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Review

UNSATURATED COMPOUNDS OF SILICON AND GROUP HOMOLOGUES

VIII *. UNSATURATED SILICON AND GERMANIUM COMPOUNDS OF THE TYPES $R_2E{=}C(SiR_3)_2$ AND $R_2E{=}N(SiR)_3)$ (E = Si, Ge)

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1. Introduction

Compounds with $p\pi$–$p\pi$ bonded silicon ("unsaturated silicon compounds") are highly unstable compared to those with $p\pi$–$p\pi$ bonded carbon ("unsaturated carbon compounds"). The generation and detection of unsaturated silicon compounds, which are stable only at very high temperatures [1] and in normal cases metastable only at very low temperatures, was considered, for a long time, to be one of the "classical problems" of silicon chemistry. Accordingly, unsaturated silicon

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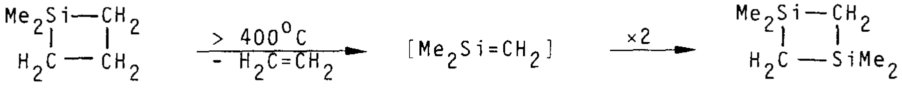
* For part VII see ref. 49. Also part LIX of compounds of silicon and group homologues. For part LVIII see ref. 49.

compounds were classified as typical examples in the curious book "Nonexistent Compounds", published in 1965 [2].

The formation of an unsaturated silicon compound, namely dimethylsilaethene $Me_2Si{=}CH_2$ (which rapidly dimerizes) was observed for the first time in 1966, by Nametkin, Gusel'nikov et al., as an intermediate in the gas phase pyrolysis of 1,1-dimethyl-1-silacyclobutane [3].


(1)

Since that time, silaethenes and other unsaturated silicon compounds as well as the corresponding germanium compounds, have been among the most intensively investigated topics in silicon and germanium chemistry. The results achieved have been summarized in many reports [4–10].

During the last few years we have been attempting to devise simple methods of generating unsaturated silicon and germanium compounds under very mild conditions [11–19]. Such techniques are the necessary prerequisites for an exhaustive and systematic study of the stability and reactivity of these compounds. Our results on the preparation, stability and reactivity of the compounds $R_2E{=}C(SiR_3)_2$ and $R_2E{=}N(SiR_3)$ (E = Si, Ge) are summarized below *.

2. Preparation

Unsaturated silicon and germanium compounds are usually observed only as reactive intermediates. They are formed, as are other unstable species, from suitable chemical precursors willingly or unwillingly, that is with evolution or absorption of energy (Fig. 1). The methods discovered so far for the generation of unsaturated silicon and germanium compounds involve thermally or photochemically induced cycloreversions, electrocyclic reactions, rearrangements and elimination reactions (e.g., retroene reactions, salt eliminations) [4–14].

We have devised suitable techniques for obtaining the title compounds under mild conditions by the use of salt eliminations and cycloreversions. By these methods, we have generated the following unsaturated systems of the $R_2E{=}C(SiR_3)_2$ and $R_2E{=}N(SiR_3)$ types (E = Si, Ge):

$Me_2E{=}C(SiMe_3)_2$
$Ph_2Si{=}C(SiMe_3)_2$
$Bu^t_2Si{=}C(SiMe_3)_2$
$Me_2Si{=}C(SiMe_3)(SiMeBu^t_2)$

$Me_2E{=}N(SiMe_3)$
$Me_2E{=}N(SiMe_2R)$ (R = Bu^t, $N(SiMe_3)_2$)
$Me_2E{=}N(SiMeR_2)$(R = Bu^t)
$Me_2E{=}N(SiR_3)$ (R = Bu^t, Ph)

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* Compounds with the $>Si{=}C<$ skeleton are designated as silaethenes (silaethylenes) or silenes, and compounds with the $>Si{=}N-$ skeleton as silaketoneimines (silaketimines), silaimines (more correctly, silaneimines) or iminosilanes (and correspondingly for compounds with the $>Ge{=}C<$ and $>Ge{=}N-$ skeletons) [4,8,11,12]. Because of the analogy between unsaturated silicon and germanium compounds and the well-known unsaturated carbon compounds, we prefer the names sila- and germa-ethenes, as well as sila- and germa-ketimines.

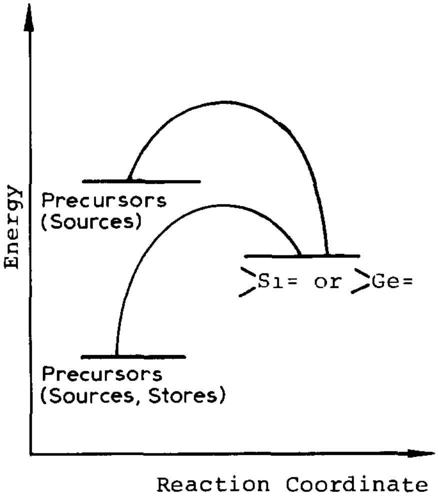
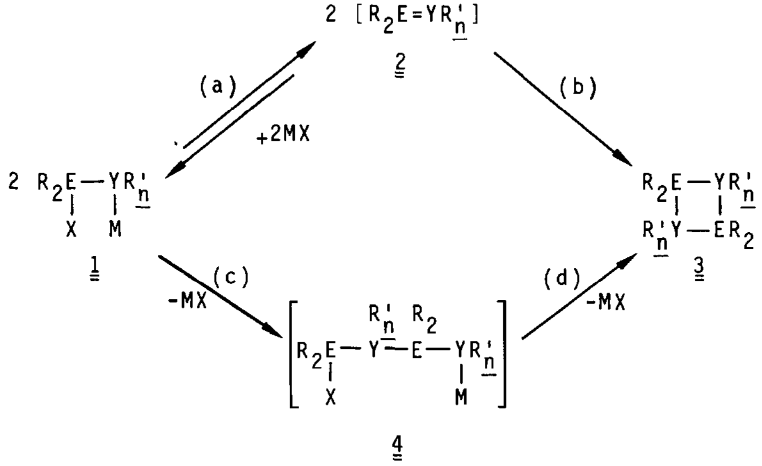


Fig. 1. Reaction profile for the formation of unsaturated silicon and germanium compounds from suitable precursors.

2.1. Salt elimination method

The formation of unsaturated silicon or germanium compounds by the salt elimination method (Scheme 1) requires starting silicon or germanium compounds **1**,

SCHEME 1



in which silicon or germanium with an electronegative substituent X (e.g. halogen) is bonded to an atom Y (e.g. C$<$, N–) bearing an electropositive metal M (e.g., alkali metal). The unsaturated silicon or germanium compounds **2**, produced by the elimination of MX from **1**, generally dimerize immediately, with the formation of four-membered rings of the type **3** *. Consequently, only compounds **3** appear as the products of the decomposition of **1**. Since the formation of **3** may not result solely

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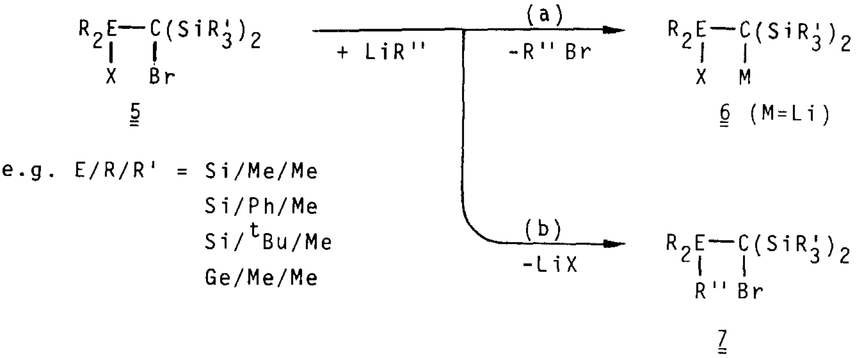
* Stable compounds **2** are formed when E and Y have very bulky substituents (cf., Section 3).

from the intramolecular MX elimination by route a/b in Scheme 1 (intermediate products **2**), but could also be formed by intermolecular MX elimination (route c/d; intermediate products **4**), the intermediate formation of **2** must be demonstrated. Subsequently, the preparation and decomposition of compounds **1**, as well as the identification of the intermediates **2**, (E = Si, Ge; Y = C, N; $R' = SiR_3$) have been discussed briefly using compounds.

Preparation of $R_2EX-YMR'_n$ (1). Preparation of precursors **1** takes place at suitable temperatures below their decomposition temperatures. Our investigations have shown that the bromo-substituted compounds **5** are useful for the synthesis of the sila- and germa-ethene precursors **6** (and the same is true for other precursors $\rangle EX-C(M)\langle$). Compounds **5** react with organolithium reagents (e.g., LiBu, LiBu^t, LiPh), in a manner similar to pure organic bromo compounds [20], even at very low temperatures (−100 °C and below), through Br/Li-exchange, according to eq. 2a [13,19,21] *.



(2)

The rate of eq. 2a increases with increasing basicity of the reaction medium (i.e., in the direction pentane < diethyl ether < tetrahydrofuran), as well as on replacement of the LiBu by LiPh. In addition, the rate depends on the steric and electronic effects of the substituents X, R and R′ [13]. An additional X/R″ exchange, leading to the formation of **7** according to eq. 2b, is also observed. This unwanted reaction can be suppressed by working at lower reaction temperatures and at lower reactant concentrations, by the use of diethyl ether or even tetrahydrofuran in place of pentane, and by the use of butyllithium instead of phenyllithium **. In addition, the relative yield of **6** increases, for different substituents X, in the order $ArSO_3 < Cl < Br < I, F, Ph_2PO_n$ [13].

If in place of organolithium reagents, the bromo compound **5** is treated with the recently-isolated silylsodium $NaSiBu^t_3$ [36] which is soluble in organic solvents, the

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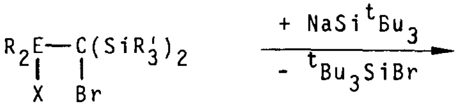
* Because the reaction represented by eq. 2a is fast, the precursors **6** (formed by the dropwise addition of LiR″ solutions to the starting materials **5** dissolved in organic media) can frequently be synthesized even in the presence of compounds which react with the sila- and germa-ethenes obtainable from **6**.

** Phenyllithium is recommended in place of butyllithium because bromobenzene, in contrast to butyl bromide (formed according to eq. 2a), does not react further with **6** to form $R_2EX-CR''(SiR'_3)_2$ (an unwanted secondary reaction which competes with the formation of the LiX eliminating compound **6**) [13]. The use of LiBu^t is also not recommended, because Bu^{t}Br, formed according to eq. 2a, reacts with **6** to form $R_2EX-CH(SiR'_3)_2 + LiBr + Me_2C{=}CH_2$ [13].

sodium derivatives **6** (M = Na) are formed by a fast Br/Na exchange, as shown in eq. 3.

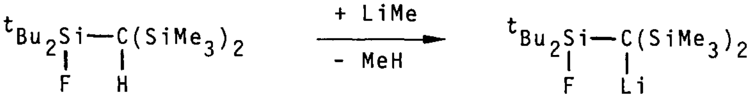


$$\underset{X}{R_2E}-\underset{Br}{C}(SiR'_3)_2 \xrightarrow[-\,{}^tBu_3SiBr]{+\,NaSi{}^tBu_3} \underset{X}{R_2E}-\underset{M}{C}(SiR'_3)_2 \qquad (3)$$

5 6 (M=Na)

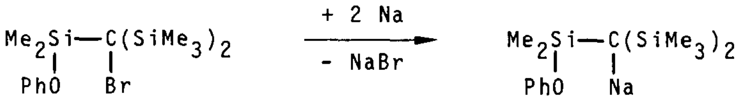
Because of the bulkiness of $NaSiBu^t_3$, the unwanted X/$SiBu^t_3$-exchange does not occur.

For the preparation of compounds with the >EX–C(M)< group, the other recommended methods such as, H/Li exchange between >SiX–CH< and organolithium compounds or lithium amides in organic media [16,22–26], R_3Si/Na exchange between >SiX–C(SiR_3)< and NaOMe in methanol [27] *, Hal/M exchange (M = alkali metal) by reaction of >SiX–C(Hal)< with M [19,25,28], or the addition of organolithium compounds to the compounds >SiX–C=C< [23,29], proceed more slowly to the required sila- and germa-ethene precursors than the Br/M exchange of >SiX–C(Br)< with MR″ (R″ = an organic or silyl group). Simultaneous formation and decomposition of the comparatively more unstable precursors >EX–C(M)< may therefore occur. As a consequence of this, the unsaturated compounds >E=C< formed, and the reactants added, then all react with the starting compounds (e.g., LiR, $LiNR_2$, MeOH, M) used for the preparation of >EX–C(M)<. On the other hand, the more stable precursors >EX–C(M)< can be synthesized by the above-mentioned routes without this disadvantage. In this way, the lithium compound **9** (which is stable up to 100 °C) can be prepared as shown in eq. 4 by the reaction of **8** with methyllithium in tetrahydrofuran at room temperature [16]. The thermostable compound **11** is also easily formed from **10** and sodium in boiling tetrahydrofuran as shown in eq. 5 [19,28].



$$\underset{F}{{}^tBu_2Si}-\underset{H}{C}(SiMe_3)_2 \xrightarrow[-\,MeH]{+\,LiMe} \underset{F}{{}^tBu_2Si}-\underset{Li}{C}(SiMe_3)_2 \qquad (4)$$

8 9



$$\underset{PhO}{Me_2Si}-\underset{Br}{C}(SiMe_3)_2 \xrightarrow[-\,NaBr]{+\,2\,Na} \underset{PhO}{Me_2Si}-\underset{Na}{C}(SiMe_3)_2 \qquad (5)$$

10 11

Hydrogen bonded to nitrogen is more easily replaced by lithium (by the action of an organolithium reagent) than hydrogen bonded to carbon. Accordingly, the sila- and germa-ketimine precursors **13** are easily obtained from the amines **12** (eq. 6a)

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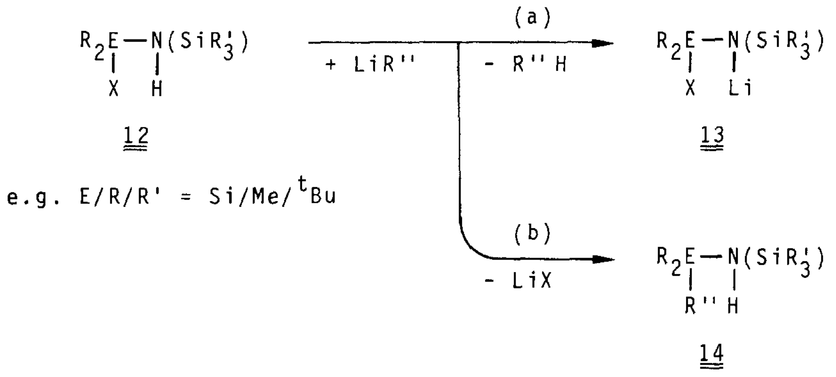
* This is possible in case of the bulkier reactants $R_2SiCl-C(SiMe_3)_3$ (R = Me, Ph). Obviously R_3Si/Na exchange follows the NaX elimination route [27].

[18,30], and the same is also true for the other precursors $>$EX–N(Li)– [31–34] *.

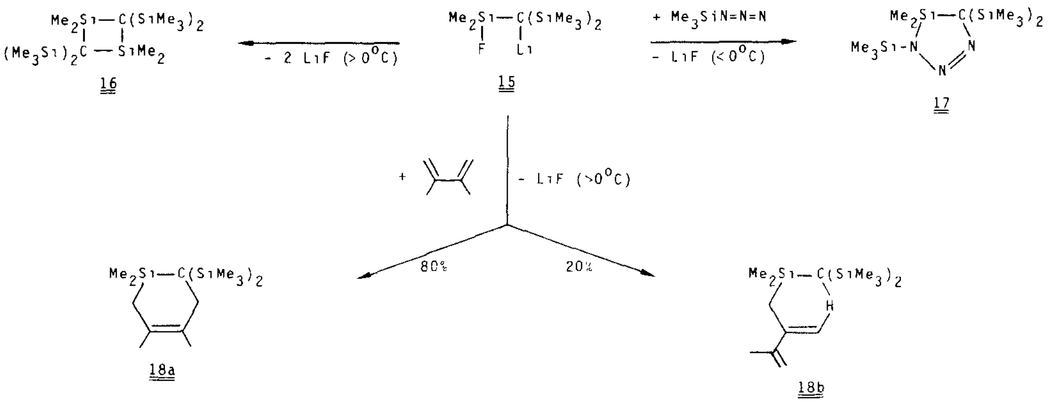


(6)

The unwanted side-reaction shown in eq. 6b, corresponding to the reaction in eq. 2b, becomes appreciable for **12** with small substituents R and R′. It can be restricted by the use of bulkier organolithium compounds.

Evidence for $R_2E{=}YR'_n$ (2). The disilacyclobutane **16** is formed exclusively in the thermal elimination of LiF from **15** (Scheme 2) (the same is also true for other

SCHEME 2



variants of $Me_2XSi\text{-}C(SiMe_3)_2$, e.g. X = Cl, Br, I, PhS, *o*-TolylSO$_3$) [14]. The formation of the four-membered ring in **16**, which is formally the dimerization product of the silaethene $Me_2Si{=}C(SiMe_3)_2$, is, however, no proof of the actual intermediate formation of $Me_2Si{=}C(SiMe_3)_2$. This is because the formation of **16** from **15** can occur through intermolecular elimination of LiF in a route involving the reaction intermediate $Me_2SiF\text{–}C(SiMe_3)_2\text{–}SiMe_2\text{–}CLi(SiMe_3)_2$ (just as well as through intramolecular elimination of LiF). Similarly the formation **17** or **18** by the decomposition of **15** in the presence of trimethylsilyl azide or 2,3-dimethyl-1,3-butadiene (Scheme 2) [11,12,15], which can easily be interpreted as a [2 + 3]

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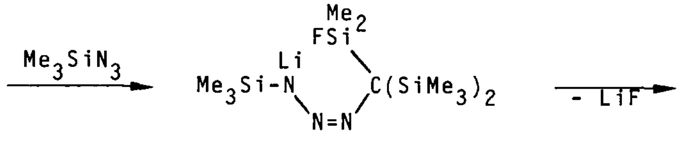
* A reaction analogous to eq. 2a is less likely because *N*-halogenamines (which are not easily accessible) can react completely with organolithium derivatives by secondary radical reactions [35].

cycloaddition of $Me_2Si{=}C(SiMe_3)_2$ with the silyl azide or as a [2 + 4] cycloaddition, as well as an ene reaction product of $Me_2Si{=}C(SiMe_3)$ with dimethylbutadiene, do not provide proof for the intermediate appearance of the silaethene; in fact, other modes of formation of **17** and **18** are conceivable.

The question of the mechanisms of the reactions depicted in Scheme 2 can be answered by kinetic and chemical investigations [14]. In probably the most acceptable hypothesis, that $Me_2Si{=}C(SiMe_3)_2$ is formed as a reactive and immediately dimerizable species, the thermal decomposition of **15** (by intramolecular elimination of LiF) should follow first-order kinetics. On the other hand, an intermolecular elimination of LiF would be expected to follow second-order kinetics. Actually, **15** undergoes a first-order decomposition in diethyl ether (the same is also true for the decomposition of the other precursors $Me_2XSi\text{-}C(SiMe_3)_2$ in diethyl ether). In addition, the intermediate presence of $Me_2Si{=}C(SiMe_3)_2$ is supported by the fact that the rate constants for the first-order thermal decomposition of **15** in diethyl ether are the same in the absence and in the presence of dimethylbutadiene, although totally different products are formed (Scheme 2). The last result supports the formation of **18a** and **18b** simultaneously by the route involving $Me_2Si{=}C(SiMe_3)_2$. Moreover, this idea is supported by the finding that the ratio of the yields of the competing trapped-products **18a** and **18b** is practically independent of the silaethene precursor $Me_2XSi{-}CM(SiMe_3)_2$ employed (X = a variety of substituents).

The thermal decomposition of **15** in diethyl ether occurs considerably faster in the presence of trimethylsilyl azide than in its absence. The formation of **17**, therefore, does not take place via $Me_2Si{=}C(SiMe_3)_2$. The reactive intermediate in this case is probably the triazenide **19**, formed by the addition of the azido group of Me_3SiN_3 to **15** [36].

15



17 (7)

19

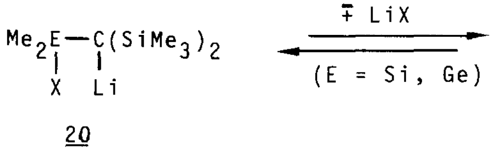
Further examples of reactions of the precursors $Me_2SiX{-}CLi(SiMe_3)_2$ which do not occur via $Me_2Si{=}C(SiMe_3)_2$ are provided by their thermolysis in tetrahydrofuran instead of diethyl ether. In this way, the disilacyclobutane **16** is formed by the thermal decomposition of $Me_2SiBr{-}CLi(SiMe_3)_2$ at −78°C in a second-order reaction. Also, the thermolysis of $Me_2SiX{-}CLi(SiMe_3)_2$ (X = Hal, SPh) in THF in the presence of dimethylbutadiene does not lead to the products **18** [14,54]. Thermal decomposition of this compound leads, through intermolecular elimination of LiX, to the reactive intermediate $Me_2SiXC(SiMe_3)_2SiMe_2CLi(SiMe_3)_2$ which tends to cyclise immediately with further elimination of LiX (cf. Scheme 1). Besides an increase in the basicity of the solvent, replacement of the Me_3Si substituents in $Me_2SiXCM(SiMe_3)_2$ by the less bulky hydrogen atoms promotes the intermolecular elimination of MX: even in diethyl ether, the thermolysis of Me_2SiXCH_2M does not occur via $Me_2Si{=}CH_2$ but via $Me_2SiXCH_2SiMe_2CH_2M$, with the formation of 1,1,4,4-tetramethyl-1,4-disilacyclobutane $[Me_2SiCH_2]_2$. Correspondingly, the thermolysis of this precursor in the presence of dimethylbutadiene leads to the disilacyclobutane and not to a [2 + 4] cycloadduct [14]. The intermediate formation of

$Me_2SiXCH_2SiMe_2CH_2M$ can be confirmed by ^1H NMR spectroscopy when one starts from Me_2SiXCH_2MgBr [17].

In contrast to the sila- and germa-ethene precursors R_2EXCMR_2 (with four R substituents), the sila- and germa-ketimine precursors R_2EXNMR contain only three R substituents. This leads to a considerable decrease in steric hindrance. The latter compounds, therefore, tend to give intermolecular instead of intramolecular elimination of LiX, and hence are of little preparative value as sources of sila- and germa-ketimines *.

Accordingly, the thermolysis of the precursors $>$EX–C(M)$<$ and EX–N(M) in the presence of reactants proceeds to the reaction products partly via unsaturated silicon and germanium compounds and partly by other routes. Minor changes in reaction conditions (e.g., change of solvent) often lead to a change in reaction mechanism. Even if the trapped products obtained from the various precursors are clearly explainable as adducts of unsaturated silicon and germanium compounds with the trapping agents, the involvement of unsaturated compounds in their formation must still be proved in all cases. In this respect, many such reactions mentioned in the literature and formulated as proceeding via unsaturated silicon and germanium compounds [4–10] should be thoroughly re-examined.

Decomposition of $R_2EX{-}YMR'_n$ (1). The position of the equilibrium (eq. a) (Scheme 1) is dependent on the basicity of X^-: a decrease leads to a shift towards the right-hand side. For a solution of the silaethene precursor **20** in diethyl ether the equilibrium, involving the silaethene **21** (E = Si), lies to the left-hand side for X = OR (R = Me, Ph), in between the left and right hand sides for X = SR, and probably also F **, and to the right hand side for X = Cl, Br, I [14,19].



$$\underset{\textbf{20}}{\mathrm{Me_2\underset{X}{E}{-}\underset{Li}{C}(SiMe_3)_2}} \underset{(E\ =\ Si,\ Ge)}{\overset{\mp\ LiX}{\rightleftharpoons}} \underset{\textbf{21}}{[\mathrm{Me_2E{=}C(SiMe_3)_2}]} \qquad (8)$$

On replacing the R in **20** (X = OR) with more electronegative groups than Me or Ph, the compounds $Me_2E(OR)CLi(SiMe_3)_2$ decompose, with the elimination of LiOR, either partly (R = e.g., 2,4,6-$Cl_3C_6H_2$, Ph_2PO, (PhO)PhPO, $(PhO)_2PO$) or fully (R = e.g. *p*-tolylSO_2). On the other hand, the elimination of LiOPh can be brought about by the addition of stoichiometric amounts of Me_3SiCl to an ethereal solution of **20** (X = OPh).

$$>XE{-}CLi< \; + \; Me_3SiCl \xrightarrow[(X\ e.g.\ OPh,\ F)]{} \; >E{=}C< \; + \; Me_3SiX \; + \; LiCl \qquad (9)$$

The same applies to other sila- and germa-ethene precursors $>$XE–C(Li)$<$ with X = e.g. OPh, F [17,16,19,49].

The rate of elimination of LiX from **20** in an ethereal solution obeys first-order

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* Intermediate formation of silaketimine by the thermal decomposition of $R_2SiFN(Li)R$ has been mentioned a number of times [31,33,34], but has never been proved conclusively.

** The equilibrium in eq. 8 does not develop clearly for X = F, because the LiF precipitates out of the reaction medium and as a result the equilibrium shifts towards the right-hand side.

TABLE 1

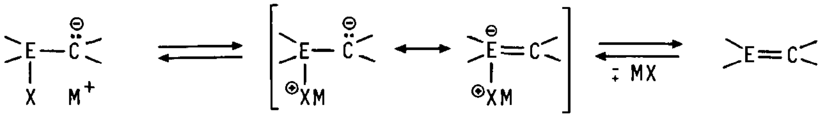
FIRST-ORDER RATE CONSTANTS k AND HALF LIVES $t_{1/2}$ OF THE DECOMPOSITION OF R_2XE–$C(M)(SiR'_3)_2$ IN DIETHYL ETHER AT T °C

Compound	T (°C)	$10^4 k$ (s^{-1})	$t_{1/2}$ (min)	Ref.
$Me_2SiXCLi(SiMe_3)_2$				
X = F	8	1.50	77	14
Cl	−90	2.06	56	14
Br	−78	1.54	75	14
I	−50	1.82	63	14
PhS [a]	34	6.35	18	14
Ph_2PO_2 [a]	15	0.60	192	14
$(PhO)_2PO_2$ [a]	−10	1.18	98	14
p-TolylSO_3	−105	1.10	105	14
$Bu^t_2SiFCLi(SiMe_3)_2$ [b]	100	[b]	[b]	16
$Me_2GeFCLi(SiMe_3)_2$	−30	0.51	135	19

[a] Thermolysis in the presence of 2,3-dimethyl-1,3-butadiene, which serves to shift the equilibrium in eq. 8 to the right. [b] $Bu^t_2SiFCLi(SiMe_3)_2$ isomerizes at 100 °C in a few min, forming the compound $Me_2SiFCLi(SiMe_3)(SiMeBu^t_2)$, which decomposes slowly (in h) with the elimination of LiF.

kinetics and increases for substituent X in the sequence $Ph_2PO_2 <$ F,SPh $< Ph_2PO_4 <$ I $<$ Br $<$ Cl $< p$-tolylSO_3 (Table 1). Also, $Me_2SiFCLi(SiMe_3)_2$ decomposes slightly more slowly than $Me_2GeFCLi(SiMe_3)_2$ but faster than $Bu^t_2SiFCLi(SiMe_3)_2$ (Table 1). The last compound eliminates LiF above 100 °C in a measurably fast decomposition. However, in the presence of Me_3SiCl at room temperature it is converted in THF into a silaethene which is stable at 0 °C (cf., eq. 9).

The mechanism of elimination of MX from compounds $\rangle$XE–C(M)$\langle$ is still not fully elucidated. Probably, the Lewis acid M^+, coordinated to the solvent molecules :D (e.g., Et_2O), first of all adds reversibly to the Lewis base X, leading to a weakening of the E–X bond. Then the MX is eliminated:



(10)

22

Therefore, the rate of MX elimination depends on the E–X bond strength, and on the effective Lewis acidity of M^+, which partly is determined by the Lewis basicity of the solvent molecules :D. Actually, the rate of loss of LiX diminishes with increasing basicity of the reaction medium (that is, in the direction, pentane > diethyl ether > tetrahydrofuran > crown ethers) * [14,37]. Also, $Me_2SiFCLi(SiMe_3)_2$ (with

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[*] $Me_2SiXCLi(SiMe_3)_2$ is formed slowly from $Me_2SiXCBr(SiMe_3)_2$ + LiR in the non-basic solvent pentane, but decomposes rapidly, whereas, in basic solvents it is formed rapidly but decomposes slowly. As a result of this, both the reactions occur simultaneously in the first case, but in the latter case, instead of slow intramolecular LiX-elimination a somewhat faster intermolecular LiX elimination is observed (see above). Thus, a solvent of intermediate basicity like diethyl ether is chosen as an appropriate medium for the formation of $Me_2SiXCLi(SiMe_3)_2$ and its decomposition into $Me_2Si{=}C(SiMe_3)_2$.

a stronger Si–X bond) decomposes much more slowly than $Me_2SiClCLi(SiMe_3)_2$ (with a weaker Si–X bond). The results show that $Me_2SiBrCLi(SiMe_3)_2$ decomposes faster than $Me_2SiClCLi(SiMe_3)_2$, and $Me_2SiFCLi(SiMe_3)_2$ faster than $Bu^t_2SiFCLi(SiMe_3)_2$ (Table 1), so that, besides M^+ coordination and the E–X bond strength, there are other effects (steric effects, solubility of MX, etc.), which also influence the rate of LiX elimination.

In this connection, it may be mentioned that $Bu^t_2SiF{-}CLi(SiMe_3)_2$ rearranges on heating at 100 °C (eq. 11) to the compound $Me_2SiFCLi(SiMe_3)(SiMeBu^t_2)$, which

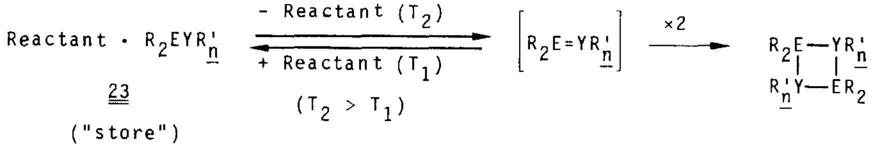
(11)

decomposes slowly with the elimination of LiF [16]. The isomerization shown in eq. 11 could also proceed through an intermediate step of the type **22** (eq. 10), because it is known that the intramolecular organo/halogen exchange process is acid-catalysed [27,38,39].

Evidently more stable towards LiX-elimination than the compounds $\rangle$XE–C(Li)$\langle$ are the comparably substituted compounds $\rangle$XE–N(Li)– * [32]. In view of this, as well as for the reasons discussed earlier, these sila- and germa-ketimine precursors are of little importance.

2.2. *Cycloreversion method*

Sila- and germa-ethenes can be prepared under very mild conditions by the salt elimination method. As a result of this and of its wide applicability, this method of preparation has considerable importance **. A definite disadvantage of this method is the use as precursors of the organometallic compounds $\rangle$XE–CM$\langle$ because, on account of their sensitivity towards hydrolysis, oxidation and thermolysis, they are difficult to handle. In addition to this, many of the reagents for trapping the sila- and germa-ethenes are unstable towards bases and react in an unwanted manner even with the precursors for the unsaturated compounds, (cf., e.g. eq. 7). In view of this, we have investigated the possibility of storing the unsaturated silicon and germanium compounds with the help of appropriate reactants, which bind the unsaturated compounds at low temperatures T_1 and set them free at higher (but not too high) temperatures $T_2 > T_1$:



(12)

Besides the unsaturated silicon and germanium compounds, which may dimerize irreversibly ***, the decomposition of the precursors **23** (subsequently referred to as

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* Still more stable are the compounds $\rangle$XE–OLi [40].

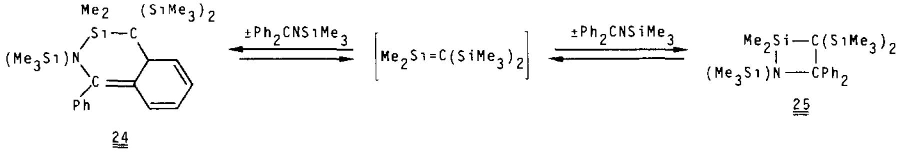
** Preparation of sila- and germa-ethenes with small substituents at the double bond is still quite difficult [17], but it should be possible using this method under appropriate conditions.

*** Stable compounds, $R_2E{=}YR'_n$, are formed when the substituents R and R′ are bulky (cf. Section 3).

"stores") also leads to reactants which combine reversibly with the unsaturated silicon and germanium compounds to form **23**. Therefore the equilibrium represented in eq. 12 shifts more to the left-hand side with increasing decomposition of **23**, that is with increasing concentration of the reactant. This results in a decrease in the first-order rate constant for the formation of the dimer in the same direction. Therefore, the "stores" are different from other precursors (subsequently referred as "sources"), which like compounds of the type $R_2EHal\text{–}CM(SiMe_3)_2$, decompose irreversibly and, therefore, with unchanged first-order rate constants, into the unsaturated silicon or germanium compounds and reactants (e.g., MX). Naturally, the same is also true for the decomposition of "stores" in the presence of fast and irreversibly reacting trapping agents for the unsaturated silicon and germanium compounds. The thermolyses of stores are always endothermic whereas thermolyses of sources may be endothermic or exothermic reactions (cf. Fig. 1).

Stores and sources of the unsaturated compounds $R_2E{=}C(SiR_3)_2$ and $R_2E{=}N(SiR_3)$, which behave according to the cycloreversion principle, are described:

Sila- and germa-ethenes. If the silaethene $Me_2Si{=}C(SiMe_3)_2$ is generated from one of the lithium-containing sources listed in Table 1, in the presence of *N*-trimethylsilyldiphenylketimine $Ph_2C{=}N(SiMe_3)$, then the yellow [2 + 4] and colorless [2 + 2] cycloadducts **24** and **25** are formed [15].



(13)

These substances can be isolated and are stable at room temperature. They both rearrange at about 60 °C into an equilibrium mixture containing 5% of **24** and 95% of **25** * [15]. As shown by kinetic investigations and competitive trapping reactions [37], the rearrangement takes place by way of [2 + 4] and [2 + 2] cycloreversions which involve $Me_2Si{=}C(SiMe_3)_2$. The intermediate formation of the silaethene by the thermolysis of **24** can be shown directly if **24** is sublimed at low pressure through a quartz tube into the ion source of a mass spectrometer. The molecular peak of $Me_2Si{=}C(SiMe_3)_2$ is observed on heating the quartz tube.

Besides the cycloadducts, a solution of the isomeric mixture **24**/**25** also always contains small amounts of $Me_2Si{=}C(SiMe_3)_2$ and $Ph_2C{=}N(SiMe_3)$. These small amounts increase with rising temperature of the solvent, but even at higher temperatures the presence of $Me_2Si{=}C(SiMe_3)_2$ cannot be shown by NMR-spectroscopy. Beyond a certain temperature, the concentration of silaethene is so large that its dimerization occurs at a measurable rate [15]. Formation of the silaethene dimer $[Me_2SiC(SiMe_3)_2]_2$ is observed on heating the cycloadducts **24** or **25** at 120 °C for a long period **. The adducts **24** and **25** are neither water- nor oxygen-sensitive and

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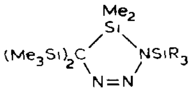
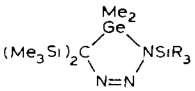
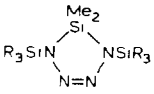
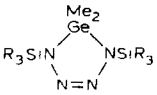
* Values for the equilibrium **24** ⇄ **25** at 80 °C in Et_2O are: $K = 7.3$, ΔH -9.1 kJ/mol, ΔG -5.8 kJ/mol, $k_{\rightarrow}$ 1.78×10^{-4} s^{-1} ($t_{1/2}$ 64 min), $k_{\leftarrow}$ 0.214×10^{-4} s^{-1} ($t_{1/2}$ 537 min) [37].

** In addition, a yellow insertion product of the silaethene into the Si–N bond of $Ph_2CNSiMe_3$ is formed (cf. Section 4.1).

TABLE 2. FIRST-ORDER RATE CONSTANTS k, HALF LIVES $t_{1/2}$, AND PRODUCTS OF DECOMPOSITION OF SILA- AND GERMA-TRIAZOLINES AND TETRAZOLINES IN DIETHYL ETHER AND BENZENE (TOLUENE) AT T °C

Compound		Diethyl ether			Benzene, toluene			Thermolysis in Et_2O		Ref.
Formula	SiR_3	T (°C)	10^4k (s^{-1})	$t_{1/2}$ (min)	T (°C)	10^4k (s^{-1})	$t_{1/2}$ (min)	% eq. 15a[a] or 17a	% eq. 15b[a] or 17b	
 **26**	$SiMe_3$	−12.0	3.40	34[b]	−12.0	1.60	72	43	57	18
	$SiMe_2Bu^t$	−14.5	4.62	25	−14.5	5.50	21	56	44	18
	$SiMeBu^t_2$	−14.5	7.22	16	−14.5	9.63	12	100	–	18
	$SiBu^t_3$	[c]			[c]			100	–	18
	$SiPh_3$	[c]			[c]			30	70	18
	$SiMe_2N(SiMe_3)_2$	−14.5	0.14	8	−14.5	0.23	5	70[e]	30	18
 **26**	$SiMe_3$	70	4.85	24	70	6.36	18	100	–	19
	$SiMe_2Bu^t$	70	7.20	16	70	7.58	15	100	–	19
	$SiMeBu^t_2$	70	3.13	37	70	4.95	23	100	–	19
	$SiBu^t_3$									
	$SiPh_3$									
	$SiMe_2N(SiMe_3)_2$	60	11.9	10	50	1.82	64	100	–	19
 **28**	$SiMe_3$	135	2.24	51	130	1.74	66	(?)	(?)	43
	$SiMe_2Bu^t$	130	3.45[d]	34	130	4.12[d]	28	100	–	18
	$SiMeBu^t_2$	130	3.91[d]	30	130	4.53[d]	26	100	–	18
	$SiBu^t_3$	101	2.38[d]	49	101	3.45[d]	34	100	–	18
 **28**	$SiMe_3$	[g]			120	3.28	35	100[f]	–	19
	$SiMe_2Bu^t$	[g]			120	> 0.8	< 150	100[f]	–	19
	$SiMeBu^t_2$	[g]			140	> 0.2	< 500	100[f]	–	19
	$SiBu^t_3$	[g]								

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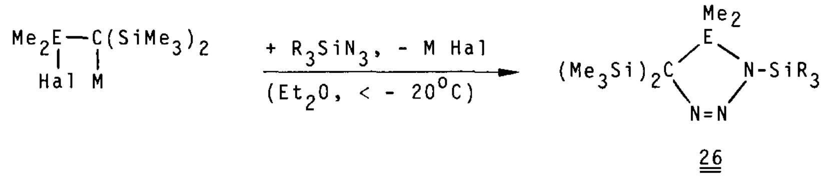
[a] Increasing the temperature of the thermolysis raises the proportion of eq 15a and lowers the proportion of eq 15b. [b] At −14.5 °C: k 1.60×10^{-4} s^{-1}, $t_{1/2}$ 72 min. [c] Not isolated. [d] Thermolysis in the presence of acetone, which serves to shift the equilibrium in eq 17a to the right. [e] Thermolysis of pure substance follows exclusively eq. 15a. [f] In benzene. [g] Not studied.

behave above 60 °C as practicable, easily manageable, "stores" for $Me_2Si{=}C(SiMe_3)_2$. For example, the products **18a** and **18b** (cf. Scheme 2) are obtained in a simple manner by refluxing a solution of **25** and 2,3-dimethyl-1,3-butadiene in toluene ($t_{1/2}$ 6.2 h at 80 °C in Et_2O).

Other stores of types **24** and **25** have been prepared with other ketimines (e.g., $Ph_2C{=}NPh$) and other silaethenes (e.g., $Ph_2Si{=}C(SiMe_3)_2$) * [17,37].

Sila- and germa-ketimines. We have observed that sila- and germa-triazolines **26** can act as good "sources" for sila- and germa-ketimines of the type $[Me_2E{=}NSiR_3]$ [15,18,19]. These are formed by the reaction of $Me_2EXCM(SiMe_3)_2$ (X = e.g., hal) with R_3SiN_3 (eq. 14; cf. Section 4.3) at lower temperatures in Et_2O, and are isolable in the form of colorless, crystalline compounds [41]. These compounds decompose (in some cases below 0 °C, when E = Si, in some cases above room temperature, when E = Ge) with [2 + 3] cycloreversion, as in eq. 15, and also with rearrangement into **27** (eq. 15b). (For the rate constants and half-lives of the decomposition of **26**, as well as the reaction ratios, eq. 15a/15b, see Table 2) **.



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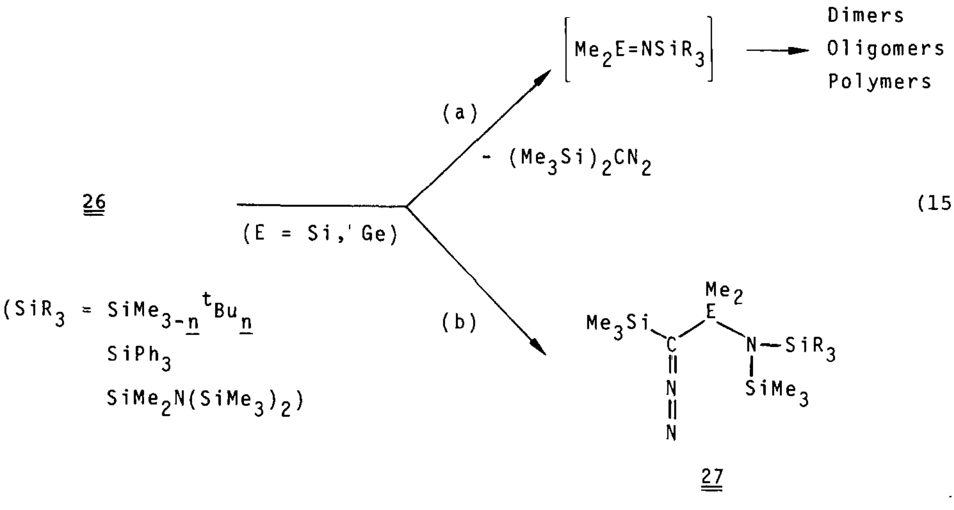

Sila- and germa-ketimines, generated according to eq. 15a, react with azides R_3SiN_3 by the route shown in eq. 16 to form colorless, crystalline sila- and germa-triazolines **28** [18,19,41], which act as "stores" (eq. 17a) and release the

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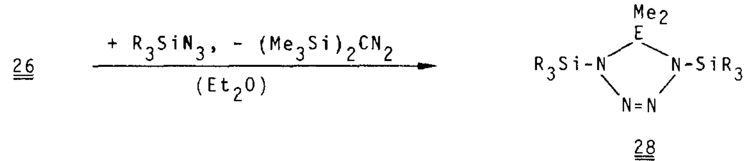
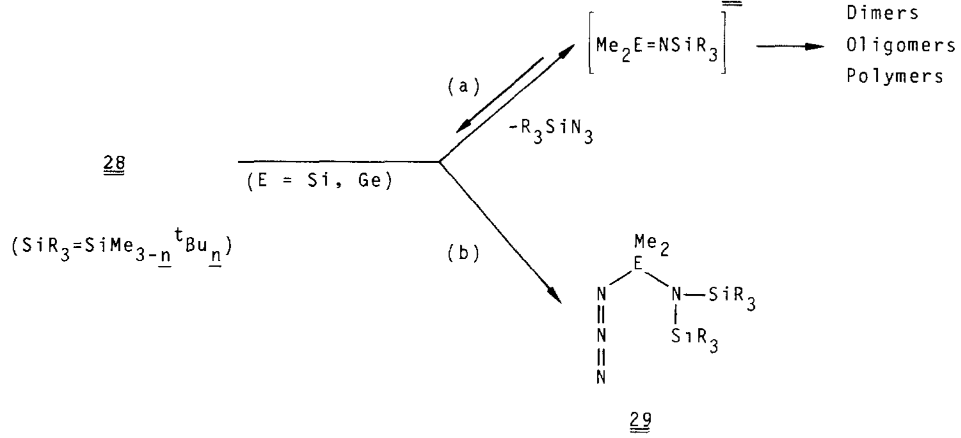
* Many of the silaethene precursors (e.g., silacyclobutanes, allylsilanes) mentioned in the literature belong in principle to the group of silaethene stores [4,8]. Of course, their use for preparative purposes is not very simple, because of the very high decomposition temperatures.

** Ketimines $Me_2E{=}NR$ with *N*-bonded organic groups (e.g., *p*-tolyl) can also be generated via triazolines by using $Me_2E{=}C(SiMe_3)_2 + RN_3$ [28].

unsaturated compounds [$Me_2E{=}NSiR_3$] at higher temperatures *.



(16)



(17)

The increasing proportion of the azide R_3SiN_3 formed as the decomposition of **28** progresses, shifts the equilibrium in eq. 17a (as already discussed) increasingly towards the left-hand side. Accordingly the total thermolysis of **28** with $ER_3 = EMe_{3-n}Bu^t_n$ (E = Si, $n > 1$; E = Ge, $n > 0$) occurs, in the absence of sila- and germa-ketimine trapping agents, only at comparatively high temperatures (around 200 °C). On the other hand, the tetrazolines **28** with $ER_3 = EMe_{3-n}Bu^t_n$ (E = Si, $n = 0,1$; E = Ge, $n = 0$) decompose faster and invariably with first-order rate constants, with isomerization into the azides **29**. Formation of the latter compounds may occur by a direct route or by an indirect route via [$Me_2E{=}NSiR_3$]. Competitive trapping experiments support the second possibility ** [18,19]. (For the rate constants and half-lives of decomposition of **28**, as well as the ratios of the reactions shown in eqs. 17a and b, see Table 2.)

3. Stability and thermolysis

The unsaturated silicon and germanium compounds $R_2E{=}YR_n$ (E = Si, Ge; Y = C, N, etc.) are only reaction intermediates, generated from appropriate starting materials ("sources", "stores"). They react, depending on the type of substituent R (which determine the energy content of the unsaturated systems in the ground state as well as in the transition state of the decomposition (Fig. 2)), more or less exothermically (cf., thermodynamic aspects) as well as more or less rapidly (cf., kinetic aspects) to the secondary products (cf., chemical aspects).

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* Sila- and germa-ketimines, generated according to eq. 15a, may react with N_2O to form [2+3] cycoadducts, which then act as sila- and germa-ketone precursors [19,30].

** Insertion of [$Me_2E{=}NSiR_3$] into the Si–N bond of R_3SiN_3 (eq. 17c) occurs only in the cases of reactants with less bulky R-groups.

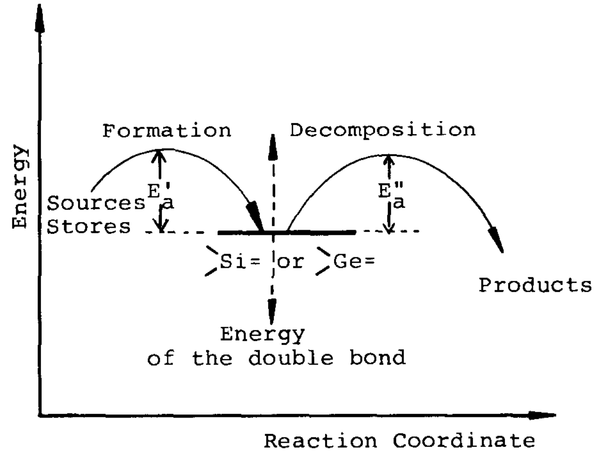
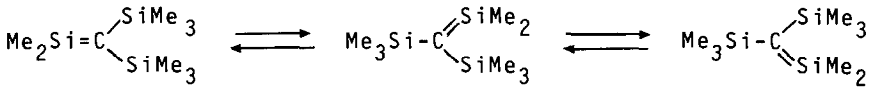


Fig. 2. "Stability" of unsaturated silicon and germanium compounds; reaction profile for their formation and decomposition.

3.1. Thermodynamic aspects

Just like many unsaturated carbon compounds, unsaturated silicon and germanium compounds are thermodynamically unstable with respect to di-, oligo- or poly-merization. Thus, sila- and germa-ethenes dimerize spontaneously. Similarly, ethylene polymerizes with release of energy. Apart from a few exceptions (e.g., N≡N, O=C=O), it is generally true that $p\pi$–$p\pi$ bonds between main group elements change to σ bonds with gain in energy, if they are not additionally stabilized. Thus, for example, benzene has a resonance stabilized π-system and is thermodynamically stable towards polymerization.

Little is known about the stabilization or destabilization of unsaturated silicon and germanium systems through steric, inductive and resonance effects of substituents. A study of the intramolecular rearrangement of $p\pi$–$p\pi$ double bonds might provide some information. Thus, the methyl groups of the silaethene $Me_2Si{=}C(SiMe_3)_2$ migrate with a rapid shift of the SiC double bond from silicon atom to silicon atom.



$$Me_2Si{=}C(SiMe_3)(SiMe_3) \rightleftarrows Me_3Si{-}C({=}SiMe_2)(SiMe_3) \rightleftarrows Me_3Si{-}C(SiMe_3)({=}SiMe_2) \qquad (18)$$

This process has been made "evident" by heating the "silaethene store" $(CD_3)_2SiC(SiMe_3)_2 \cdot Ph_2CNSiMe_3$ (cf. **24**,**25**) in C_6D_6 at 120 °C [17]. At this temperature, it gives (in a reversible reaction) a small amount of the silaethene (cf. eq. 13), whose concentration remains so small that dimerization does not occur. After five hours of this thermal treatment, the NMR spectra of the store show that the CD_3 groups of the silaethene, held in the store, are distributed among the three silicon atoms in the expected statistical proportions *. Methyl group migration of the type

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* The half-life for a methyl-rearrangement step is ca. 30 min at 120 °C.

shown in eq. 18 was, in fact, previously observed by Eaborn et al. [43] in the case of $Ph_2Si{=}C(SiMe_3)_2$ (generated by gas phase thermolysis of $Ph_2SiFC(SiMe_3)_3$ at 450 °C), and we have also observed it in the case of $Bu^t_2Si{=}C(SiMe_3)_2$ [37]. The latter silaethene, formed by LiF-elimination from $Bu^t_2SiFCLi(SiMe_3)_2$ in the presence of Me_3SiCl at room temperature, is a short-lived, NMR spectroscopically-detectable species, which rapidly rearranges into the "stable" silaethene $(MeBu^t_2Si)C(SiMe_3){=}SiMe_2 \equiv Me_2Si{=}C(SiMe_3)(SiMeBu^t_2)$. Callote models indicate that the substituents on the Si=C double bond in this silaethene offer less steric hindrance than in the unrearranged silaethene. Evidently the "pressure" of the substituents causes the rearrangement: increasingly adverse steric influences of double bond substituents raise the angular strain and with that the energy content of the double bond.

Unsaturated silicon and germanium compounds with mixed substituents, $R_2E{=}Y(SiR'_3)_n$ (E = Si, Ge; Y = C, N) have been rearranged to the most stable double-bonded system through organic group migrations, as in eq. 18, at as low a temperature as possible. From the position of the double bonded substituents in these systems inferences can be drawn in a simple way about their effects upon the energy content.

The kinetic data in Table 2 show that silatriazolines decompose faster by [2 + 3] cycloreversions than the comparable germatriazolines *, and this could indicate that the silaketimines $Me_2Si{=}NSiMe_{3-n}Bu^t_n$ are more stable than the germaketimines $Me_2Ge{=}NSiMe_{3-n}Bu^t_n$. Also, the rate of formation of silaketimines from silatriazolines increases with an increasing number of t-butyl groups, which, as is known, exert an electron-releasing inductive effect **. Possibly, therefore, the energy content of the silaketimines decreases with increasing n. This follows also from the thermolysis of silatetrazolines with different silyl groups $SiMe_{3-n}Bu^t_n$ on the ring: the silaketimine with the larger number, n, of t-butyl groups is the one preferentially formed by [2 + 3] cycloreversion [18]. Since the initial and transition states of this [2 + 3] cycloreversion cannot be exactly compared energetically, the statements are naturally somewhat uncertain.

The double bond system of unsaturated silicon and germanium compounds may also be stabilized mesomerically. However, the incorporation of silicon or germanium in the aromatic system of benzene has not led to thermodynamic stabilization of unsaturated silicon and germanium compounds (sila- and germa-benzene) relative to their dimerization [23,44,45].

3.2. *Kinetic aspects*

In contrast to unsaturated carbon compounds, unsaturated silicon and germanium compounds are normally kinetically unstable with respect to di-, oligo- or poly-merization. The kinetic stability of the carbon compounds, which like the others, are thermodynamically unstable (see above), depends on the fact that no pathway with a favourable activation energy exists to the di-, oligo- or poly-merization products.

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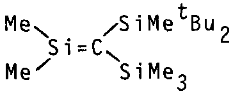
* As compared with $Me_2E{=}NSiMe_3$ (E = Si, Ge), the ketimines $Me_2E{=}NCMe_3$ are formed more slowly by [2 + 3] cycloreversion from the sila- and germa-triazolines.

** As according to the equations $>E{=}C< + -N{=}C< \rightarrow >E{=}N- + >C{=}C<$ and $>E{=}N- + O{=}C< \rightarrow >E{=}O + -N{=}C<$, sila- and germa-ethenes give sila- and germa-ketimines, which then give sila- and germa-ketones, the energy content of the double bond obviously decreases in the same direction.

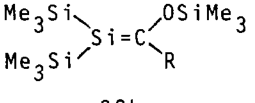
Thus, the thermal supra-suprafacial [2 + 2] cycloaddition of two ethylenes $>C=C<$ is forbidden on the basis of the non-conservation of orbital symmetry [46]. As a consequence of this, a high activation energy of about 200 kJ/mol has been found for this cyclodimerization. In case of the unsaturated silicon and germanium compounds $R_2E{=}YR'_n$, because of the lower symmetry of the reactive centres, the symmetry restriction for a [2 + 2] cycloaddition is lowered [4,8,47]. The activation energy for silaethene dimerization is estimated to be ca. 40 kJ/mol.

Although thermodynamically stable unsaturated silicon and germanium compounds $R_2E{=}YR'_n$ (E = Si, Ge; Y = C, N, etc.) are unlikely (see above), kinetic stabilization of them is possible. Dimerization involves an increase in the coordination number of the double bonded atoms, E and Y, by one in each case. Bulky substituents R and R′ in $R_2E{=}YR'_n$ may thus raise the activation energies E_a'' (cf., Fig. 2) of dimerization or polymerization, and so hinder the reactions of the unsaturated silicon and germanium compounds: with increasing substitution of the title compounds $R_2E{=}C(SiR_3)_2$ and $R_2E{=}N(SiR_3)$ by bulky organic groups R (e.g., Bu^t), that is, by increasing the steric hindrance, the kinetic stability must increase *.

The replacement of two of the Me groups of the Me_3Si substituents of the reactive silaethene $Me_2Si{=}C(SiMe_3)_2$ (which dimerizes even at −100 °C) [15] by two t-butyl groups leads to a considerable increase in kinetic stability: the silaethene **30a** decomposes comparatively slowly to give secondary products [16]. After the discovery of the compounds **30b** (R = 1-adamantyl, CEt_3) by Brook et al. [48], the air-



30a



30b

and hydrolysis-sensitive and comparatively “stable” silaethene **30a** is the second type of compound of this kind. It is almost at the limit of isolability and, in contrast to **30b**, has the high reactivity shown by otherwise not isolable silaethenes. Accordingly, it forms (mostly in very fast reactions) insertion and ene reaction products, as well as [2 + 2], [2 + 3] and [2 + 4] cycloadducts (cf., ref. 16 and Section 4.)

3.3 Chemical aspects

The mostly short-lived unsaturated silicon and germanium compounds $R_2E{=}YR'_n$ (E = Si, Ge; Y = C, N) normally stabilize themselves through dimerization, to give $[R_2EYR_n]_2$, which contain EYEY four-membered rings [4,8,10]. The formation of such “head to tail dimers” is observed also in the systems $R_2E{=}C(SiMe_3)_2$ (R = Me, Ph) and $R_2E{=}N(SiMe_{3-n}Bu^t_n)$ which are being considered here [14,18,19,21]. If the double bond system is only slightly protected sterically, then oligomers and polymers of the reactive intermediate, $R_2E{=}YR_n$, can also be formed. Thus, the germaketi-

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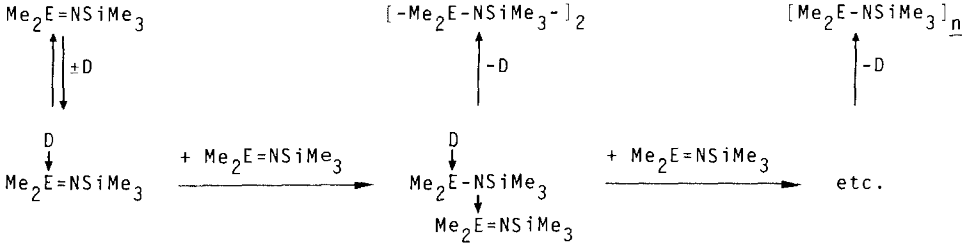
* Nothing is known about the kinetic stabilization of unsaturated silicon and germanium compounds by means of inductive or mesomeric effects (stabilization may be due to a decrease in the polarity of the unsaturated system, which in turn would lead to an increase of the symmetry restriction to [2+2] cycloaddition).

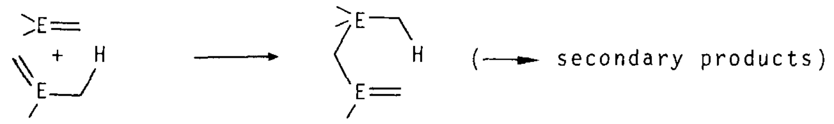
mine $Me_2Ge{=}NSiMe_3$ (from germatriazoline) reacts in diethyl ether at 70 °C to form (in addition to the dimer) the polymers $[Me_2GeN(SiMe_3)]_n$, which are insoluble in organic media (the same is true, but is less pronounced, with $Me_2Si{=}NSiMe_3$) [19,28]. Possibly Et_2O acts as a polymerization catalyst (Scheme 3, D = e.g. Et_2O; E = Si, Ge).

SCHEME 3

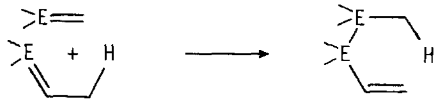


None of the title compounds investigated by us dimerize to give products which contain YEEY four-membered rings. The formation of such a "head to head dimer" has however been observed with silaethenes of type **30b** (R = e.g., Ph, Bu^t) [48].

If one of the groups R or R′ in the compound $R_2E{=}YR'_n$ is an alkyl group with hydrogen in the α-position (e.g., methyl) then, in principle, a "dimerization" of the unsaturated system, by an ene reaction, is also conceivable.



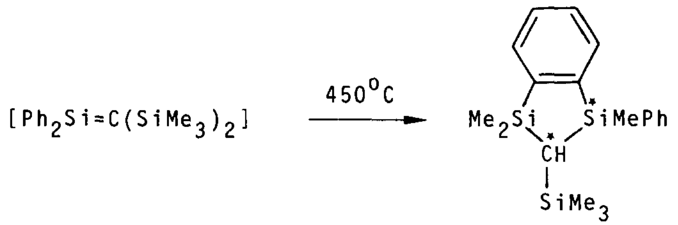
(19a)



(19b)

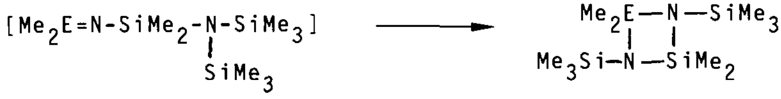
According to the results reported so far, the title compounds do not stabilize themselves as in eq. 19a. A stabilization according to eq. 19b has been reported in the case of the silaethene **30b** (R = Me) [48].

Under special conditions (high temperatures, reactive or bulky substituents at the E=Y double bonded system, etc.), unsaturated silicon and germanium compounds also stabilize themselves by rearrangement. Thus, decomposition of the compound $Ph_2SiFC(SiMe_3)_3$ in the gas phase at 450 °C gives, ultimately, the products **31a**, via $Ph_2Si{=}C(SiMe_3)_2$ [43], and sila- and germa-triazolines with appropriate substituents give, at room temperature, the products **31b**, via $Me_2E{=}NSiMe_2N(SiMe_3)_2$ [18,19]. Obviously, **31a** is the product of insertion of the Si=C system of $Me_2Si{=}C(SiMe_3)(SiMePh_2)$ (derived from $Ph_2Si{=}C(SiMe_3)_2$ through methyl group migration) into the C–H bond of a phenyl ring, and **31b** is the product of insertion of the E=N system into an Si–N bond of the $N(SiMe_3)_2$ group in $Me_2E{=}N{-}SiMe_2N(SiMe_3)_2$ (cf. Section 4.1).



31a

(19c)



31b

(19d)

4. Reactivity

Unsaturated silicon and germanium compounds, generated from appropriate starting materials in the presence of reactants ("trapping agents"), often combine with these reactants more rapidly, to form secondary products, rather than dimerizing, because the activation barrier of the trapping reactions is lower than that of the dimerization reaction (Fig. 3). This offers an opportunity to study the reactivity of unsaturated silicon and germanium compounds *.

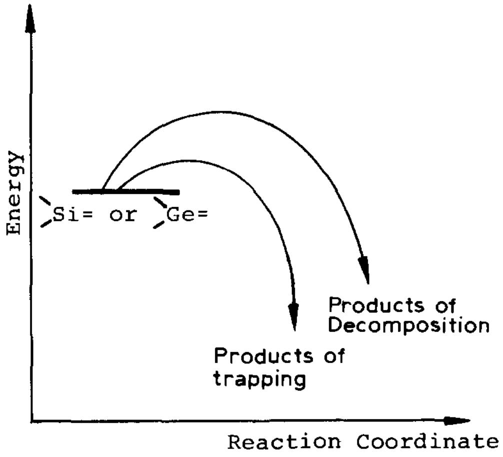


Fig. 3. Reaction profile for the decomposition or trapping of unsaturated silicon or germanium compounds.

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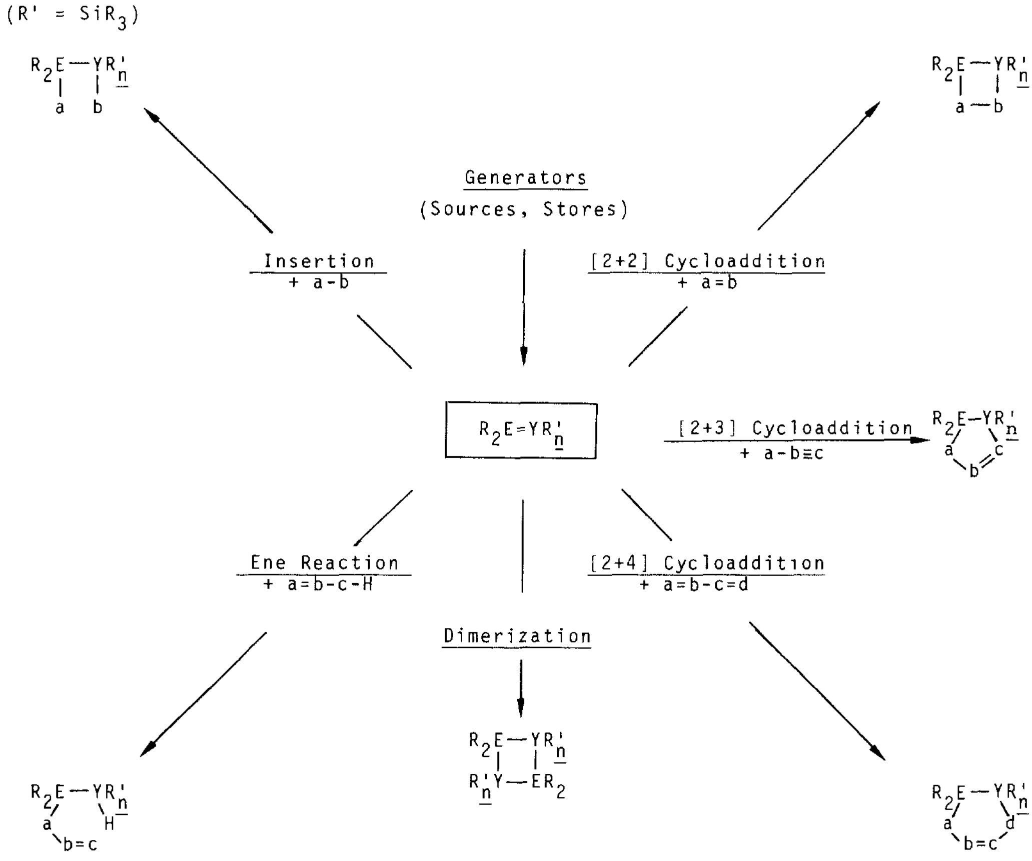
[*] With smaller differences in activation barriers, the dimers of unsaturated silicon and germanium compounds are formed as well as the products with trapping agents, in more or less large yields (the kinetically more unstable systems, therefore, are more difficult to trap). The unwanted side reactions can be reduced by adding a sufficient excess of trapping agent, by the slow generation of the unsaturated compounds, and by increasing the reaction temperature.

Our investigations on the reactivity of the title compounds have led to the results summarized in Scheme 4. According to this, the unsaturated systems $R_2E{=}C(SiR_3)_2$ and $R_2E{=}N(SiR_3)$ (E = Si, Ge) add to polar a–b single bonds of many compounds with the formation of insertion products, combine with a=b–c–H double bond systems to give ene reaction products, and react with the unsaturated systems a=b, a–b=c and a=b–c=d to give [2 + 2], [2 + 3] and [2 + 4] cycloadducts. All the investigated reactions support the view that the unsaturated silicon and germanium compounds concerned are not diradicals but possess $p\pi$–$p\pi$ multiple bonds analogous to those in unsaturated carbon compounds.

SCHEME 4

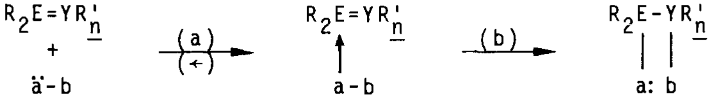


Characteristic examples of insertion, ene reactions and cycloadditions are discussed below for the unsaturated systems, which were generated as follows:

System	Precursor	Name
$R_2E{=}C(SiR_3)_2$	$Me_2SiC(SiMe_3)_2 \cdot Ph_2CNSiMe_3$	Silaazetdine (**25**)
	$R_2EX{-}CM(SiR_3)_2$	Salt sources (**6**)
$R_2E{=}N(SiR)_3$	$R_2EC(SiR_3)_2 \cdot R'N_3$	Sila- or germa-triazolines (**26**)
	$R_2EN(SiR_3) \cdot R'N_3$	Sila- or germa-tetrazolines (**28**)

4.1. Insertion reactions

According to present ideas, the insertion of unsaturated silicon and germanium compounds $R_2E{=}YR'_n$ (E = Si, Ge; Y = C, N, etc.) into polar a–b single bonds, or, synonymous, addition of a–b groups to the double bond of $R_2E{=}YR'_n$ (see below and refs. 4,8,10), occurs in steps (single step insertion reactions are not allowed on the basis of the non-conservation of orbital symmetry [46]): $R_2E{=}YR'_n$ acts as a Lewis acid, and in the first reaction step it interacts with the more electronegative atom a of the a–b group acting as a Lewis base (eq. 20a), the Lewis acid/base complex **32** so-formed rearranges in the second reaction step to give the end product of the insertion reaction. Therefore, the rearrangement in eq. 20b can be interpreted as an intramolecular nucleophilic substitution of atom a on the more electropositive Lewis acid-acting atom b of the a–b group. Eq. 20b co-determines the rate of consumption of $R_2E{=}YR'_n$ if the complex-forming eq. 20a is reversible.

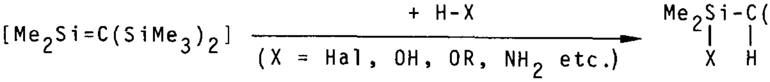


$$\begin{array}{c}R_2E{=}YR'_n\\ +\\ \ddot{a}{-}b\end{array} \xrightarrow[(\leftarrow)]{(a)} \begin{array}{c}R_2E{=}YR'_n\\ \uparrow\\ a{-}b\end{array} \xrightarrow{(b)} \begin{array}{c}R_2E{-}YR'_n\\ |\quad |\\ a{:}\ b\end{array} \qquad (20)$$

32

The formation of an adduct **32** has been confirmed. The stable silaethene $Me_2Si{=}C(SiMe_3)(SiMeBu^t_2)$, **30a**, forms an adduct **30** · THF with tetrahydrofuran in which, according to an X-ray structure analysis [49], the tetrahydrofuran is bonded through its oxygen atom to the unsaturated silicon atom of **30a**.

Insertion into element-hydrogen bonds. If a solution of the silaethene store **25** (silaazetidine) in moist tetrahydrofuran is heated at 90 °C, the product **33** (X = OH) of insertion of the silaethene $Me_2Si{=}C(SiMe_3)_2$ into an OH bond of water * is formed [37], and this, in the case of a limited amount of water, reacts further with the $Me_2Si{=}C(SiMe_3)_2$ to give an insertion product **33** (X = $(Me_2Si)_2CH{-}SiMe_2O$):



$$[Me_2Si{=}C(SiMe_3)_2] \xrightarrow[(X\,=\,Hal,\ OH,\ OR,\ NH_2\ etc.)]{+\ H{-}X} \begin{array}{l}Me_2Si{-}C(SiMe_3)_2\\ \quad |\qquad |\\ \quad X\qquad H\end{array} \qquad (21)$$

33

That the water does not react directly with **25** is indicated by the fact that the formation of **33** occurs at the same rate as the formation of other trapped products from $Me_2Si{=}C(SiMe_3)_2$, generated from **25**.

In a manner analogous to that of water, hydrogen chloride, ammonia, alcohols, thioalcohols and amines ** react with $Me_3Si{=}C(SiMe_3)_2$ (from **25**) to give the insertion products **33** (X = RO, RS, RHN). For these reactions, the relative reactivities shown in Fig. 4, have been obtained from competitive trapping experiments [17]. Thus, and completely in agreement with the nucleophilic addition mechanism

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* Besides this, the ketimine $Ph_2C{=}NSiMe_3$ is formed, and slowly hydrolyses to give $Ph_2C{=}NH$ and $(Me_3Si)_2O$.

** Even the insertion of $Me_2Si{=}C(SiMe_3)_2$ into the α-C–H bond of pyridine is possible [28].

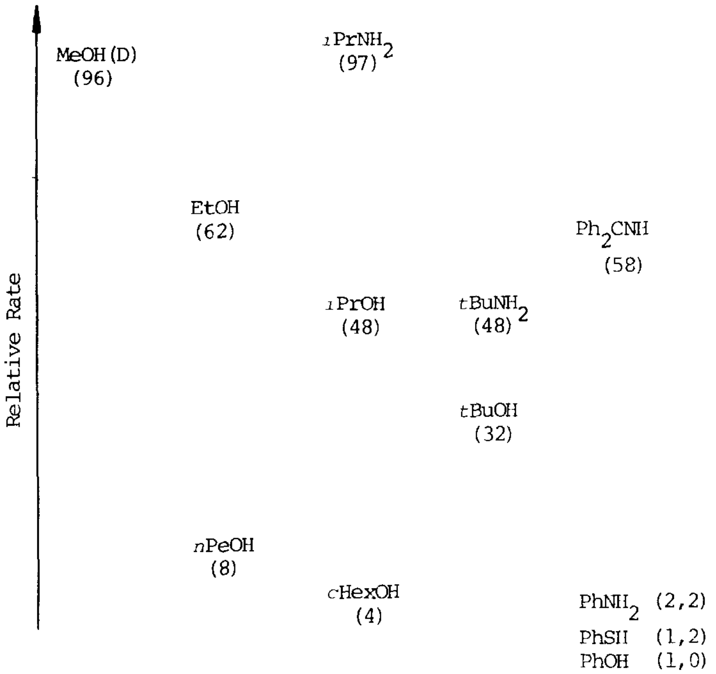

Fig. 4. Relative rates (in brackets) of insertion of $Me_2Si{=}C(SiMe_3)_2$ (generated from **25**) into the O–H, S–H and N–H bonds of alcohols, thioalcohols, and amines at 100 °C in Et_2O [17]. (Reactivity with PhOH compared with dimethylbutadiene, 30 : 1, cf., Fig. 6. n-PeOH = n-pentanol, c-HexOH = cyclohexanol.)

outlined in eq. 20, the more basic methanol (pK_a 16) reacts faster than the less basic phenol (pK_a 10). Had it been an electrophilic addition mechanism [50], as in the case of the addition of alcohol to an organic double bond, the more acidic phenol would have added faster than the less acidic methanol. The postulated nucleophilic addition mechanism is also supported by the agreement of the rates of addition of MeOH and MeOD [17] *, and the finding that even acetic acid reacts more slowly than methanol with $Me_2Si{=}C(SiMe_3)_2$ (with formation of **33**, $X = CH_3CO_2$). Besides basicity, the addition rates are also considerably influenced by steric factors. Thus, the more basic pentanol (pK_a 17) reacts with $Me_2Si{=}C(SiMe_3)_2$ much more slowly than methanol (pK_a 16) and the more basic t-butanol (pK_a 19) more slowly than 2-propanol (pK_a 18). Amines, on the other hand, add slightly faster to $Me_2Si{=}C(SiMe_3)_2$ than the comparably substituted alcohols; obviously they develop a higher Lewis basicity relative to the unsaturated compound [17,37]. Other unsaturated compounds in the $R_2E{=}C(SiMe_3)_2$ and $R_2E{=}N(SiR_3)$ series can be similarly inserted into element–hydrogen bonds; for example, the stable silaethene $Me_2Si{=}C(SiMe_3)(SiMeBu^t_2)$ combines with water to form $Me_2Si(OH)$-$CH(SiMe_3)(SiMeBu^t_2)$ [16], and the silaketimine $Me_2Si{=}N(SiBu^t_3)$ (from silatetrazo-

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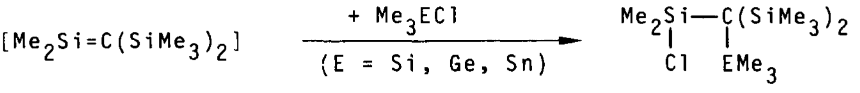
* In this case, the rate of insertion is determined only by the reaction in eq. 20a. The same holds certainly for other insertions into element–hydrogen bonds.

line) gives $\mathrm{Me_2Si(OR)NH(SiBu^t_3)}$ ($\mathrm{R = H}$ or $\mathrm{Me_2SiNH(SiBu^t_3)}$) [30].

Insertion into element–halogen bonds. The silaethene $\mathrm{Me_2Si{=}C(SiMe_3)_2}$, generated from **25**, inserts directly and quantitatively into the Sn–Cl bond of $\mathrm{Me_3SnCl}$ to form **34** (E = Sn). $\mathrm{Me_3GeCl}$ reacts more slowly and no longer quantitatively, and besides **34** (E = Ge), typical thermolysis products of silaazetidine **25** appear in this case (cf. Section 2.2). Practically no insertion of $\mathrm{Me_2Si{=}C(SiMe_3)_2}$ into the Si–Cl bond of $\mathrm{Me_3SiCl}$ occurs [15,17].



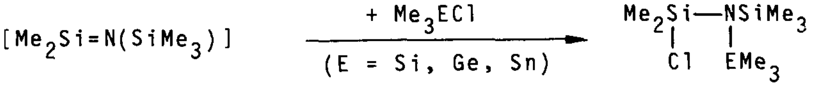
$$[\mathrm{Me_2Si{=}C(SiMe_3)_2}] \xrightarrow[(\mathrm{E\ =\ Si,\ Ge,\ Sn})]{+\ \mathrm{Me_3ECl}} \begin{array}{ll} \mathrm{Me_2Si} & \!\!—\ \mathrm{C(SiMe_3)_2} \\ \quad\ | & \quad\ \ | \\ \ \ \mathrm{Cl} & \quad \mathrm{EMe_3} \end{array} \qquad (22a)$$

34

The chlorine-rich silanes $\mathrm{Me_2SiCl_2}$ and $\mathrm{SiCl_4}$ are also inert towards $\mathrm{Me_2Si{=}C(SiMe_3)_2}$, whereas $\mathrm{MeSiCl_3}$ reacts in trace amounts to give $\mathrm{Me_2SiCl{-}C(SiMe_3)(SiMe_2Cl)}$. $\mathrm{Me_2Si{=}C(SiMe_3)_2}$ (from **25**) inserts faster into the E–F bond than into the E–Cl bond. In contrast to $\mathrm{SiCl_4}$, $\mathrm{SiF_4}$ interacts with the silaethene [17]. A smooth insertion into the B–F bond of $\mathrm{BF_3}$, to form $\mathrm{Me_2SiFC(SiMe_3)_2(BF_2)}$, has also been observed [17]. The corresponding addition product is formed by the stable silaethene $\mathrm{Me_2Si{=}C(SiMe_3)(SiMeBu^t_2)}$ [16].

These results support the presence of a reversible first reaction step, involving insertion into the polar a–b bond (cf. eq. 20). As a consequence of this, the rate of insertion increases the more basic atom a is relative to E (i.e., $F\text{–}\mathrm{SiR_3} > Cl\text{–}\mathrm{SiR_3}$; $Cl\text{–}\mathrm{SnR_3} > Cl\text{–}\mathrm{GeR_3} > Cl\text{–}\mathrm{SiR_3}$; with decrease in n in $\mathrm{Me_{4-\mathit{n}}Si}Cl_n$); the more electrophilic b is relative to C (i.e., $\mathrm{Cl\text{–}}Sn\mathrm{R_3} > \mathrm{Cl\text{–}}Ge\mathrm{R_3} > \mathrm{Cl\text{–}}Si\mathrm{R_3}$; and with decreasing size and increasing electronegativity of R in $\mathrm{Hal\text{–}}Si\mathrm{R_3}$) *.

The silaketimine $\mathrm{Me_2Si{=}N(SiMe_3)}$, generated from a silatriazoline, adds to the E–Cl bond of $\mathrm{Me_3ECl}$ with good (E = Si) or quantitative yield (E = Ge, Sn) of compounds **35** [12,18]:



$$[\mathrm{Me_2Si{=}N(SiMe_3)}] \xrightarrow[(\mathrm{E\ =\ Si,\ Ge,\ Sn})]{+\ \mathrm{Me_3ECl}} \begin{array}{ll} \mathrm{Me_2Si} & \!\!—\ \mathrm{NSiMe_3} \\ \quad\ | & \quad\ \ | \\ \ \ \mathrm{Cl} & \quad \mathrm{EMe_3} \end{array} \qquad (22b)$$

35

Accordingly, $\mathrm{Me_2Si{=}N(SiMe_3)}$ is more capable of insertion into an E–Cl bond than $\mathrm{Me_2Si{=}C(SiMe_3)_2}$, which can be explained by the higher nucleophilicity of the nitrogen atom (with less steric protection). As a consequence, the ketimine also inserts into the Si–Cl bonds of the chlorine-rich silanes $\mathrm{Me_{4-\mathit{n}}SiCl_\mathit{n}}$ [18].

Insertion into element–oxygen and element–nitrogen bonds. The silaethene $\mathrm{Me_2Si{=}C(SiMe_3)_2}$ (from silaazetidine **25**, as well as from the salt sources **6**) adds to the Si–O bond of monosilyl ethers such as $\mathrm{Me_3Si{-}OMe}$ or $\mathrm{Me_3Si{-}OPh}$ with the formation of compounds **36** [15,17].

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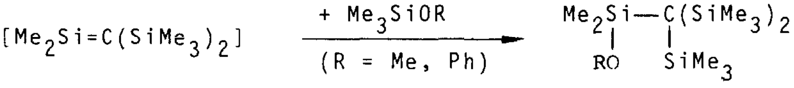
* The stable silaethene $\mathrm{Me_2Si{=}C(SiMe_3)(SiMeBu^t_2)}$ is similar to alkenes in that it adds bromine very easily, but the mechanism is not yet known.



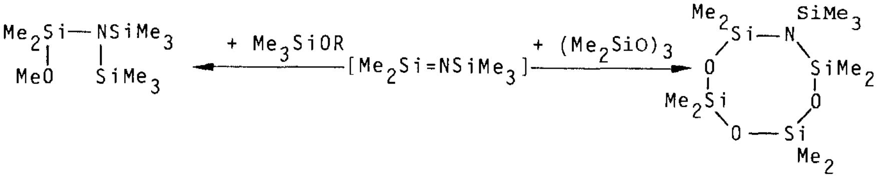
$$[\mathrm{Me_2Si{=}C(SiMe_3)_2}] \xrightarrow[(\mathrm{R} = \mathrm{Me,\ Ph})]{+\ \mathrm{Me_3SiOR}} \underset{\mathrm{RO}}{\mathrm{Me_2Si}}{-}\underset{\mathrm{SiMe_3}}{\mathrm{C(SiMe_3)_2}} \qquad (23a)$$

36

On the other hand, siloxanes such as $Me_3Si{-}O{-}SiMe_3$ or $[Me_2SiO]_3$, in which oxygen is less basic than in $Me_3Si{-}OR$, do not add to $Me_2Si{=}C(SiMe_3)_2$ generated from **25** [28].

The aminosilanes Me_3SiNMe_2 and $Me_3SiNCPh_2$ react with $Me_2Si{=}C(SiMe_3)_2$ (from **25**), more slowly than Me_3SiOMe (but faster than Me_3SiCl), to form $Me_2Si(NMe_2)C(SiMe_3)_3$ and $Me_2Si(NCPh_2)C(SiMe_3)_3$ [15]. No Si–N insertion product is formed with Me_3SiN_3 because of the considerably faster [2 + 3] cycloaddition of silylazide to the silaethene (cf. Section 4.4; the same is true for $Me_2Ge{=}C(SiMe_3)_2$).

The silaketimine $Me_2Si{=}NSiMe_3$ (from silatriazoline) adds to Si–O and Si–N bonds more easily than the silaethene $Me_2Si{=}C(SiMe_3)_2$ (cf., behaviour towards Si–Hal bonds). Accordingly, it forms an insertion product with $[Me_2SiO]_3$ as well as with Me_2SiOR [12,18].



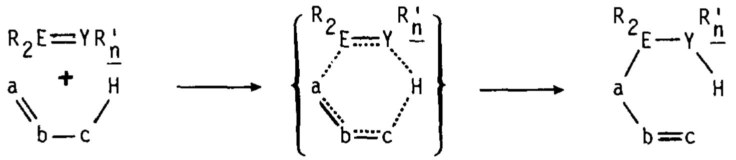
(23b)

However, the disiloxane $Me_3SiOSiMe_3$ does not add to $Me_2Si{=}N(SiMe_3)$ (from silatriazoline). As expected, insertion products are formed with Me_3SiNMe_2 and $Me_3SiNCPh_2$, and $Me_2Si{=}N(SiMe_3)$ adds to the Si–N bond even in Me_3SiN_3 [12,28]. Of course, in the latter case, the yield of insertion product decreases with increase in temperature in favour of the [2 + 3] cycloadduct (cf., 4.4) [37]. Also, the proportion of insertion decreases strongly with increasing size of the groups R in the silaketimines $Me_2Si{=}N(SiR_3)$, as well as in the silylazides R_3SiN_3. Thus, at $-10\,^\circ C$ $Me_2Si{=}N(SiMe_2Bu^t)$ and Me_3SiN_3 form only 56% of the Si–N insertion product, with 44% of the [2 + 3] cycloadduct, whereas, $Me_2Si{=}N(SiMe_3)$ and $Bu^tMe_2SiN_3$ form only the silaketimine dimer, and no insertion product. For an interesting example of an (intramolecular) insertion of the E=N group of the sila- and germa-ketimines, $Me_2E{=}NSiMe_2N(SiMe_3)_2$, into the Si–N bond of their $N(SiMe_3)_2$ group, see Section 3.3, eq. 19d.

Insertion into metal–element bonds. The silaethene $Me_2Si{=}C(SiMe_3)_2$ (and the same is probably also true for other unsaturated silicon and germanium compounds) is able to insert into the Li–element bond of compounds such as LiSPh, $LiOPO(OPh)_2$, etc. (cf. also Section 2.1).

4.2. Ene reactions

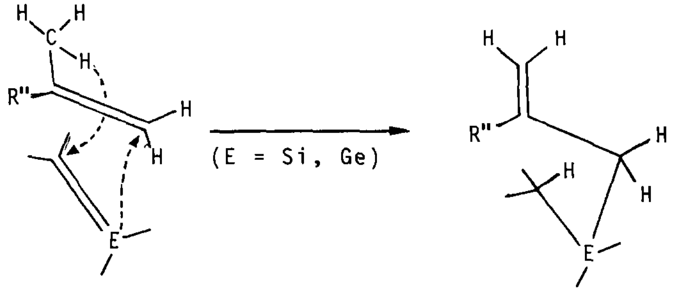
An ene reaction consists of the addition of an (as a rule electrophilic) unsaturated compound ("enophile"; here: $R_2E{=}YR'_n$ with E = Si, Ge; Y = C, N, etc.) to a (as a rule nucleophilic) double bond system a=b–c–H (e.g., $\rangle C{=}\underset{|}{C}{-}C{\lessdot}H$, $-N{=}\underset{|}{C}{-}C{\lessdot}H$, O=C–C<H) with an allylic hydrogen H [51].



37 38 (24)

The reactions, which involve double bond and hydrogen displacements, occur with conservation of orbital symmetry [46]. Therefore, ene reaction products **38** can result from a single step synchronous process, via concerted complexes **37** of comparatively low energy content.

Ene reactions with alkenes. The sila- and germa-ethenes $Me_2E{=}C(SiMe_3)_2$, generated from salt sources $Me_2EHal{-}CLi(SiMe_3)_2$ (E = Si, Ge), react readily with propene $CH_2{=}CHCH_3$ and isobutene (2-methylpropene) $CH_2{=}CMeCH_3$ to form the ene products **39** (R″ = H or Me) [15,19]:

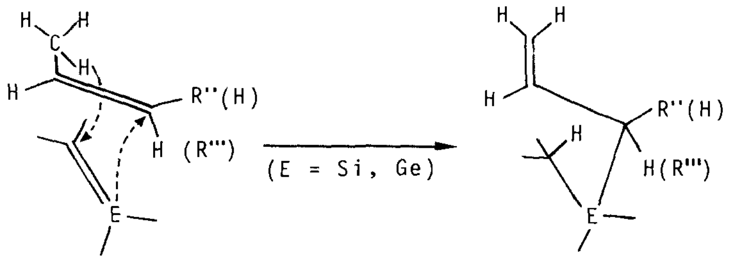


39 (25)

2-Methylbutadiene (2-vinylpropene; R″ in eq. 25 $CH_2{=}CH$) and 2,3-dimethylbutadiene (2-methylvinylpropene; R″ in eq. 25 CH_2CMe) also react with $Me_2E{=}C(SiMe_3)_2$ according to eq. 25, but in both cases, as well as in certain other cases still to be discussed, [2 + 4] cycloadducts are also formed (cf. Section 4.3) [15,17,19]. As is evident from Fig. 5, the rate of the ene reaction of $Me_2Si{=}C(SiMe_3)_2$ with these alkenes decreases in the order propene > isobutene > 2-methylbutadiene > 2,3-dimethylbutadiene. The ene reaction of $Me_2Si{=}C(SiMe_3)_2$ with the propenes $CH_2{=}CR''CH_3$ with increasingly large substituents in the 2-position (R″ = H < Me < $CHCH_2$ < $CMeCH_2$) are obviously increasingly sterically hindered.

Substituents in the 1-position (of propene) hinder the progress of the ene reaction to a much greater extent. Accordingly, $Me_2Si{=}C(SiMe_3)_2$ reacts comparatively slowly with such propenes, as in eq. 26, to give the ene products **40** (cf. Fig. 5) [17].

Propenes $R''CH{=}CHCH_3$ with *cis*-positioned substituents R″ react faster than the propenes $R'''CH{=}CHCH_3$ with *trans*-positioned substituents R‴. Thus, $Me_2Si{=}C(SiMe_3)_2$ reacts faster with *cis*-$MeCH{=}CHCH_3$ than with *trans*-$MeCH{=}CHCH_3$ (Fig. 5). Similarly, *cis*-(*trans*-$MeCH{=}CH)CH{=}CHCH_3$ is more reactive than *trans*-(*trans*-$MeCH{=}CH)CH{=}CHCH_3$, and *cis*-$(CH_2{=}CH)CH{=}CHCH_3$



40

(26)

is more reactive than *trans*-$(CH_2{=}CH)CH{=}CH{-}CH_3$. Also, of the two $MeCH{=}CH$ sections of the compound *cis*-(*trans*-$MeCH{=}CH)CH{=}CHCH_3$ only that with a *cis*-configuration reacts with $Me_2Si{=}C(SiMe_3)_2$ [17]. It also follows from Fig. 5 that rate at which $Me_2Si{=}C(SiMe_3)_2$ reacts with the propenes $R''HC{=}CH{-}CH_3$ increases in the sequence $(H_2CCH)CH{=}CHCH_3 < (MeHCCH)CH{=}CHCH_3 < (Me_2CCH)$-$CH{=}CHCH_3$ in forming the ene product. Since the nucleophilicity of propenes increases in the same order (i.e., with increasing methyl substitution), the alkenes

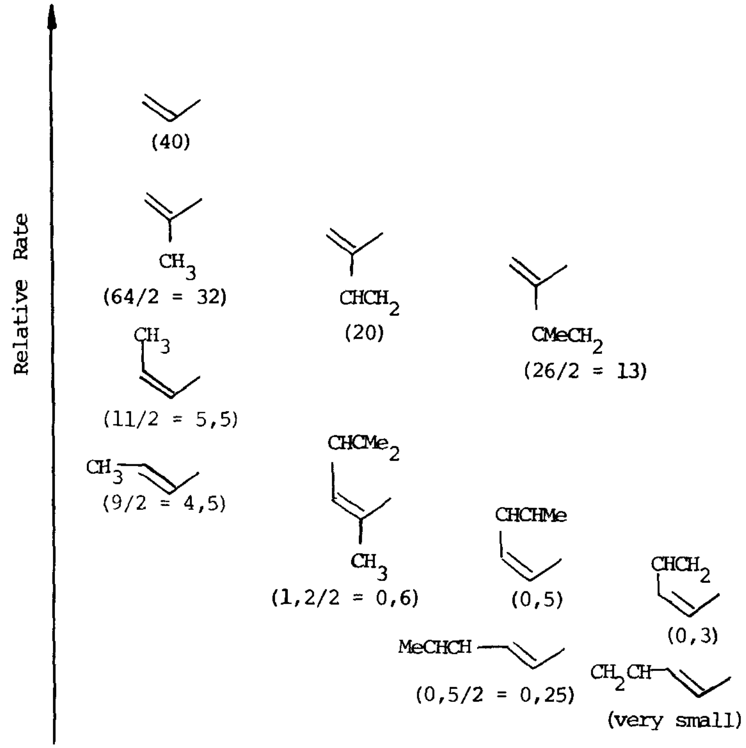
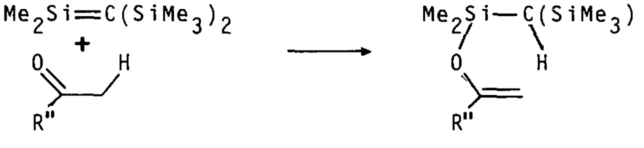


Fig. 5. Relative rates (in brackets), relative to the [2 + 4] cycloaddition of 2,3-dimethylbutadiene (taken as 100), of the ene reactions of $Me_2Si{=}C(SiMe_3)_2$ (generated from **25**) with various alkenes at 115 °C in Et_2O [17]. (The relative rate r of an alkene is equal to the experimental value $r(\exp)$ divided by the number n of equivalent propene sites: $r = r(\exp)/n$.)

obviously act as nucleophiles, relative to $Me_2Si{=}C(SiMe_3)_2$ and consequently the silaethene is the electrophile.

In a manner analogous to $Me_2E{=}C(SiMe_3)_2$, the unsaturated silicon and germanium compounds $Me_2Si{=}C(SiMe_3)(SiMeBu^t_2)$ and $Me_2E{=}N(SiMe_{3-n}Bu^t_n)$ also react with alkenes (e.g., isobutene) to form ene products [18,19,37].

Other ene reactions. The silaethene $Me_2Si{=}C(SiMe_3)_2$ (from the silaazetidine **25**) reacts with acetone or ethyl acetate much faster than with isobutene, according to eq. 27, to give the ene products **41** ($R'' = Me$ or EtO) [17,37].



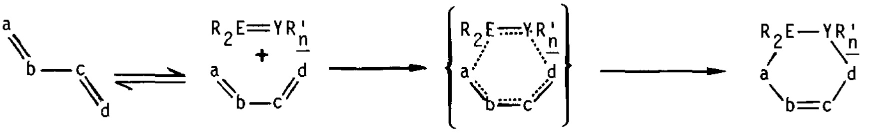
(27)

41

The relative rates are 32 (with isobutene) and 5760 (with acetone). In an analogous manner, the unsaturated silicon and germanium compounds $Me_2Si{=}C(SiMe_3)(SiMeBu^t_2)$ and $Me_2E{=}N(SiMe_{3-n}Bu^t_n)$ combine with acetone to form ene reaction products [16,18,19].

4.3. [2 + 4] Cycloadditions

The [2 + 4] cycloaddition of a (generally electrophilic) alkene $>C{=}C<$ ("dienophile") to a (generally nucleophilic) alkadiene $>C{=}\overset{|}{C}{-}\overset{|}{C}{=}C<$ ("diene"), which is also known after its discoverers as the Diels–Alder reaction, occurs with conservation or orbital symmetry [46], and hence, as a rule, as a synchronous process. The same is generally true for reactions of other unsaturated compounds (here: $R_2E{=}YR'_n$ with $E = Si$, Ge; $Y = C$, N, etc.) with the conjugated double bond systems a=b–c=d to give the [2 + 4] cycloadducts **43**.



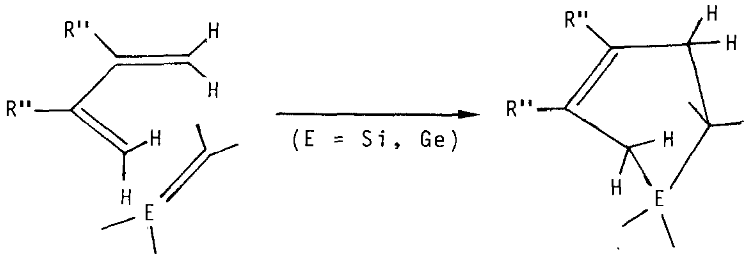
(28)

42 **43**

The concerted course of the reaction shown in eq. 28, which proceeds via the activated complex **42**, requires the existence of diene in the *cisoid* conformation and this generally exists in equilibrium with the *transoid* form. At low temperatures, the equilibrium generally lies over the side of the *transoid* conformer, and certainly more so in the case of the butadiene with *cis*-methyl substituents in the 1- and 4-positions than in the case with *trans* methyl substituents. With increasing temperature, the equilibrium shifts increasingly towards the *cisoid* conformer [52].

[2 + 4] Cycloadditions with alkadienes. The sila- and germa-ethenes $Me_2E{=}C(SiMe_3)_2$, generated from the salt sources $Me_2EHalCLi(SiMe_3)_2$ ($E = Si$, Ge), react smoothly according to eq. 29 with butadiene ($R'' = H$), 2-methylbutadiene (R'', $R'' = Me$, H), and 2,3-dimethylbutadiene ($R'' = Me$) to give the [2 + 4] cycloadducts **44** [15,19] (in the last cases, and in cases still to be discussed, ene reaction

products are also formed cf. Section 4.2.).



44

(29)

The yield of product **44** increases with increasing reaction temperature, and in case of the reaction of $Me_2Si{=}C(SiMe_3)_2$ with an equimolar quantity of 2,3-dimethylbutadiene at −80°, −60°, and −40° it amounts to ca. 12, 40 and 72% (in addition, 3, 10 and 18% of the ene product and 85, 50 and 10% of the silaethene dimer are formed) [14]. The results support the suggestion that **44** is formed by a route similar to that of an organic Diels-Alder reaction, which, as a typical synchronous process, is favoured by an increase in temperature *. Under similar reaction conditions (with butadiene at −30 °C), the yield of the [2 + 4] cycloadduct from $Me_2Ge{=}C(SiMe_3)_2$ is smaller, and that from $Ph_2Si{=}C(SiMe_3)_2$ is larger, than that from $Me_2Si{=}C(SiMe_3)_2$ [19,21]. Thus, $Me_2Ge{=}C(SiMe_3)_2$ is more reactive, and $Ph_2Si{=}C(SiMe_3)_2$ less reactive towards dimerization than $Me_2Si{=}C(SiMe_3)_2$. As expected, the stable silaethene $Me_2Si{=}C(SiMe_3)(SiMeBu^t_2)$ reacts with butadiene at −30 °C to give only the [2 + 4] cycloadduct [16].

As is evident from Fig. 6, the rate of the [2 + 4] cycloaddition of $Me_2Si{=}C(SiMe_3)_2$ with dienes increases in the order butadiene < 2-methylbutadiene < 2,3-dimethylbutadiene. Since the nucleophilicity of the dienes increases in the same direction (that is, with increasing methyl substitution), the alkadienes act as nucleophiles relative to $Me_2Si{=}C(SiMe_3)_2$; consequently the silaethene behaves as an electrophile.

Butadienes with methyl groups in the 1- and 4-positions react (as in eq. 30) more slowly than butadienes with methyl groups in the 2- and 3-positions with the silaethene $Me_2Si{=}C(SiMe_3)_2$ (generated from **25**) to give products **45**. The same is also true for the germaethene. Butadienes with two such methyl groups react more slowly than those with one **, and butadienes with *cis*-positioned methyl groups R''' more slowly than those with *trans*-positioned methyl groups R'' (cf. eq. 30 and Fig. 6).

These results with butadienes clearly indicate the synchronous course of [2 + 4] cycloaddition, because the formation of the transition state is evidently hindered more by 1,4-substituents than by 2,3-substituents, and the formation of *cisoid* dienes

---

* Part of the increase in yield, that is the increase in the ratio of the rate of formation of **44** and of the sila- or germa-ethene dimer, could result from the increasing amount of the diene in the *cisoid*-conformation with increasing temperature. Since the yield of the ene reaction product increases in the same order as for **44**, the shift in the *transoid* diene $\rightleftarrows$ *cisoid* diene equilibrium with the temperature obviously does not play any significant role.

** 1,1,4,4-Tetramethylbutadiene does not form any [2 + 4] cycloadduct with $Me_2SiC(SiMe_3)_2$ (generated from **25**), but gives only an ene reaction product.

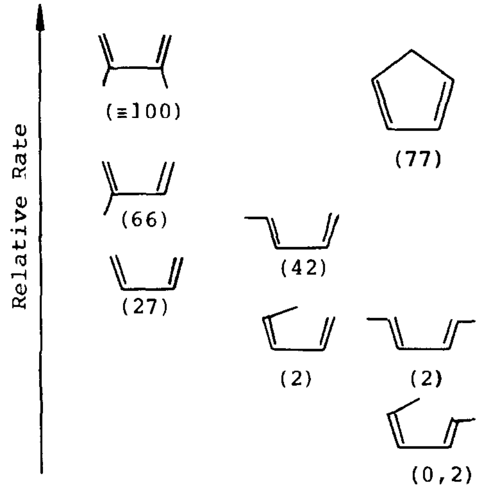
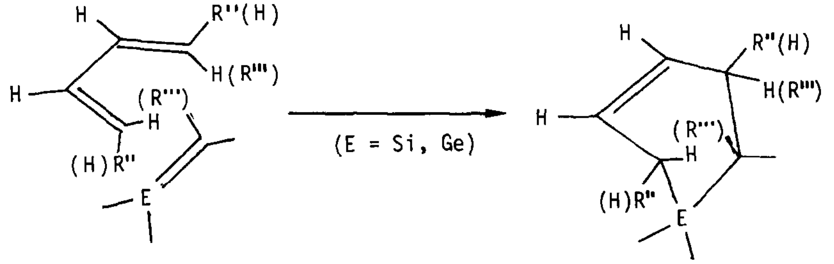


Fig. 6. Relative rates (in brackets) of the [2+4] cycloaddition of $Me_2Si{=}C(SiMe_3)_2$ (generated from **25**) to various alkadienes at 115 °C in Et_2O [17].

from their *transoid* isomers is reduced more by *cis*-substituents than by *trans*-substituents. Because of its 1,4-substituted diene system, cyclopentadiene reacts more



45

(30)

slowly than 2,3-dimethylbutadiene with $Me_2Si{=}C(SiMe_3)_2$ *; however, because of its ideal *cisoid*-diene system it adds much faster than *trans*-1,*trans*-4-dimethylbutadiene **. The fact that *trans*-1-methylbutadiene is more reactive than butadiene towards $Me_2Si{=}C(SiMe_3)_2$ evidently depends on the effect of the increased nucleophilicity of the diene, which in this case overcomes the effect of increased steric hindrance.

Of the two possible [2 + 4] cycloadducts, the reaction of 2-methylbutadiene with $Me_2Si{=}C(SiMe_3)_2$, the 1-methyl-4-silacyclohexene derivative is the major product (the yield ratio of the adduct isomers is 13 : 1). The [2 + 4] cycloaddition of *trans*-

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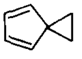
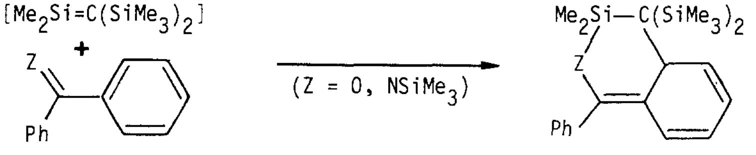
* The spiro compound  does not form a [2+4] cycloadduct at all with $Me_2Si{=}C(SiMe_3)_2$ (generated from **25**). *Only the silaethene thermolysis is observed.*

** This is also true for anthracene. $Me_2Si{=}C(SiMe_3)_2$ (from **25**) does not react with the "aromatics" furan, triophene and *N*-methylpyrrole.

and *cis*-1-methylbutadiene even leads exclusively to one adduct isomer in each case, namely to the 3-methyl-4-silacyclohexene derivative with the former and to the 6-methyl-4-silacyclohexene derivative with the latter. In an analogous manner, *cis*-1-*trans*-4-dimethylbutadiene gives only one 3,6-dimethyl-4-silacyclohexene derivative * [17]. Clearly the silaethene $Me_2Si{=}C(SiMe_3)_2$ possesses a high substrate specificity; it is not too active a species to be selective.

In a manner analogous to $Me_2E{=}C(SiMe_3)_2$, the more stable sila- and germaketimines $Me_2E{=}N(SiMe_{3-n}Bu^t_n)$ ($n > 0$) also form [2 + 4] cycloadducts with dienes such as butadiene or 2,3-dimethylbutadiene [18,19].

[2 + 4] Cycloadditions with other dienes. As illustrated by the following example, hetero-substituted 1,3-dienes have a similar ability to react with $Me_2Si{=}C(SiMe_3)_2$ (from salt sources) to form [2 + 4] cycloadducts [15]:



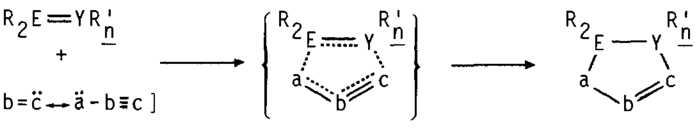
(31)

46

In stoichiometric reactions, a yellow benzophenone adduct **46** (Z = O) is formed quantitatively, and the similar yellow adduct **46** ($Z = NSiMe_3$, cf., Section 2.2) is formed at 0 °C in 60% yield, as well as the [2 + 2] cycloadduct (cf., Section 4.5). Similarly, azobenzene PhN=NPh, phenylazotrimethylsilane $PhN{=}NSiMe_3$, benzophenoneanil $Ph_2C{=}NPh$ and benzil Ph–CO–CO–Ph react with $Me_2Si{=}C(SiMe_3)_2$ as in eq. 31 [17,28]. No [2 + 4] cycloadduct is formed between $Me_2Si{=}C(SiMe_3)_2$ and the azine $Me_2C{=}N{-}N{=}CMe_2$ [37].

4.4. [2 + 3] Cycloadditions

Corresponding to [2 + 4] cycloaddition, the [2 + 3] cycloaddition of unsaturated compounds ("1,3-dipolarophiles"; here $R_2E{=}YR'_n$ with E = Si, Ge; Y = C, N, etc.) to the double bonded systems a–b≡c ("1,3-dipoles"; e.g., >C–N≡N, –N–N≡N, O–N≡N) [53] occurs with conservation of orbital symmetry [46] and frequently as a synchronous process, via activated complexes, **47**, to give the [2 + 3] cycloadducts, **48**:



(32)

47 **48**

Formation of a [2 + 3] cycloadduct of the unsaturated silicon and germanium compounds $R_2E{=}Y(SiR_3)_n$ with the diazomethane $(Me_3Si)_2C{=}N{=}N$ has not so far

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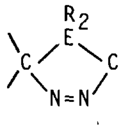
* The reaction of *cis*-1-*trans*-4-dimethylbutadiene with $Me_2Si{=}C(SiMe_3)_2$ (generated from **25**) leads, with change in configuration, to the same [2 + 4] cycloadduct as *trans*-1-*trans*-4-dimethylbutadiene forms without any change in diene configuration [17]. Obviously the former diene does not exist sufficiently long in the *cisoid* conformation. The [2 + 4] cycloaddition therefore follows a faster stepwise path than concerted path to the cycloadduct.

been observed. As already discussed, the [2 + 3] cycloadducts (**50**) of $R_2E{=}N(SiMe_3)$ with $(Me_3Si)_2C{=}N{=}N$, synthezised by other methods, decompose easily in a reverse manner by cycloreversion to sila- or germa-ketimine and bis(trimethylsilyl)diazomethane (cf. Section 2.2). In an analogous manner, the [2 + 3] cycloadducts **49**, not obtained so far from $R_2E{=}C(SiR_3)_2$ and $(Me_3Si)_2C{=}N{=}N$, would probably decompose easily, with the elimination of bis(trimethylsilyl)diazomethane, to the sila- and germa-ethene, and hence might act as good precursors for these compounds. On the other hand, azides N=N=N (e.g., Bu^tN_3, PhN_3, $Me_{3-n}Bu^t_nSiN_3$,



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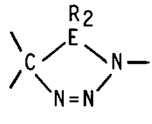

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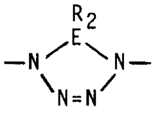
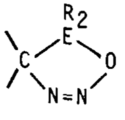


51

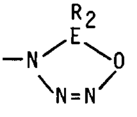
Ph_3SiN_3, $((Me_3Si)_2N)$, Me_2SiN_3) react, as already indicated in Section 2.2, with the sila- and germa-ethenes $R_2E{=}C(SiMe_3)_2$ to give the sila- and germa-triazolines **50***, and with the sila- and germaketimes $R_2E{=}N(SiMe_3)$ to form sila- and germa-tetrazolines **51** (with the ketimines, especially at low temperatures, besides the [2 + 3] cycloadducts, insertion products may also be formed to some extent, cf., Section 4.1 and Table 2) [15,18,19,37,41]. The cycloaddition rate with azides is comparatively high, and so $Me_3Si{=}C(SiMe_3)_2$ (from the silaazetidine **25**) in a 2,3-dimethylbutadiene medium in the presence of Me_3SiN_3 (mol ratios, silaethene : azide : dimethylbutadiene = 1 : 1 : 70) does not form the [2 + 4] but only the [2 + 3] cycloadduct ** [37].

The rate of [2 + 3] cycloaddition decreases with increasing size of the reactants. Thus, $Me_2Si{=}NSiMe_2Bu^t$ and $Me_2Si{=}NSiMeBu^t_2$ (from the silatriazolines) still react with $Bu^t_2MeSiN_3$ at −10 °C but not at all with $Bu^t_3SiN_3$. Also, $Me_2Si{=}NSiBu^t_3$ reacts only at higher temperatures (100 °C) with $Bu^t_3SiN_3$ to give a [2 + 3] cycloadduct **51**.

Nitrous oxide, N_2O, forms [2 + 3] cycloadducts with $R_2E{=}Y(SiR_3)_n$ (E = Si, Ge; Y = C, N). The products with sila- and germa-ethenes are of the type **52**, and with sila- and germa-ketimines, of the type **53**. The [2 + 3] cycloadduct **55**, formed by the



52



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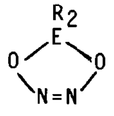

54

reaction of $Me_2Si{=}C(SiMe_3)_2$ (from the silaazetidine **25**) with N_2O at 150 °C, is thermolabile under the reaction conditions; it decomposes 2/3 according to eq. 33a

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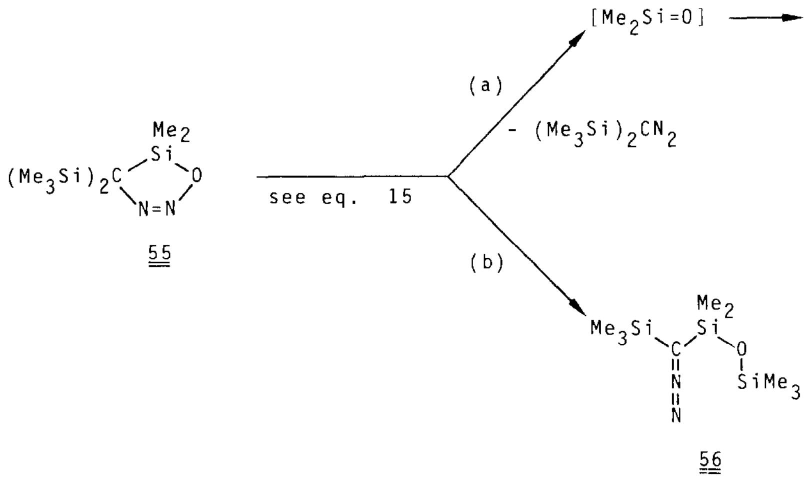
* In these cases, salt sources are not recommended as sila- and germa-ethene precursors because they may react directly with azides to form the products **50** (cf., Section 2.1). The silaazetidine **25** is the preferred precursor.

** The rate of cycloaddition of Me_3SiN_3 with $Me_2Si{=}C(SiMe_3)_2$ (from **25**) is definitely more than 1000 times greater than the rate of addition of 2,3-dimethylbutadiene. As expected, the rate of thermolysis of **25** is independent of whether it is decomposed in the presence of 2,3-dimethylbutadiene or trimethylsilylazide.

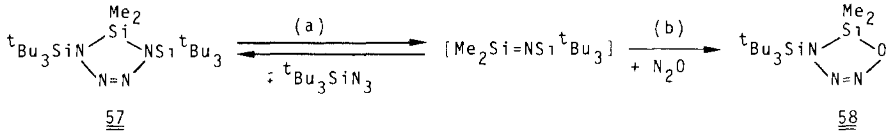
by [2 + 3] cycloreversion to give $(\mathrm{Me_3Si})_2\mathrm{CN_2}$ and polymers of dimethylsilaketone, $\mathrm{Me_2Si{=}O}$, and 1/3 according to eq. 33b to give the diazomethane derivative **56** [15,28]:



(33)

The silaketone so formed can also be trapped with trimethylchlorosilane (with formation of the insertion product $\mathrm{Me_2SiClOSiMe_3}$).

The [2 + 3] cycloadduct **58**, obtained by the reaction of $\mathrm{Me_2Si{=}NSiBu^t_3}$ (from **57**) with $\mathrm{N_2O}$ at 100 °C (eq. 34), is, like **55**, unstable under the reaction conditions [30]; it decomposes quantitatively, as shown in eq. 35a, into $\mathrm{Bu^t_3SiN_3}$ and dimethylsilaketone which, in the absence of an appropriate trapping agent, combines with $\mathrm{Me_2Si{=}NSiBu^t_3}$ (from **57**) (eq. 35b), but in the presence of a trapping agent, such as $\mathrm{Et_3SiH}$, it reacts according to eq. 35c.



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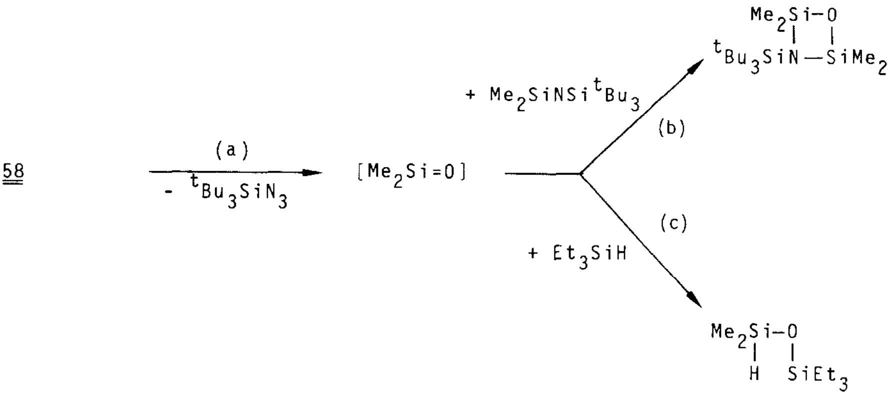


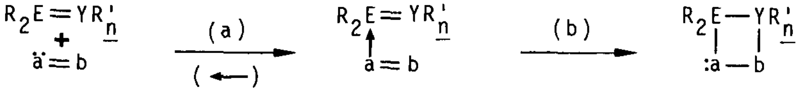
(35)

The cyclic compound **58** acts as an especially good precursor of dimethylsilaketone, which has also been obtained by other methods [4,8]. The cyclic compound **54**

($R_2E = Me_2Si$) may be even more valuable as a precursor of $Me_2Si{=}O$, but it has not so far been synthesized.

4.5. [2 + 2] Cycloadditions

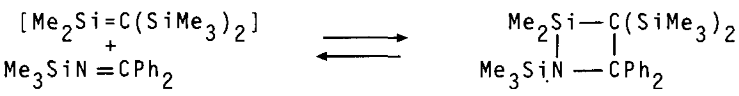
The [2 + 2] cycloaddition of the unsaturated silicon and germanium compounds $R_2E{=}YR'_n$ (E = Si, Ge; Y = C, N, etc.) to double bond systems a=b such as alkenes, azo compounds, ketones, ketimines, etc., obviously proceeds in steps, according to eq. 36 (single-step supra-suprafacial [2 + 2] cycloadditions are more or less restricted on the basis of the non-conservation of orbital symmetry [46], cf., insertions, Section 4.1.):



$$\begin{array}{c} R_2E{=}YR'_n \\ + \\ \ddot{a}{=}b \end{array} \xrightarrow[(\leftarrow)]{(a)} \begin{array}{c} R_2E{=}YR'_n \\ \uparrow \\ a{=}b \end{array} \xrightarrow{(b)} \begin{array}{c} R_2E{-}YR'_n \\ |\quad\ | \\ :a{-}b \end{array} \qquad (36)$$

In order that the [2 + 2] cycloaddition of unsaturated silicon and germanium compounds occurs fast even at lower temperatures, the more electronegative atom of the reaction partner a=b must possess a free electron pair. Consequently, no [2 + 2] cycloadduct formation between $R_2E{=}Y(SiR_3)_n$ (from the precursors discussed in Section 2) and the unsaturated hydrocarbon systems $\rangle C{=}C\langle$ and $-C{\equiv}C-$ has so far been observed [15,28]. Obviously, the [2 + 2] cycloaddition of silicon and germanium compounds with alkenes and alkynes only occurs at higher temperatures by a radical mechanism [4] *. In contrast to alkenes, sila- and germa-ethenes undergo cycloaddition with sila- and germa-ethenes (cf., Sections 3.2. and 3.3.).

As already mentioned (cf., Sections 2.2. and 4.3.), $Me_2Si{=}C(SiMe_3)_2$ (from salt sources) reacts with the ketimine $Ph_2C{=}N(SiMe_3)$ at ca. 0 °C, not only according to eq. 31, to give a yellow [2 + 4] cycloadduct **46** (Z = $NSiMe_3$) in 60% yield, but also in accordance with eq. 37 to give a colorless [2 + 2] cycloadduct, **59**, in 34% yield



$$\begin{array}{c} [Me_2Si{=}C(SiMe_3)_2] \\ + \\ Me_3SiN{=}CPh_2 \end{array} \rightleftarrows \begin{array}{c} Me_2Si{-}C(SiMe_3)_2 \\ |\qquad | \\ Me_3Si\dot{N}{-}CPh_2 \end{array} \qquad (37)$$

59

[15]. The insoluble adduct isomers **46** and **59** are thermolabile and rearrange above 60 °C, by a route involving free $Me_2Si{=}C(SiMe_3)_2$ and $Ph_2C{=}NSiMe_3$, to give an equilibrium mixture of the two compounds which contains 95% **59**. Thus, the formation of **46** at low temperatures is kinetically controlled; the [2 + 4] cycloaddition in the present case occurs faster than the [2 + 2] cycloaddition of $Ph_2C{=}NSiMe_3$; and, in fact, faster than the [2 + 4] cycloaddition of 2,3-dimethylbutadiene [15]. In the end, of course, the thermodynamically stable [2 + 2] cycloadduct is formed.

Benzophenoneanil, $Ph_2C{=}NPh$, reacts with $Me_2Si{=}C(SiMe_3)_2$ (from salt sources) to give exclusively the [2 + 4] cycloadduct, which at higher temperatures (90 °C)

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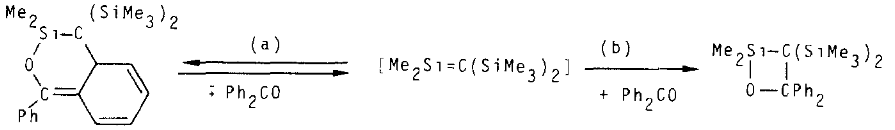
* The mechanism of the occasionally-observed formation of [2 + 2] cycloadducts from unsaturated silicon and germanium compounds and alkenes and alkynes at low temperatures [4,8,10] should be thoroughly investigated. Possibly the [2 + 2] cycloadducts in these cases are formed by reaction of the unsaturated hydrocarbons with the precursors of the unsaturated silicon and germanium compounds.

rearranges, via [2 + 4] cycloreversion and [2 + 2] cycloaddition to **59** (with PhN instead of Me_3SiN [37]. The direct formation of a [2 + 2] cycloadduct is observed in the reaction of $Me_2Si{=}C(SiMe_3)_2$ (from salt sources) with the azine $Me_2C{=}N{-}N{=}CMe_2$ [37].

In contrast to $Me_2Si{=}C(SiMe_3)_2$, the more reactive germa-ethene $Me_2Ge{=}C(SiMe_3)_2$ (from salt sources) forms neither a [2 + 4] nor a [2 + 2] cycloadduct with $Ph_2C{=}NSiMe_3$, but gives only the germaethene dimer.

The thermolysis of the salt precursors $Me_2SiX{-}CLi(SiMe_3)_2$ at low temperatures in the presence of the ketone $Ph_2C{=}O$, leads exclusively to a [2 + 4] cycloadduct **60** (cf., eq. 31) [15]. This rearranges thermally in the [2 + 2] cycloadduct **61** [15], which, in contrast to the [2 + 2] cycloadduct **59**, does not decompose thermally into $Me_2Si{=}C(SiMe_3)_2$ and Ph_2CO [30] *:



60 61 (38)

The intermediate silaethene $Me_2Si{=}C(SiMe_3)_2$, formed in the course of the rearrangement, can be trapped with the help of a good silaethene trapping agent, such as Bu^tN_3, Bu^tOH or CH_3CO_2H, which is able to compete with the Ph_2CO.

Also at higher temperatures, $[Me_2Si{=}C(SiMe_3)_2]$ reacts with Ph_2CO to form **60** almost exclusively at first, with only a trace amount (or no) **61**. As in the case of the reaction with $Ph_2C{=}NSiMe_3$, the reaction of $Me_2Si{=}C(SiMe_3)_2$ with $Ph_2C{=}O$ leads faster to the thermodynamically less stable [2 + 4], than to the thermodynamically more stable [2 + 2] cycloadduct. Because of this, benzophenone acts as a very good silaethene trapping agent, whose relative reactivity with respect to $Me_2Si{=}C(SiMe_3)_2$ at 100 °C is ca. 500 times greater than of 2,3-dimethyl butadiene [37] **.

The more reactive germaethene $Me_2Ge{=}C(SiMe_3)_2$ (from salt sources) gives just as little [2 + 4] or [2 + 2] cycloadduct with Ph_2CO as with $Ph_2C{=}NSiMe_3$ (see above). On the other hand, the silaketimine $Me_2Si{=}NSiMe_3$ (from silatriazoline) reacts with benzophenone to form $(Me_2SiO)_n$ and $Ph_2C{=}NSiMe_3$. The reactive intermediate is probably a [2 + 2] cycloadduct, which could not be isolated because of its thermolability under the reaction conditions (−10 °C).

[2 + 2] Cycloadducts of acetone with the unsaturated silicon and germanium compounds $R_2E{=}Y(SiR_3)_n$ have not so far been observed, because acetone reacts faster to form ene reaction products (cf., Section 4.2.). (For an adduct of the silaketone $Me_2Si{=}O$ with the silaketimine $Me_2Si{=}NSiBu^t_3$, see eq. 35b).

The azo compounds $Me_3SiN{=}NSiMe_2$ and $Me_3SiN{=}NPh$ combine with the silaethene $Me_2Si{=}C(SiMe_3)_2$ (from salt precursors) to form the colorless [2 + 2] cycloadducts **62** (cf. eq. 39) [15,54]. Analogous cycloadducts are not formed with the more reactive germaethene $Me_2Ge{=}C(SiMe_3)_2$ (from salt precursors). The products

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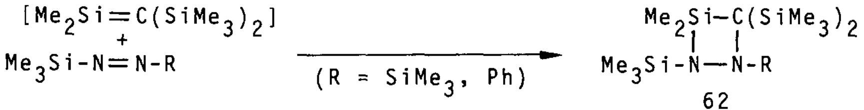
* The thermolysis occurs by a radical route to give a mixture of many products [30].

** Me_3SiN_3 reacts much faster than Ph_2CO, $Ph_2CNSiMe_3$ much more slowly than Ph_2CO.

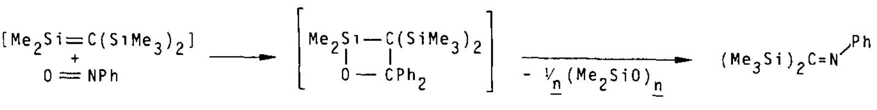


62

(39)

62 are thermolabile: the trimethylsilyl compound ($R = SiMe_3$) decomposes above 50 °C by [2 + 2] cycloreversion to give $Me_2Si{=}NSiMe_3$ and $(Me_3Si)_2C{=}NSiMe_3$, and also by rearrangement to $(Me_3Si)_2C{=}NSiMe_2N(SiMe_3)_2$ [15]; the phenyl compound ($R = Ph$) at ca. 100 °C gives an isomer whose structure has not yet been determined [54]. The azo compound $Me_3SiN{=}NSiMe_3$ does not enter into any reaction with the silaketimine $Me_2Si{=}NSiMe_3$ (from silatriazoline).

The nitroso compound PhNO reacts both with $Me_2Si{=}C(SiMe_3)_2$ (from silaazetidine **25**) and with $Me_2Si{=}N(SiMe_3)$ (from silatriazoline) [28]. In the former case, an orange-red ketimine $(Me_3Si)_2C{=}NPh$ *, and Me_2SiO-polymers are obtained. The non-isolable reaction intermediate is perhaps the [2 + 2] cycloadduct **63** **:



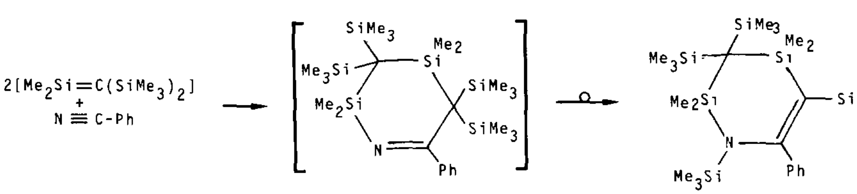
63

(40)

The products of the reaction of $Me_2Si{=}NSiMe_3$ with PhNO have not so far been completely characterized.

Obviously, dioxygen also reacts with compounds of the $R_2E{=}C(SiMe_3)_2$ type, as indicated by the high sensitivity towards oxygen of the "stable" silaethene $Me_2Si{=}C(SiMe_3)(SiMeBu^t_2)$. This reaction, which has not so far been fully explained, possibly occurs via the [2 + 2] cycloadduct of the silaethene and oxygen to give, among other products, Me_2SiO-polymers and the deep blue $O{=}C(SiMe_3)$-$(SiMeBu^t_2)$ [37].

A comparatively complex process takes place in the reaction of the silaethene $Me_2Si{=}C(SiMe_3)_2$ (from salt sources) with the nitrile $PhC{\equiv}N$ in Et_2O at −10 °C: a cycloadduct **65**, consisting of two molecules of $Me_2Si{=}C(SiMe_3)_2$ and one molecule of PhCN is formed [15]:



64 65

(41)

Surprisingly then, **65** is formed in higher yields (compared with the silaethene dimer), when PhCN is added in excess. Obviously, therefore, the product formation involves an adduct $Ph_2C{\equiv}N{\rightarrow}SiMe_2{=}C(SiMe_3)_2$, which, because of steric considera-

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* The ketimine exhibits two Me_3Si-proton signals, which coalesce at 64 °C.

** Perhaps an additional intermediate, the [2+4] cycloadduct, is also formed; cf. eq. 38.

tions does not cyclize to a four-membered ring but decomposes reversibly to give only the reactants, or reacts irreversibly with another molecule of $Me_2Si{=}C(SiMe_3)_2$ to form the [2 + 2 + 2] cycloadduct **64**. As a result, PhCN initiates the polymerization of $Me_2Si{=}C(SiMe_3)_2$ (cf. Section 3.3.); this process is broken by cyclization, with the formation of compound **64**, which rearranges further into **65**.

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