
The formation of $\text{MeSiCH}_2\text{SiCl}$ type products upon treating XIII and XIV with K/Na alloy vapours is explained by the addition of silylmethyl radicals (derived from the abstraction of the chlorine atom from carbon by the alkali metal) to the silicon-carbon double bond followed by H-atom abstraction:



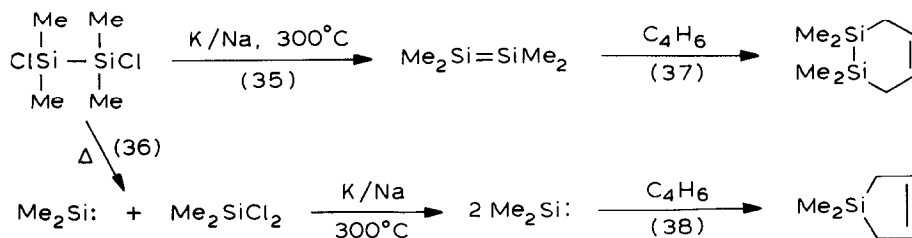
Presumably, this is the addition reaction of monoradicals to the Si=C double bond (reactions 30 and 32) which is responsible for the formation of cyclic trimers, because cyclotrimerization is known not to be an inherent property of silaethylenes [35]:



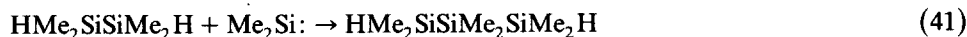
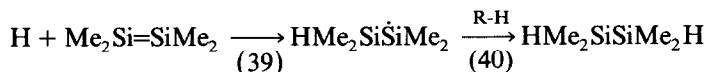
The reaction of K/Na alloy vapours with 1,1,2,2-tetramethyl-1,2-dichlorodisilane yields tetramethyldisilane and hexamethyltrisilane, but not 1,3-disilacyclobutanes, which are the rearrangement products in the pyrolytic generation of tetramethyldisilene [36].



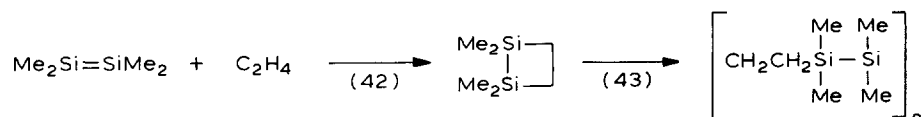
Apparently, at a much lower temperature (than that in the case of pyrolysis), tetramethyldisilene does not transform into a 1,1,2-trimethyldisilirane intermediate, from which dimethyl-1,3-disilacyclobutanes are obtained. The participation of tetramethyldisilene was proved by carrying out the reaction in excess buta-1,3-diene. However, not only a Diels-Alder reaction adduct of tetramethyldisilene, but also a cycloaddition product of dimethylsilylene was obtained. Possibly, the latter is derived from XV via a thermal α -elimination reaction.



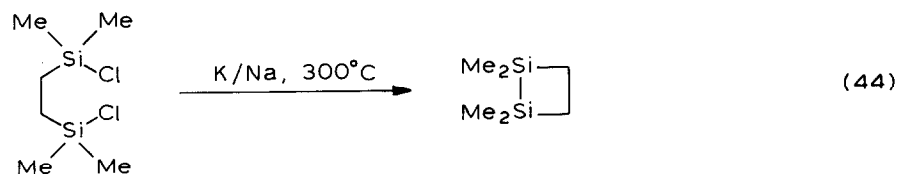
In the absence of an interceptor, tetramethyldisilene changes into tetramethyldisilane with the addition of an H-atom; subsequent insertion of dimethylsilylene into the Si-H bond of disilane yields hexamethyltrisilane:



The generation of tetramethyldisilene in excess ethylene apparently gives 1,1,2,2-tetramethyl-1,2-disilacyclobutane, which, however, was not isolated because of its polymerization (eq. 42; 43).

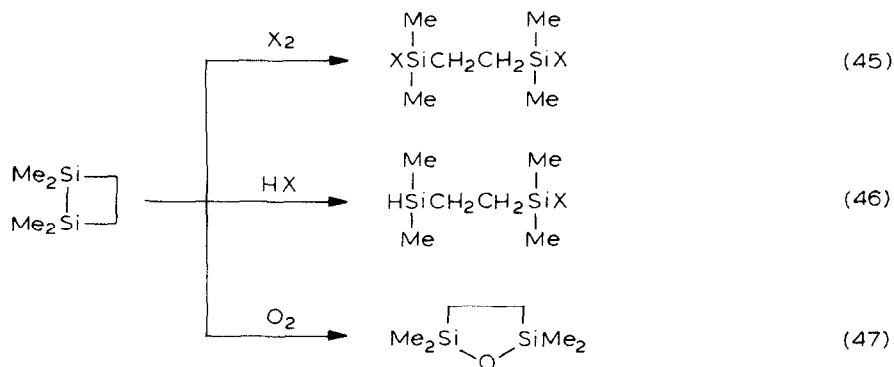


1,1,2,2-Tetramethyl-1,2-disilacyclobutane was isolated in the reaction of 1,2-bis(dimethylchlorosilyl)ethane with K/Na alloy vapours [6,10]. It is a colourless liquid smelling of geranium. At room temperature, it readily polymerizes (reaction 43) with the liberation of heat [7,10]:



At low temperatures, polymerization does not take place. Thus, vacuum-distilled

1,1,2,2-tetramethyl-1,2-disilacyclobutane was stored at 77 K for several months. Ring-opening reactions of 1,1,2,2-tetramethyl-1,2-disilacyclobutane with halogens and hydrohalides were observed. It oxidizes in air [10] (eq. 45–47). The addition

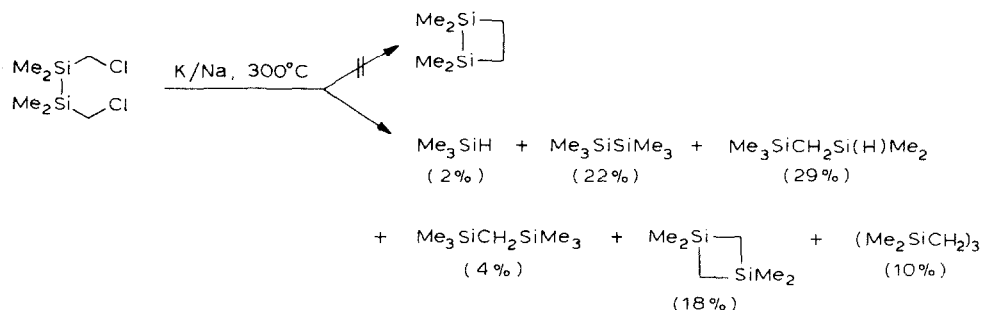


(X = Cl, Br)

reactions proceed with the liberation of large amounts of heat; therefore they were carried out at -20°C .

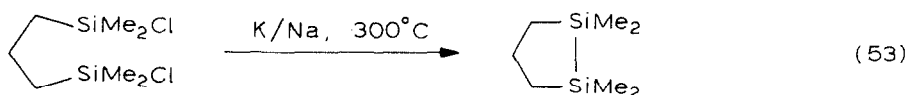
We did not succeed in synthesizing 1,1,2,2-tetramethyl-1,2-disilacyclobutane by a method based on the cyclization of 1,2-bis(chloromethyl)tetramethyldisilane in a reaction with K/Na alloy vapours (Scheme 1). Instead of the expected heterocycle, we obtained a reaction mixture containing 1,1,3,3-tetramethyl-1,3-disilacyclobutane in particular.

SCHEME 1

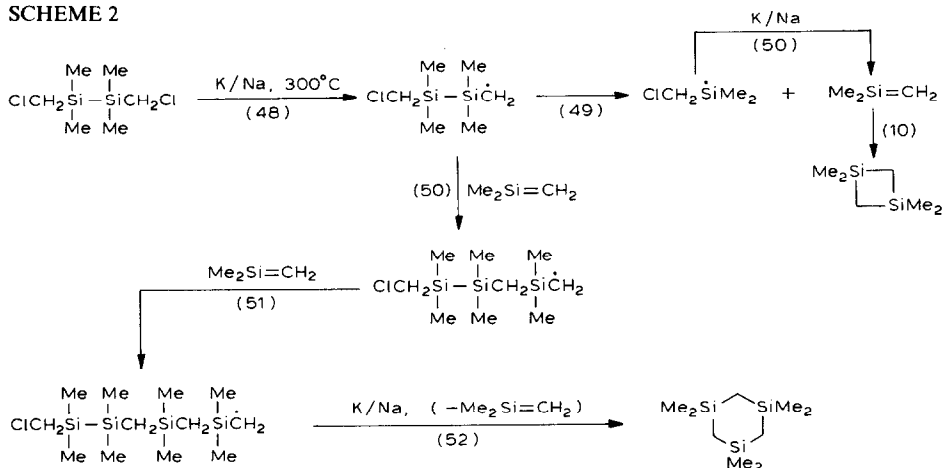


In the light of the results given earlier on the decomposition of the pentamethyldisilanylmethyl radical, the formation of the products of Scheme 1 was interpreted as shown in Scheme 2.

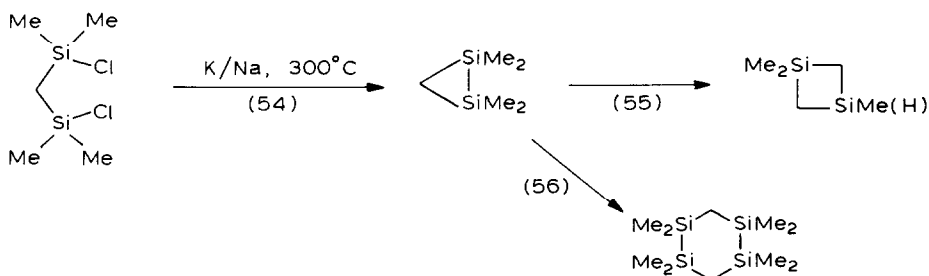
Similar to the dehalogenation of XX, the reaction of K/Na alloy vapours with XXI proceeds as intramolecular cyclization to give 1,1,2,2-tetramethyl-1,2-disilacyclopentane:



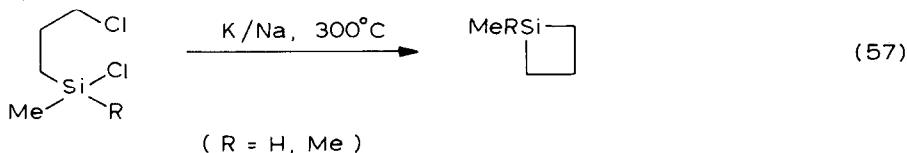
SCHEME 2



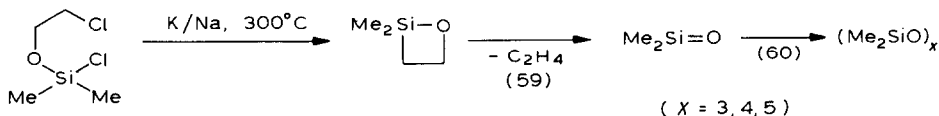
However, we failed to obtain 1,1,2,2-tetramethyl-1,2-disilacyclopentane by this method. Instead of the expected silacyclopentane, its isomer and dimer were obtained:



Cyclization of γ -chloropropylmethylchlorosilanes gives monosilacyclobutanes upon treatment with K/Na alloy vapours, the yield being 30–40% [15,18]:



Similar cyclization of 2-chloroethoxydimethylchlorosilane [16] yields only the products derived from the decomposition of the 2,2-dimethyl-2-silaoxetane intermediate:



Conclusion

The dehalogenation reactions of organochlorosilanes with alkali metal vapours considered reveal that the use of this method for generating unstable silicon compounds in the gas phase enables us to solve various problems concerning the chemistry of silyl and silyl-containing radicals, silylenes, intermediates with a

double-bonded silicon atom, and others. Also, it is possible to synthesize small-ring silicon-carbon heterocycles, including those which cannot be synthesized by other methods. Thanks to the use of readily available starting materials, simple apparatus, and facilities for safe experimental work, the dehalogenation of organohalosilanes with alkali metal vapours can be extensively employed for synthesizing organosilicon compounds.

Experimental

Method of dehalogenating organohalosilanes with alkali metal vapours. The reactions were carried out in a flow system similar to that described in [37]. In the vertical reactor (diameter 80 mm and height 300 mm), potassium (100 g) and sodium (13 g) were placed in an argon current. The lower part and bottom of the reactor were heated. The upper part was connected to a vacuum pump via traps cooled by liquid nitrogen. Vapours of the organochlorosilanes were passed over the sodium-potassium alloy heated to 280–320°C so that the pressure in the reactor was within 0.1 and 1 Torr. The reaction products were analysed by GLC and GC/MS techniques. In some cases, the products were isolated and identified by IR spectroscopy, NMR, and chemical methods.

Dechlorination of Me₃SiCl (I). Using the procedure above, I (2.17 g, 20 mmol) was dehalogenated to give 1.21 g of liquid and 21 cm³ of gas (under normal conditions). The gas mainly contained trimethylsilane. The main reaction products were: Me₃SiH (7%), M^+ , m/z 74 (6)*; $[M-1]^+$, 73 (62); $[M-15]^+$, 59 (100); Me₃SiSiMe₃ (64%), M^+ , 146 (6); $[M-15]^+$, 131 (19); Me₃Si⁺, 73 (100); Me₃SiCH₂SiMe₂H (2%), $[M-1]^+$, 145 (3); $[M-15]^+$, 131 (100); Me₃Si⁺, 73 (52); Me₃SiCH₂SiMe₂Cl (16%), $[M-15]^+$, 165 (100); ClMe₂Si⁺, 93 (8); Me₃Si⁺, 73 (40). (The yield of the converted organochlorosilanes is given in parentheses.)

Dechlorination of Me₂PrSiCl (II). Using the procedure above, II (4.08 g, 30 mmol) was dehalogenated to give 2.89 g of liquid and 10 cm³ of gas. The liquid contained: Me₂PrSiH (12%), M^+ , m/z 102 (5); $[M-1]^+$, 101 (13); $[M-15]^+$, 87 (19); $[M-43]^+$, 59 (100); PrMe₂SiSiMe₂H (3%), M^+ , 160 (14); $[M-43]^+$, 117 (16); PrMe₂SiSiMe₂Pr (51%), M^+ , 202 (32); $[M-15]^+$, 187 (3); $[M-43]^+$, 159 (8); $[M-85]^+$, 117 (40); $[M/2]^+$, 101 (100). The gas fraction consisted of Me₂SiH₂, Me₃SiH, CH₃CH=CH₂, and C₃H₈ in the ratio 8/1/4/5.

Dechlorination of Me₃SiSiMe₂Cl (III). Using the procedure above, III (1.66 g, 10 mmol) was dehalogenated to give 0.95 g of reaction products: Me₃SiSiMe₂H (8%), M^+ , m/z 132 (7); $[M-1]^+$, 131 (2); $[M-15]^+$, 117 (16); Me₃Si⁺, 73 (100); Me₃SiSiMe₂SiMe₂H (4%), M^+ , 190 (10%); $[M-1]^+$, 189 (1); $[M-15]^+$, 175 (15); $[M-59]^+$, 131 (45); $[M-73]^+$, 117 (26); $[M-74]^+$, 116 (75); Me₃Si⁺, 73 (100); HMe₂Si⁺, 59 (16); (Me₃SiSiMe₂)₂ (82%), M^+ , 262 (28); $[M-15]^+$, 247 (9); $[M-73]^+$, 189 (57); $[M/2]^+$, 131 (73); Me₃Si⁺, 73 (100).

Dechlorination of Me₃SiCH₂SiMe₂Cl (IV). Using the procedure above, IV (1.65 g, 10 mmol) was dehalogenated to give 1.09 g of reaction products: Me₃SiCH₂SiMe₂H (6%); (Me₃SiCH₂SiMe₂)₂ (58%), M^+ , m/z 290 (3); $[M-15]^+$,

* Here and below are given the intensities (%) of the characteristic ions in the mass spectra of the products.

275 (0.5); $[M - 103]^+$, 187 (15); $[M/2]^+$, 145 (100); $[(M/2) - 15]^+$, 130 (19); $[(M/2) - 16]^+$, 129 (18); Me_3Si^+ , 73 (85).

Dechlorination of $\text{Me}_3\text{SiCH}_2\text{Cl}$ (V). Using the procedure above, V (3.66 g, 30 mmol) was dehalogenated to give 2.84 g of reaction products: Me_4Si (6%), M^+ , m/z 88 (0.6); $[M - 15]^+$, 73 (100); $(\text{Me}_2\text{SiCH}_2)_2$ (1%), M^+ , 144 (23); $[M - 15]^+$, 129 (100); $[M - 43]^+$, 101 (11); $\text{Me}_3\text{SiCH}_2\text{SiMe}_3$ (5%), $[M - 15]^+$, 145 (100%); Me_3Si^+ , 73 (45%); $\text{Me}_2\text{SiCH}_2\text{CH}_2\text{SiMe}_2\text{CH}_2$ (3%), M^+ , 158 (32); $[M - 15]^+$, 143 (100); $[M - 28]^+$, 130 (36); $[M - 43]^+$, 115 (80); $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{SiMe}_3$ (73%), M^+ , 174 (7); $[M - 15]^+$, 159 (12); $[M - 43]^+$, 131 (7); Me_3Si^+ , 73 (100).

Dechlorination of $\text{ClCH}_2(\text{Me}_2)\text{SiSiMe}_3$ (VI). Using the procedure above, VI (3.60 g, 20 mmol) was dehalogenated to give 2.74 g of reaction products: Me_3SiH (5%), $\text{Me}_3\text{SiSiMe}_3$ (17%); $\text{Me}_3\text{SiCH}_2\text{SiMe}_2\text{H}$ (19%); $(\text{Me}_2\text{SiCH}_2)_2$ (26%); $\text{Me}_3\text{SiCH}_2\text{SiMe}_3$ (4%); $\text{Me}_3\text{Si}(\text{Me})\text{SiCH}_2\text{SiMe}_2\text{CH}_2$ (2%), M^+ , m/z 202 (27); $[M - 15]^+$, 187 (100); $[M - 73]^+$, 129 (25); $[M - 89]^+$, 113 (28); $[M - 101]^+$, 101 (10); $\text{Me}_3\text{SiCH}_2\text{SiMe}_2\text{SiMe}_3$ (5%), M^+ , 218 (4); $[M - 15]^+$, 203 (10); $[M - 73]^+$, 145 (84); Me_3Si^+ , 73 (100); $(\text{Me}_2\text{SiCH}_2)_3$ (1%), $[M - 15]^+$, 201 (100); $[M - 87]^+$, 129 (7); Me_3Si^+ , 73 (18); $(\text{Me}_3\text{SiCH}_2\text{SiMe}_2)_2$ (7%).

Dechlorination of a mixture of $\text{ClCH}_2\text{SiMe}_3$ (V) and Me_3SiCl (I). Using the procedure above, a mixture of V (1.22 g, 10 mmol) and I (1.08 g, 10 mmol) was dehalogenated to give 1.05 g of reaction products: Me_3SiH (1%); Me_4Si (5%), $\text{Me}_3\text{SiSiMe}_3$ (10%), $\text{Me}_3\text{SiCH}_2\text{SiMe}_3$ (58%), $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{SiMe}_3$ (traces).

Dechlorination of $\text{ClCH}_2\text{Me}_2\text{SiSiMe}_2\text{CH}_2\text{Cl}$ (VII). Using the procedure above, VII (2.14 g, 10 mmol) was dehalogenated to give the following products (1.15 g): Me_3SiH (2%), $\text{Me}_3\text{SiSiMe}_3$ (22%), $\text{Me}_3\text{SiCH}_2\text{SiMe}_2\text{H}$ (29%), $(\text{Me}_2\text{SiCH}_2)_2$ (18%), $\text{Me}_3\text{SiCH}_2\text{SiMe}_3$ (4%), $(\text{Me}_2\text{SiCH}_2)_3$ (10%).

Dechlorination of Me_2SiCl_2 (VIII) in the presence of buta-1,3-diene. Using the procedure above, a mixture containing VIII (2.58 g, 20 mmol) and buta-1,3-diene (20.8 g, 0.4 mol) was dehalogenated to give 2.40 g of liquid. 1.61 g (72%) of $\text{Me}_2\text{SiCH}_2\text{CH}=\text{CHCH}_2$ was obtained from the liquid by preparative GLC. ^1H NMR spectrum (δ , ppm): 1.10 (6H, s), 2.76 (4H, d), 5.52 (2H, t); mass spectrum: M^+ , m/z 112 (16); $[M - 15]^+$, 97 (100); $[M - 54]^+$, 58 (11).

Dechlorination of MePrSiCl_2 (IX). Using the procedure above, IX (3.12 g, 20 mmol) was dehalogenated to give 0.95 g of liquid and 66 cm³ of gas. The liquid contained: MePrSiH_2 (56%), M^+ , m/z 88 (10); $[M - 1]^+$, 87 (12); $[M - 2]^+$, 86 (32); $[M - 15]^+$, 73 (28); $[M - 43]^+$, 45 (100); Me_2PrSiH (5%), M^+ , m/z 102 (5%); $[M - 1]^+$, m/z 101 (13); $[M - 15]^+$, m/z 87 (19); $[M - 43]^+$, 59 (100); $\text{Me}(\text{Pr})\text{HSiSiMeH}_2$ (6%), M^+ , 132 (9); $[M - 1]^+$, 131 (4); $[M - 15]^+$, 117 (2); $[M - 45]^+$, 87 (31); $\text{Pr}(\text{Me})\text{HSiSiH}(\text{Me})\text{Pr}$ (6%), M^+ , 174 (18); $[M - 15]^+$, 159 (1); $[M - 43]^+$, 131 (8); $[M/2]^+$, 87 (36); $[(M/2) - 1]^+$, m/z 86 (73); $[M - 115]^+$, m/z 59 (100); $[M - 116]^+$, m/z 58 (71). The gas fraction consisted of C_2H_4 , $\text{CH}_3\text{CH}=\text{CH}_2$, and C_3H_8 in the ratio 1/18/1.

Dechlorination of IX in the presence of diethyl ether vapours. Using the procedure above, a mixture of IX (0.78 g, 5 mmol) and diethyl ether (3.90 g, 50 mmol) was dehalogenated to give 3.97 g of liquid and 28 cm³ of gas. The liquid contained the same products as those in the previous experiment. n-Hexane (9%), $[M - 29]^+$, m/z 57 (100); $[M - 29 - 1]^+$, 56 (44); $M/2^+$, 43 (82) was detected in addition to MePrSiH_2 (52%) and PrMe_2SiH (4%). The gas contained C_2H_4 , C_4H_6 , $\text{CH}_3\text{CH}=\text{CH}_2$, and C_3H_8 in the ratio 3/1/5/2.

Dechlorination of $\text{Me}_3\text{SiCH}_2\text{SiMeCl}_2$ (X). Using the procedure above, X (2.01 g, 10 mmol) was dehalogenated to give 0.92 g of products: $\text{Me}_3\text{SiCH}_2\text{SiMeH}_2$ (65%), M^+ , m/z 132 (1); $[M-1]^+$, 131 (6); $[M-2]^+$, 130 (1); $[M-15]^+$, 117 (100); $[M-59]^+$, 73 (40); $[M-73]^+$, 59 (10); $\text{Me}_3\text{SiCH}_2\text{SiMe}_2\text{H}$ (4%); $\text{Me}_3\text{SiCH}_2\text{SiMe}_3$ (2%).

Dechlorination of $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{SiMeCl}_2$ (XI). Using the procedure above, XI (2.15 g, 10 mmol) was dehalogenated to give 1.03 g of products; $\text{Me}_3\text{SiCH}=\text{CH}_2$ (55%), M^+ , m/z 100 (13); $[M-15]^+$, 85 (100); $[M-27]^+$, 73 (87); $\text{Me}_2\text{SiCH}_2\text{CH}_2\text{SiMe(H)CH}_2$ (8%), M^+ , 144 (43); $[M-1]^+$, 143 (3); $[M-15]^+$, 129 (65); $[M-28]^+$, 116 (100); $[M-43]^+$, 101 (67); $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{SiMeH}_2$ (25%), M^+ 146 (5); $[M-1]^+$, 145 (3); $[M-15]^+$, 131 (18); $[M-43]^+$, 103 (20); Me_3Si^+ , 73 (100); $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{SiMe}_2\text{H}$ (2%), M^+ , 160 (6); $[M-1]^+$, 159 (2); $[M-15]^+$, 145 (18); $[M-43]^+$, 117 (18); $[M-74]^+$, m/z 86 (51); Me_3Si^+ , 73 (100); Me_2SiH , 59 (18). The first two products were isolated by preparative GLC and identified by IR spectroscopy in the gas phase: $\text{Me}_3\text{SiCH}=\text{CH}_2$, IR spectrum (cm^{-1}): 949, 1000, 1008, 1590, 3008; $\text{Me}_2\text{SiCH}_2\text{CH}_2\text{SiMe(H)CH}_2$, IR spectrum (cm^{-1}): 978, 1021, 1125, 2110.

Dechlorination of $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{SiMeCl}_2$ (XII). Using the procedure above, XII (2.19 g, 10 mmol) was dehalogenated to give the following products (1.07 g): $\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2$ (46%), M^+ , m/z 114 (4); $[M-15]^+$, 99 (18); Me_3Si^+ , 73 (100); $\text{Me}_2\text{Si(CH}_2)_3\text{SiMe(H)CH}_2$ (4%), M^+ , 158 (22); $[M-15]^+$, 143 (15); $[M-42]^+$, 116 (100); $[M-57]^+$, 101 (42); $[M-85]^+$, 73 (42); $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{SiMeH}_2$ (30%), M^+ , 160 (2); $[M-1]^+$, 159 (1); $[M-15]^+$, 145 (23); $[M-43]^+$, 117 (5); Me_3Si^+ , 73 (100); $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{SiMe}_2\text{H}$ (4%), M^+ 174 (2); $[M-15]^+$, 159 (23); $[M-43]^+$, 131 (3); $[M-58]^+$, 116 (29); Me_3Si^+ , 73 (100); Me_2SiH , 59 (24).

Dechlorination of $\text{ClCH}_2\text{SiMe(H)Cl}$ (XIII). Using the procedure above, XIII (1.28 g, 10 mmol) was dehalogenated to give 0.96 g of products; Me_2SiHCl (5%), M^+ , m/z 94 (10); $[M-1]^+$, 93 (100); $[M-15]^+$, 79 (56); $\text{HMe}_2\text{SiCH}_2\text{SiMeH}_2$ (11%), M^+ , 118 (5); $[M-1]^+$, 117 (13); $[M-2]^+$, 116 (12); $[M-15]^+$, 103 (18); $[M-1-45]^+$, 72 (100); $(\text{HMeSiCH}_2)_2$ (32%), M^+ , 116 (81); $[M-1]^+$, 115 (25); $[M-15]^+$, 101 (100); $\text{Me}_2\text{SiCH}_2\text{SiMe(H)CH}_2$ (4%); M^+ , 130 (49); $[M-1]^+$, 129 (10); $[M-15]^+$, 115 (100); $\text{Cl(H)MeSiCH}_2\text{SiMe}_2\text{H}$ (8%), M^+ , 152 (5); $[M-1]^+$, 151 (21); $[M-15]^+$, 137 (100); $[M-59]^+$, 93 (17); $[M-79]^+$, 73 (20); $(\text{H(Me)SiCH}_2)_3$ (5%), M^+ , 174 (20); $[M-1]^+$, 173 (29); $[M-15]^+$, 159 (100).

Dechlorination of $\text{ClCH}_2\text{SiMe}_2\text{Cl}$ (XIV). Using the procedure above, XIV (14.3 g, 100 mmol) was dehalogenated to give 8.0 g of products: Me_3SiH (2%); Me_4Si (0.7%); Me_3SiCl (5%), M^+ , m/z 108 (2); $[M-15]^+$, 93 (100); $\text{ClCH}_2\text{SiMe}_2\text{H}$ (0.3%), M^+ , 108 (2); $[M-1]^+$, 107 (3); $[M-15]^+$, 93 (22); $[M-49]^+$, 59 (100); $\text{Me}_3\text{SiCH}_2\text{SiMe}_2\text{H}$ (1%); $(\text{Me}_2\text{SiCH}_2)_2$ (48%); $\text{Me}_3\text{SiCH}_2\text{SiMe}_3$ (2%); $\text{Me}_3\text{SiCH}_2\text{SiMe}_2\text{Cl}$ (15%); $(\text{Me}_2\text{SiCH}_2)_3$ (3%).

Dechlorination of XIV in the presence of buta-1,3-diene. Using the procedure above, XIV (2.8 g, 20 mmol) was dehalogenated in a 20-fold excess of C_4H_6 to give 1.4 g of liquid which contained 1,1-dimethylsilacyclohex-3-ene (10%), M^+ , m/z 126 (45); $[M-15]^+$, 111 (48); $[M-28]^+$, 98 (100); $[M-43]^+$, 83 (31); $[M-54]^+$, 72 (70).

Dechlorination of $\text{ClMe}_2\text{SiSiMe}_2\text{Cl}$ (XV). Using the procedure above, XV (1.87 g, 10 mmol) was dehalogenated to give 1.24 g of products: $\text{HMe}_2\text{SiSiMe}_2\text{H}$ (58%), M^+ , m/z 118 (23); $[M-1]^+$, 117 (7); $[M-15]^+$, 103 (26); $[M-45]^+$, 73 (71);

M^+ , m/z 118 (23); $[M - 1]^+$, 117 (7); $[M - 15]^+$, 103 (26); $[M - 45]^+$, 73 (71); Me_2SiH 59 (100); $\text{Me}_3\text{SiSiMe}_2\text{H}$ (10%), M^+ , 132 (7); $[M - 1]^+$, 131 (3); $[M - 15]^+$, 117 (16); Me_3Si^+ , 73 (100); $\text{HMe}_2\text{SiSiMe}_2\text{SiMe}_2\text{H}$ (8%), M^+ , 176 (9); $[M - 1]^+$, 175 (3); $[M - 15]^+$, 161 (15); $[M - 59]^+$, 117 (91); $[M - 60]^+$, 116 (100); Me_2SiH , 59 (26).

Dechlorination of XV in the presence of buta-1,3-diene. Using the procedure above, XV (0.19 g, 1 mmol) was dehalogenated in a 20-fold excess of buta-1,3-diene to give 0.15 g of liquid. The liquid contained, in addition to $\text{HMe}_2\text{SiSiMe}_2\text{H}$ (31%), $\text{Me}_3\text{SiSiMe}_2\text{H}$ (6%), and $\text{HMe}_2\text{SiSiMe}_2\text{SiMe}_2\text{H}$ (4%), the following: $\text{Me}_2\text{SiCH}_2\text{CH}=\text{CHCH}_2$ (18%) and $\text{Me}_2\text{SiCH}_2\text{CH}=\text{CHCH}_2\text{SiMe}_2$ (10%), M^+ , m/z 170 (30); $[M - 15]^+$, 155 (34); $[M - 54]^+$, 116 (100); $[M - 54 - 15]^+$, 101 (20).

Dechlorination of XV in the presence of ethylene. Using the procedure above, XV (0.19 g, 1 mmol) was dehalogenated in a 100-fold excess of C_2H_4 to give 0.09 g of product, which on defrosting turned into a mobile, transparent liquid smelling of geranium. At room temperature, the liquid soon became dull and finally solidified. After vacuum separation of the volatile products, a white solid (0.06 g) was obtained, which dissolved in benzene and toluene on heating, and separated from the solution at room temperature. The ^1H NMR spectrum of the product obtained was found to be identical with that of the 1,1,2,2-tetramethyl-1,2-disilacyclobutane polymer (δ , ppm, C_6H_6 , T 60°C): 0.275 (12H, s), 0.875 (4H, s).

Dechlorination of $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{SiMe}_2\text{HCl}$ (XVI). Gas-phase synthesis of 1-methyl-1-silacyclobutane. Using the procedure above, XVI (5.23 g, 33 mmol) was dehalogenated to give 3.12 g of products: $\text{Me}(\text{H})\text{SiCH}_2\text{CH}_2\text{CH}_2$ (58%); PrMeSiH_2 (7%); $\text{Me}_2\text{SiCH}_2\text{CH}_2\text{CH}_2$ (4%). A liquid (4.17 g) was obtained on dehalogenating XVI (0.78 g, 0.005 mol) with diethyl ether (3.9 g, 0.05 mol). The composition of the liquid hardly differed from those of the liquids obtained in the absence of diethyl ether.

Dechlorination of $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{SiMe}_2\text{Cl}$ (XVII). Gas-phase synthesis of 1,1-dimethyl-1-silacyclobutane. Using the procedure above, XVII (1.71 g, 10 mmol) was dehalogenated to give 0.72 g of liquid. A pure sample of 1,1-dimethyl-1-silacyclobutane (0.42 g, 42%) was obtained by the preparative GLC method. ^1H NMR spectrum (δ , ppm, C_6H_6 external): 2.15 (2H, m), 1.06 (4H, m), 0.258 (3H, s).

Dechlorination of $\text{ClCH}_2\text{CH}_2\text{OSiMe}_2\text{Cl}$ (XVIII). Using the procedure above, XVIII (3.3 g, 20 mmol) was dehalogenated to give 1.5 g of liquid and 35 cm^3 (under normal conditions) of gas. The latter contained mostly ethylene. Cyclosiloxanes D_3 , D_4 , and D_5 in the ratio 1/3/1 were isolated from the liquid. The total yield of oligomers was 30%. Mass spectra: D_3 , M^+ , m/z 222 (0.05); $[M - 15]^+$, 207 (100); $[M - 31]^+$, 191 (8); D_4 , M^+ , 296 (0.05); $[M - 15]^+$, 281 (100); $[M - 31]^+$, 265 (8); $[M - 89]^+$, 207 (10); D_5 , M^+ , 370 (0.05); $[M - 15]^+$, 355 (100).

Dechlorination of $\text{ClMe}_2\text{SiCH}_2\text{SiMe}_2\text{Cl}$ (XIX). Using the procedure above, XIX (2.01 g, 10 mmol) was dehalogenated to give 1.24 g of liquid. From the liquid were obtained: $\text{Me}_3\text{SiSiMe}_2\text{H}$ (2%), $\text{HMe}_2\text{SiCH}_2\text{SiMe}_2\text{H}$ (10%), $\text{Me}_2\text{SiCH}_2\text{SiMe}(\text{H})\text{CH}_2$ (8%), M^+ , m/z 130 (52); $[M - 1]^+$, 129 (17); $[M - 15]^+$, 115 (100); $(\text{Me}_2\text{SiCH}_2\text{SiMe}_2)_2$ (18%), M^+ , 260 (46); $[M - 15]^+$, 245 (34); $[M - 59]^+$, 201 (11); $[M - 73]^+$, 187 (100); $[M - 89]^+$, 171 (31); $[M/2]^+$, 130 (47); $[M - 131]^+$, 129 (22); Me_3Si^+ , 73 (98). ^{29}Si NMR spectrum (δ , ppm, C_6H_6) - 19.6.

Dechlorination of ClMe₂SiCH₂CH₂SiMe₂Cl (XX)

A. Formation of the 1,1,2,2-tetramethyl-1,2-disilacyclobutane polymer. Using the procedure above, XX (2.14 g, 10 mmol) was dehalogenated to give 1.15 g of product, which on defrosting turned into a mobile, transparent liquid. At room temperature, the liquid soon became dull and finally turned into a white solid mass resembling polyethylene. After elimination of the impurities by heating the sample continuously in a vacuum, 1.07 g of polymer was obtained. The polymer, according to the DTA data, melts at 113°C; in air it starts to decompose at 240°C. It does not dissolve in organic solvents at 20°C. Above 55°C it dissolves in benzene, toluene, *o*-, *m*-, and *p*-xylenes. The elementary composition, NMR and IR spectra are in agreement with a polymer with the main chain made up of CH₂CH₂Me₂SiSiMe₂ links. IR spectrum of polyethylenetetramethyldisilene (PETMDS): 300(m), 605(s), 688(s), 719(s), 765(vs), 829(vs), 1050(m), 1127(s), 1237(s), 1282(vs), 1398(m), 1450(w), 2790(m), 2875(s), 2895(s), and 2944(s). ¹H NMR spectrum (δ, ppm, C₆H₆, *T* 60°C) 0.275 (12H, s), 0.875 (4H, s); ¹³C NMR spectrum (δ, ppm, C₆H₆, *T* 60°C); -0.4 (4C, s), 13.84 (2C, s); ²⁹Si NMR spectrum: (δ, ppm, solid state): -15.5. The intrinsic viscosity of PETMDS (60°C, benzene) equals 0.21 dl/g.

B. Synthesis of 1,1,2,2-tetramethyl-1,2-disilacyclobutane. Using the procedure above, XX (21.4 g, 100 mmol) was dehalogenated to give 12.8 g of liquid. Pure 1,1,2,2-tetramethyl-1,2-disilacyclobutane (1,2-TMDSCB) was obtained after distillation at a low pressure (b.p. 45–46°C/29 mmHg); it smelled of geranium. A large amount of 1,2-TMDSCB was lost because of its polymerization. Thus, the yield of 1,2-TMDSCB was 24% (only 3.5 g of the product was isolated). ¹H NMR spectrum (δ, ppm, without a solvent, -50°C, external standard CHCl₃): -0.23 (12H, s), 0.63 (4H, s); ¹³C NMR spectrum (δ, ppm, without a solvent, -40°C, external standard CD₃OD): -2.95 (4C, s), 8.70 (2C, s). 1,2-TMDSCB can be stored for a long period at 77 K. At room temperature, 1,2-TMDSCB readily polymerizes.

Dechlorination of ClMe₂SiCH₂CH₂CH₂SiMe₂Cl (XXI). Gas-phase synthesis of 1,1,2,2-tetramethyl-1,2-disilacyclopentane. Using the procedure above, XXI (2.28 g, 10 mmol) was dehalogenated to give 1.74 g of liquid. A pure sample of 1,1,2,2-tetramethyl-1,2-disilacyclopentane (1.04 g, 70%) was obtained by the preparative GLC method. Mass spectrum: *M*⁺, *m/z* 158 (81); [*M* - 15]⁺, 143 (58); [*M* - 28]⁺, 130 (61); [*M* - 41]⁺, 117 (50); [*M* - 42]⁺, 116 (42); [*M* - 43]⁺, 115 (100); Me₃Si⁺, 73 (77).

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