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Synthesis and reactivity of functional 1-methyl-silacyclopentenes

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Abstract

The silylenes MeSiCl, MeSiOMe and $MeSiNMe_2$ can be thermally generated from disilanes and trapped by butadiene, isoprene and 2,3-dimethylbutadiene to give functionally-substituted silacyclopentenes. Some examples of cycloadditions to heterodienes are included to demonstrate the scope and mechanism of the reaction. The reactivity of 1-chloro-1-methyl-silacyclopent-3-ene has been studied.

Key words: Silane; Silylene; Cycloaddition; Diolefin; π-Bonding; Cothermolytic synthesis

1. Introduction

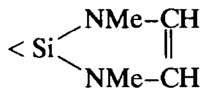
Thermolysis or photolysis of suitable disilanes or unsaturated organosilanes produces silylenes (silandiyls) which are known to react with high chemo- and regio-selectivity with element–H bonds, dienes, alkynes and a number of element halides. Such reactions have mainly been the subject of mechanistic studies, but some preparative applications are known too [1–7]. Most of the work involved inorganic silylenes such as $SiCl_2$, $Si(OMe)_2$, SiH_2 or SiHCl, and symmetrical organic silylenes such as $SiMe_2$ or silylsilylenes. We became interested in the rather rarely investigated heterosubstituted organosilylenes RSiX [8–12] for three main reasons:

(a) trapping reactions furnish functionally-substituted silanes which may be modified or used in further syntheses;

(b) silandiyls RSiX containing α-C–H bonds should (in addition to isomerization in competition with the trapping reaction) undergo HX-elimination from intermediate species or adducts and so show a wider variety of reactions;

(c) (p–p)–π interactions between the lone pair of the heteroatom and the empty p_z-orbital increase in the order

$$MeSiCl < MeSiOMe < MeSiNMe_2 < Si(NMe_2)_2$$



as shown by the coefficients of the π-MOs [13] (selected π-MOs are given in Fig. 1) and such increase should lengthen the life time of the silandiyl and so inhibit competing decompositions in the slower trapping reactions.

The study described below has concentrated mainly on the first of these aspects, *i.e.* on the synthesis and reactivity of 1-heterosubstituted 1-methyl-silacyclopent-3-enes.

2. Results and discussion

1,2-Dimethyltetrachlorodisilane (**1a**) (b.p. 152–153°C) comprises an appreciable part of the higher boiling by-products of the Direct-Synthesis and is the most readily available reactive disilane. Fractionation gives this compound contaminated by *ca.* 15–20% $Me_2ClSiSiMeCl_2$ (**1b**) (b.p. 144–146°C [14]) which may be converted into **1a** by prolonged treatment with $HCl/AlCl_3$ [15].

As shown below and by recent thermolysis-mass spectrometric investigations [16] both disilanes undergo

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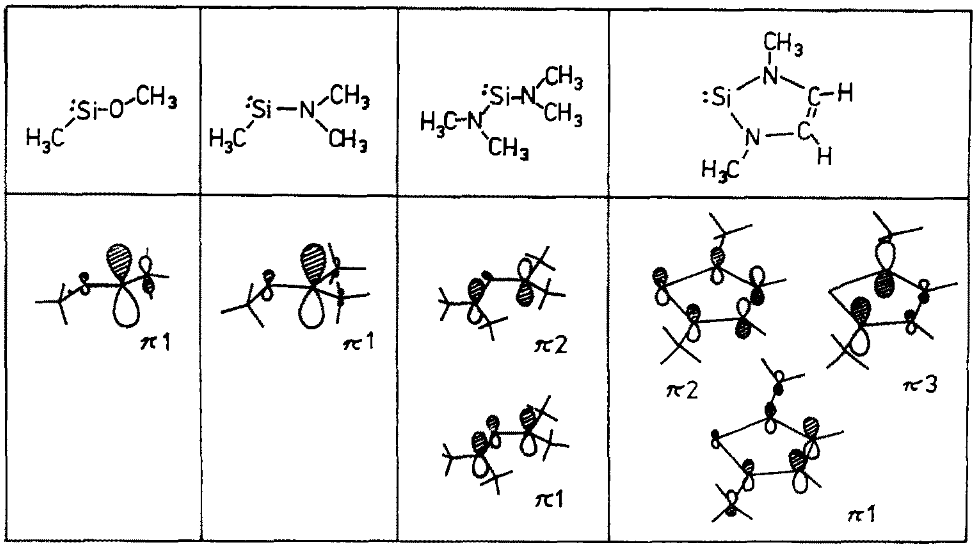
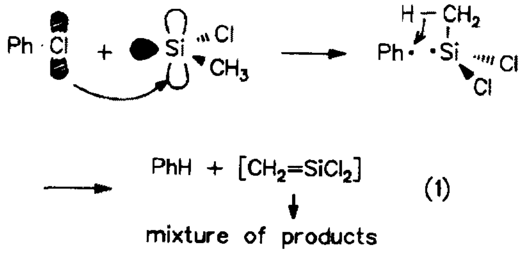


Fig. 1. Coefficients of the p_z-orbitals in selected bonding π-MOs as calculated by the PM3 method [13].

thermolysis above 500°C to give the same silylene ClMeSi along with the respective volatile chloromethylsilanes $MeSiCl_3$ and Me_2SiCl_2. Since only the silylene determines the reaction behaviour in most experiments we used the disilane fraction containing 80% of **1a** (δ^{29}Si 18.09 ppm) and 20% of **1b** (δ^{29}Si 25.03 and 15.43 ppm) without further treatment.

Thermolysis of **1a**, **b** in a flow-tube without trapping reagents gave, in addition to $MeSiCl_3$ and some Me_2SiCl_2, an ill-defined pale-yellow solid with half of the chlorine content of $(ClMeSi)_n$ (^{29}Si-CP/MAS: broad maxima at 16 and −51 ppm, ^{29}Si-MAS: broad maximum at 31 ppm). Pyrolysis in the presence of chlorobenzene gave mixtures of no value. Much of the chlorobenzene was reduced to benzene, while the silylene insertion (which works well for $SiCl_2$ [6,7]) gives only a little $PhMeSiCl_2$ (5–10%, in the presence of Cu on silica up to 20%). The strong preference for reduction may be the result of a favourable cyclic transition state for hydrogen transfer within the radical cage (as assumed for insertion of $SiCl_2$ into the C–Cl bond [6,7]) but isomerization and subsequent abstraction of SiH cannot be excluded (eqn. (1)).

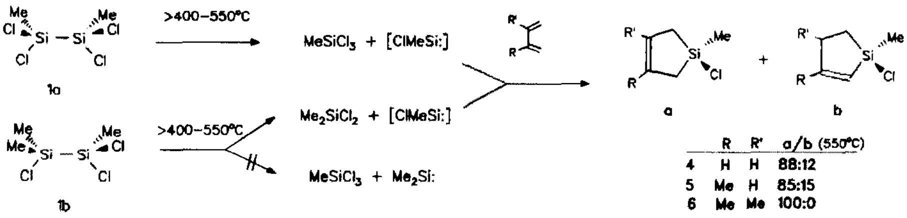


(1)

2.1. Syntheses of unsaturated silicon heterocycles

Well defined reactions of thermally-generated ClMeSi take place with 1,3-dienes as traps. Though the copyrolysis of $Me_2Si_2Cl_4$ and butadiene was mentioned in a patent by Atwell [8] and the copyrolysis of $Me_3SiSiMeCl_2$ and butadiene was described by Clarke and Davidson [11] we are aware of no systematic study of monofunctionally-substituted silylenes. The silylene MeHSi behaves somewhat unusually because of the easy intramolecular H-shift in the primary adducts [11].

From thermolysis of **1a**, **b** in a stream of butadiene at 500–550°C we obtained mixtures of $MeSiCl_3$, and a little Me_2SiCl_2, 1-chloro-1-methyl-silacyclopent-3-ene



	R	R'	a/b (550°C)
4	H	H	88:12
5	Me	H	85:15
6	Me	Me	100:0

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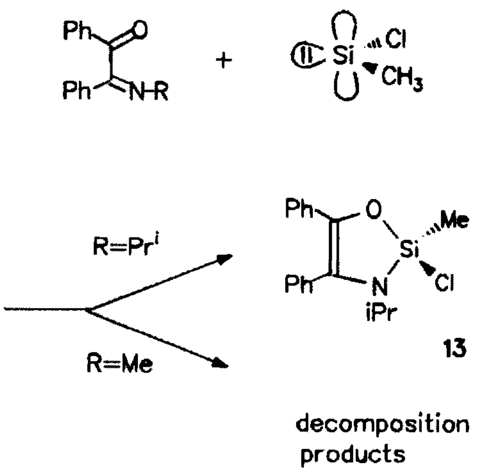

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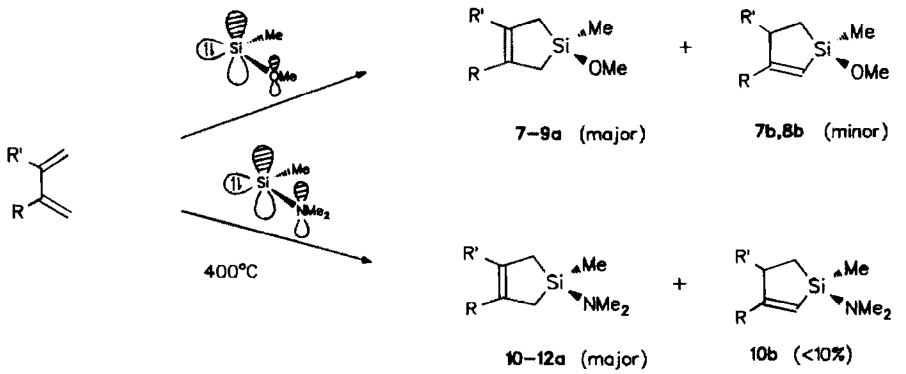
(4a), 1-chloro-1-methyl-silacyclopent-2-ene (4b) and vinylcyclohexene. The latter is not easy to remove by distillation but its formation can be much reduced by there being excess of the disilane (about 50%) over butadiene. A competing insertion of the silylene into the Si–Cl bond of the chlorodisilanes was not observed, and seems not to be of importance. The absence of dimethyl- or dichloro-silacyclopentenes in the products of all experiments demonstrates the high selectivity in the generation of the silylene in the temperature range used (eqn. (2)).

The reaction with isoprene proceeds similarly, giving 1-chloro-1,3-dimethyl-silacyclopent-3-ene (**5a**) (major product) and 1-chloro-1,3-dimethyl-silacyclopent-2-ene (**5b**) (minor product). The formation of **5a** and **5b** as well as the absence of 1-chloro-1,4-dimethyl-silacyclopent-2-ene are entirely consistent with a stepwise mechanism involving initial (2 + 1)-cycloaddition followed by a ring-opening-rearrangment, as proposed by Lei *et al.* [17] for additions of silylenes to dienes.

The presence of an excess of pyridine in the reaction between **1a**, **b** and isoprene caused no substantial change, though the yield and purity of **5a**, **b** were lowered. This provides evidence for the low efficiency of an intermolecular amine-induced HCl elimination in the flow-pyrolysis.

The scope for the use of heterodienes in place of dienes is limited by side reactions. The cycloadditions can be used to make oxygen- and nitrogen-containing silicon heterocycles only if elimination or substitution reactions are suppressed. Copyrolysis of **1a**, **b** with a solution of α-iminoketone PhC(O)C(=N^{i}Pr)Ph in benzene, gave (see eqn. (3)) the desired 2-chloro-1,3,2-oxazasiloline-4 (**13**), a moisture- and air-sensitive viscous liquid (yield 54%). The related but less bulky iminoketone PhC(O)–C(=NMe)Ph, however, produced a white precipitate just on addition of **1a**, **b** to the benzene solution, and the pyrolysis of the mixture gave an undistillable resin.

It thus seemed desirable to use less reactive functional silylene precursors which allow reactions at silicon without severe restrictions on the scope of the cycloadditions. The methoxydisilanes **2a**, **b** and dimethyltetrakis(dimethylamino)disilane (**3a**), (obtained by treatment of **1a** and **b** with MeOH/urea and an excess of Me_2NH, respectively), are less sensitive towards nucleophiles. On the other hand they generate methoxymethylsilylene and dimethylaminomethylsilylene, at 400° and 420°C, respectively, in good yield, *i.e.* about 100°C below the temperature needed for chlorodisilanes. At 400°C with a 50 s flowtime in the presence of 2,3-dimethylbutadiene all the $Me_2Si_2(OMe)_4$ is decomposed whereas about 1/4 of $Me_2Si_2(NMe_2)_4$ and 2/3 of $Me_2Si_2Cl_4$ remain unchanged. The fact that the formation of the more π-stabilized aminosilylene needs somewhat higher temperatures than the methoxysilylene suggests that the rate of the α-elimination is controlled by the stronger 2n–3d(Si) interactions in the



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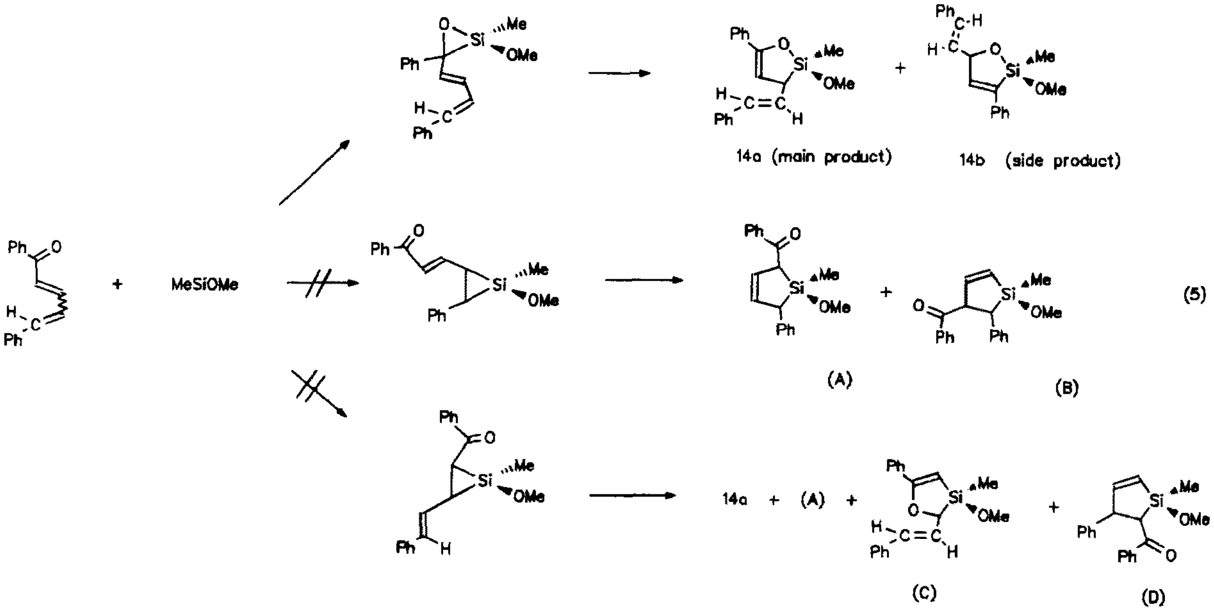
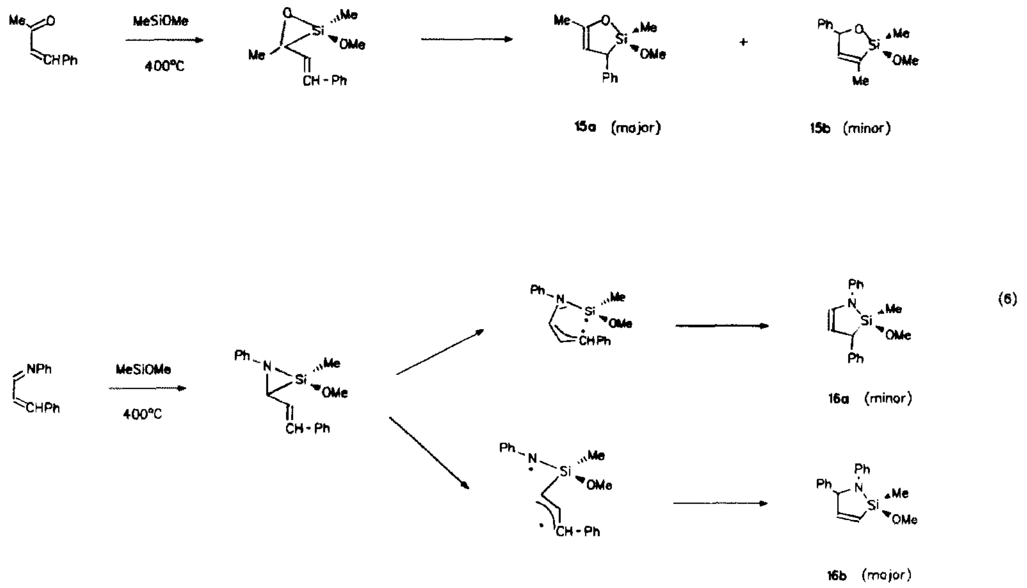


transition state. The reactivities of the three silylenes towards dienes, however, are not markedly different and the corresponding 1-methoxy- and 1-dimethylaminosilacyclopentenes **7–12** are, like **4–6**, formed in good yields (eqn. (4)). The silacyclopent-2-enes content increases with the temperature of the copyrolysis, pointing to cleavage of the more stable C–C bond in the silirane intermediate, and seems to be lower for the aminosilylene. In the case of 2,3-dimethylbutadiene these isomers were not observed.

Because methoxy- and amino-disilanes are stable towards a large variety of heterodienes, cycloadditions to unsaturated aldehydes, ketones (see the example in eqn. (6)), Schiff bases, diketones, diimines or iminoketones are possible and provide an easy route to many unsaturated heterocycles containing Si–N– or Si–O– and both Si–O and Si–N– as described elsewhere [18]. We mention here only two special features. Conjugated heterodienes react more rapidly than dienes, as shown by competition experiments and by copyrolysis with



oxa- and azatrienes. As shown for the reaction with PhCH=CH-CH=CH-CPh=O (eqn. (5)) the observed regiochemistry is in accordance with an initial addition to the C=O bond. Attack on the terminal C=C bond would result in benzoylated-silacyclopentenes, and initial reaction at the internal C=C bond would give a mixture of styryloxasilacyclopentenes and benzoylsilacyclopentenes.

We suggest that the course taken is due to initial Lewis acid-base interactions prior to the (2 + 1)-cycloaddition step. The formation of isomers with the double bond in the α- and β-position relative to silicon is again consistent with the stepwise mechanism.

The greatly increased proportion of the α-Si-unsaturated azasilacyclopentenes from cycloadditions to 1-azabutadienes, *e.g.* of **16b** as shown in eqn. (6), is the main difference compared with the outcome of the reactions of dienes and α,β-unsaturated ketones. It is in accordance with cleavage of the thermodynamically least stable bond, *i.e.* C–N [19] in the azasiliridine intermediate.

It is noteworthy that two mechanisms have been suggested for the ring-opening-rearrangement. Lei *et al.* [17] proposed a diradical cleavage of the bond opposite to the Si atom as well as that of the Si–C(alkenyl) bond to account for the formation of silacyclopent-2-enes and -3-enes, respectively. Since later studies [20] have shown that the dissociation energy of Si–C bonds is not less than that of C–C bonds, Clarke and Davidson [11] suggested a 1,3-silyl shift mechanism to account for the predominance of silacyclopent-3-enes in cycloadditions of dienes. Our results seem to support the radical mechanisms. Since the silyl shift is initiated by nucleophilic attack at silicon, the presence of two alkoxy groups on Si in the oxasilacyclopropane intermediate or of alkoxy and amino substituents in the azasiliridin intermediate shown in eqn. (6) should favour the formation of Si-allyl type isomers **15a** and **16a**. However, the ratio **15a**/**15b** is rather smaller than the corresponding **a**/**b** ratios of the diene adducts and **16b** predominates over **16a**. Since bond dissociation energies and charge distribution in the three-membered intermediates may differ strongly from those in acyclic models the possibility of silyl-shift-induced ring-openings cannot be excluded.

2.2. Reactivity of 1-chloro-1-methylsilacylopentenes

The 1-chloro-silacyclopent-3-enes have three reaction sites, the Si–Cl bond, the allylic double bond, and the CH_2 centre, which is activated by the double bond as well as the silicon atom. Because of this and the ease of their preparation they are regarded as valuable reagents for the synthesis of unsaturated and saturated five-membered silicon heterocycles. The examples outlined below, involving classical procedures, demonstrate the versatility of these compounds.

In presence of bases to remove HCl and so inhibit attack of the latter at the Si–allyl bond, the chlorine is

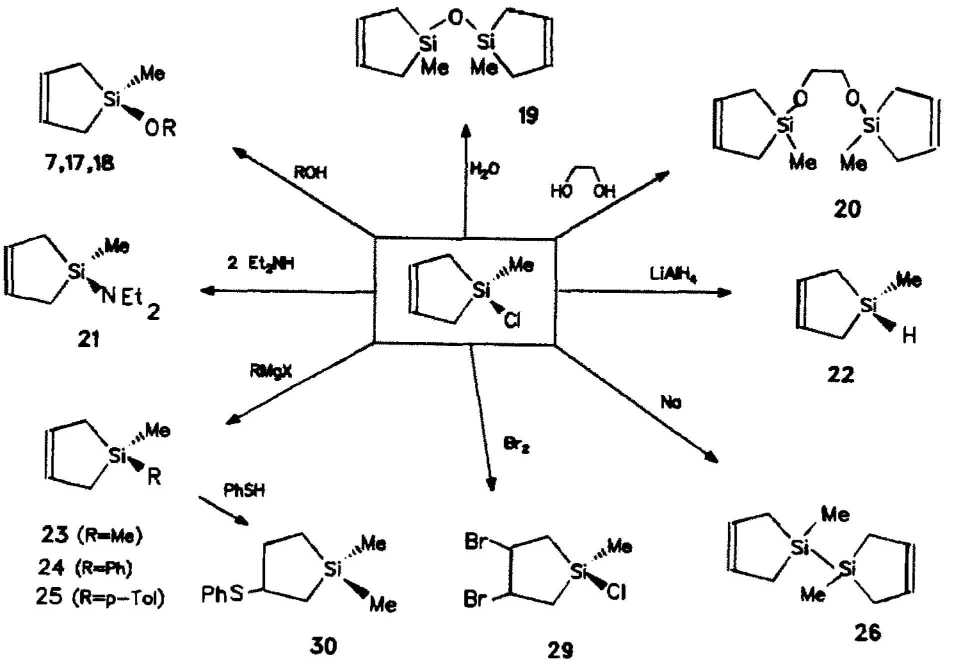


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TABLE 1. ^{13}C- and ^{29}Si-NMR data of silacyclopent-3-enes [a] δ_{TMS} in $CDCl_3$ (ppm)

	C(1)	C(2)	C(3)	C(4)	C(5)	$R^{3/4}$	X(Me)	^{29}Si
4a	1.0	20.1	129.9	129.9	20.1	–	–	43.3
5a	1.3	24.8	138.9	123.5	21.1	22.5/–	–	
6a	1.2	18.9	129.8	129.8	18.9	27.4	–	
7a	−2.6	15.8	131.1	131.1	15.8	–	50.7	32.6
8a	−2.8	20.4	139.5	124.1	16.6	22.8/–	49.9	
9a	−2.5	19.7	130.8	130.8	19.7	23.8	51.1	28.3
10a	−3.0	16.1	131.6	131.6	16.1	–	38.7	22.5
11a	−2.8	23.6	140.4	125.2	17.3	21.1/–	38.7	24.2
12a	−3.1	19.8	131.1	131.1	19.8	23.9	38.5	17.1
27a	0.1	36.5 [b]	134.6/	133.3	18.5	–	–	
28a	−2.5	38.7 [b]	135.6/	135.2	16.5	–	−3.7	

[a] Assignments based on DEPT spectra, comparison with data of known derivatives [12,26,30] and increment estimations.

[b] CHBr.

TABLE 2. ^{13}C- and ^{29}Si NMR data of silacyclopent-2-enes [a] δ_{TMS} in $CDCl_3$ (ppm)

Comp.	C(1)	C(2)	C(3)	C(4)	C(5)	$R^{3/4}$	X(Me)	^{29}Si
4b	2.2	128.9	157.0	31.0	11.0	–	–	39.3
5b	2.5	122.3	168.1	35.0	12.8	22.6/–	–	
7b	−1.6	128.1	157.8	31.2	18.3	–	50.4	17.0
8b	−1.8	123.8	161.9	34.7	19.2	22.9/–	50.6	
trans-**27b**	2.2	130.3	157.2	50.4 [b]	25.4	–	–	
cis-**27b**	1.7	130.3	156.5	49.3 [b]	24.5	–	–	
28b	−1.2	133.5	153.6	54.4 [b]	23.4	–	−1.8	

[a] Assignments based on DEPT spectra, comparison with data of known derivatives [12,26,30] and increment estimations.

smoothly replaced by hydroxy- or NH-nucleophiles to give, *e.g.*, **7a** and **17a–21a** (eqn. (7)). Treatment with organometallic reagents yields 1-methyl-1-organosilacyclopentenes **23a–25a** and $LiAlH_4$ brings about selective reduction at silicon to **22a**. Even lithium in THF or sodium in toluene attack mainly the Si–Cl bond to produce 35–40% of the disilane **26a**. Anionic ring opening polymerizations [21] may be responsible for the occasional low yields but they appear to predominate only in the presence of the strong donor HMPA.

The allylic double bond in **4a** is less reactive. Attempts to bring about its hydrosilylation by $HSiCl_3$ and $HSiEt_3$ in the presence of $H_2PtCl_6/{}^{i}PrOH$ were unsuccessful. Even long heating in benzene or toluene (in a closed Schlenk tube) gave only low yields of adducts. A similarly low tendency towards addition was observed towards phosphines (Ph_2PH, PhMePH) and thiophenol in refluxing benzene or toluene in the presence of AIBN. Use of diisopropyl perdicarbonate as radical initiator was much more effective, and gave **30**, the adduct from thiophenol and **23**, in 47% yield.

The stereospecific *trans*-addition of bromine to the double bond of **4a** in CCl_4 occurs much more readily and results, in a mixture of the two pairs of diastereoisomers [22*] of 1-chloro-3,4-dibromo-1-methylsilacyclopentane **29**. Bromination of **4a** and **23a** with N-bromosuccinimide gave isomeric mixtures of 4-bromo-silacyclopent-2-enes **27b**, **28b** (major) and 2-bromo-silacyclopent-3-enes **27a**, **28a** (minor component). A radical mechanism, as shown in eqn. (8), involving an allyl radical accounts for the formation of both products. The main product results from attack at the sterically exposed carbon atom (4), reaction at carbon (2) to give the side product being hindered by the methyl groups on silicon. The presence of chlorine on silicon seems completely to prevent formation of the product with Si–Cl and C–Br bonds *cis* to each other (perhaps because of electron pair repulsion) since we find only one of the two possible isomers *viz.* **27a**. In the analogous reaction of 1,1-dichloro-silacyclopent-3-ene no 2-bromosilacyclopentenes were detected [23].

The compounds were identified mainly by the differing ^{13}C-NMR chemical shifts for silacyclopent-3-enes and -2-enes (Tables 1, 2). ^{1}H-NMR data for silacyclopentenes (Table 3) are often less informative, and complicated by higher order spectra [24]. They are helpful, however, in the determination of the ratio of

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* Reference number with asterisk indicates a note in the list of references.

TABLE 3. ^{1}H-NMR data of the silacyclopentenes [a] δ_{TMS} in $CDCl_3$ (ppm) (coupling constants in Hz)

	SiMe	X(Me)	H(2, 2′)	H(5, 5′)	H(3)/R(3)	H(4)/R(4)
4a	0.61(s)	–	1.60(m)		5.90(br)	
4b	0.87(s)	–	6.10(m) [b]		7.15(m)	2.55(m)
5a	0.56(s)	–	1.56(m)		1.76(br)	5.51(m)
6a	0.59(s)	–	1.66/1.61(m, $J_{AB} \approx 18$)		1.73(m)	
7a	0.22(s)	3.34(s)	1.32/1.09(m, $J_{AB} \approx 19$)		5.81(br)	
8a	0.22(s)	3.51(s)	1.32(m)		1.72(s)	5.36(m)
9a	0.21(s)	3.38(s)	1.40/1.18(m, $J_{AB} \approx 18.3$)		1.65(m)	
10a	0.32(s)	2.53(s)	1.42/1.19(m, $J_{AB} \approx 16.7$)		5.96(m, 1.1)	
11a	0.23(s)	2.45(s)	1.34/1.23(m, $J_{AB} \approx 21$) 1.11/1.05(m, $J_{AB} \approx 18$)		1.72(m) (J(HH) ≈ 1.1)	5.49(m) (J(HH) ≈ 1.8)
12a	0.20(s)	2.44(s)	1.38/1.14(m, $J_{AB} \approx 17$)		1.68(br)	
17a	0.30 (s)	3.60(q) 1.20(t)	1.30(m)		5.90(m)	
18a	0.46(s)	6.8–7.3(m)	1.25(m)		5.94(br)	
19a	0.24(s)	–	1.21(m)		5.85(t)	
20a	0.28(s)	3.64(s)	1.27(m)		5.86(t)	
21a	0.23(s)	2.90(q) 0.98(t)	1.20(m)		5.88(br)	
22a	0.20(s)	4.21(m)	1.28(m)		5.87(br)	
23a	0.18(s)/	0.175(s)	1.28(m)		5.84(t)	
24a	0.47(s)	7.3–7.5(m)	1.55(m)		5.98(t)	
25a	0.46(s)	2.36(s), 7.2–7.4(m)	1.54(m)		5.96(br)	
26a	0.20(s)	–	1.42(m)		5.86(br)	

[a] Measurements were carried out with Bruker WP200 and ARX300 instruments, in the latter case giving separated 2,2′- and 5,5′-signals which are broadened or split by small long-range couplings with H(3, 4) and/or Me(3, 4). For ^{1}H-NMR analysis of dichlorsilacyclopent-3-ene see [24].
[b] Signal superimposed on the $SiCH_2$-signal of **4a**.

isomers and sometimes of their stereochemistry. The structural elucidation of the two stereoisomers of **27b** was based on analysis of their ^{1}H-NMR data by a spectra simulation [25*] (signals from **27a** are weak, and except for SiMe, overlapping). If there were a nearly planar structure as in silacyclopent-3-enes [26], the coupling constants ^3J(H3H4) (torsion angles near 0°) should be larger than ^3J(H3H5) and the high-field signals of the *AB*X-part assigned to H(5), the others to H(4) and H(3), respectively (Fig. 2). The downfield shift caused by vicinal chlorine is probably larger from the *cis*- than the *trans*-position, and therefore the low-field H(4) signal is assigned to the *trans*-isomer (highest abundance) and the low-field H(5) signal to the *cis*-isomer of **27b**.

3. Experimental details

All operations with moisture sensitive substances were carried out in sodium-dried solvents with exclusion of moisture. Pyrolyses and operations with air sensitive substances were carried out under dry argon. Butadiene and isoprene were purified before use. The heterodienes were prepared by published procedures and characterized by ^{13}C-NMR spectroscopy. NMR spectra were recorded in $CDCl_3$ solution relative to TMS on Bruker instruments (AC80, WP200, ARX300). The IR spectra were recorded on a Specord instrument (Zeiss Jena).

3.1. Disilanes

3.1.1. $Me_2Si_2Cl_4/Me_3Si_2Cl_3$ 1a, b

From the crude high boiling fraction of the methylchlorosilane production a disilane fraction at 145–165°C was distilled off and then rectified by use of a bubble-cap column (150–160°C) to give $Me_2Si_2Cl_4$/$Me_3Si_2Cl_3$ **1a**, **b** (80/20%). NMR (ppm), δ^{29}Si: **1a** 18.1, **1b** 25.0 (Me_2ClSi), 15.4 ($MeCl_2Si$); δ^1H: **1a** 1.00, **1b** 0.65 (Me_2ClSi), 0.92 ($MeCl_2Si$).

3.1.2. $Me_2Si_2(OMe)_4/Me_3Si_2(OMe)_3$ 2a, b

Compare [27,28]. The mixture of **1a**, **b** (20 g, 0.089 mol) was mixed with 21 g of urea (0.35 mol), and 18.2 ml of anhydrous MeOH (0.45 mol) was added dropwise with ice cooling. After stirring for 1–2 h at room temperature the upper phase was decanted off. To these impure **2a**, **b**, containing a few percent of unreacted silicon chloride, was added an excess of Et_3N in ether. Filtration and distillation at 41–43°C/5 mmHg yielded 17.2 g (92%) of **2a**, **b**. NMR (ppm), δ^1H: **2a** 0.24, 3.54; **2b** 0.20, 3.52 {SiMe(OMe)$_2$}, 0.28, 3.44 (SiMe$_2$OMe). **2a** : **2b** ≈ 80 : 20%.

3.1.3. $Me_2Si_2(NMe_2)_4/Me_3Si_2(NMe_2)_3$ *3a, b*

Freshly condensed dry Me$_2$NH (54.1 g, 1.2 mol) was dissolved in cold (−40°C) pentane (300 ml) and 34.2 g of **1a**, **b** (0.153 mol) was added dropwise with stirring below −10°C. After 2 h stirring at room temperature and standing overnight the mixture was refluxed for 2 h and the solid filtered off and washed thoroughly with pentane. The solvent was stripped from the filtrate and washings and the residue distilled at 119–123°C/17 mmHg to yield 22.1 g (56%) of waxy-solid **3a**, **b**, m.p. 79–82°C. NMR (ppm), δ^{29}Si: **3a** −7.3; **3b** −9.5/+7.8; **3a** : **3b** ≈ 87 : 13%. **3a** $C_{10}H_{30}Si_2N_4$ (262.55); found/calc.: C 46.2/45.75, H 12.0/11.52, N 20.9/21.34%.

3.2. *Cothermolyses*

The gas phase flow-reactions were carried out in an electrically heated, nearly vertical empty quartz tube of diameter 25 and length 500 mm. The apparatus was filled with argon, the pyrolyzer heated to the selected temperature, and the pure or dissolved components (See Table 4) were added slowly from a dropping funnel (or dosing pump) to the top of the pyrolyzer and any gases used were introduced via a calibrated flow-meter. Addition and flow rate were chosen normally to give $t_{\text{residence}}$ of *ca.* 50 s and calculated by use of the approximation [29]:

$$t_{\text{total}}(\text{s}) = t_{\text{res}}(\text{s}) \cdot n_{\text{total}}(\text{mol}) \cdot T(\text{K})/273(\text{K}) \cdot 22400(\text{ml/mol})/v_{\text{react}} \cdot 760(\text{mmHg})/p(\text{mmHg}).$$

dropping rate (1 drop ≈ 0.05 ml) = volume$_{\text{soln.}}$(ml)/(0.05(ml) · t_{total}(s). The products were collected in a

TABLE 4. Experimental data on silacyclopentenes **4–12**, obtained by copyrolysis

	X	R^1	R^2	products (mmol)	T$_{\text{pyr}}$ [°C]	b.p. [°C/mmHg]	yield g(%) isom. ratio	composition (mol. mas)	found/calc. [a] (%)
4a, b	Cl	H	H	**1a, b** 120 g (540) butadiene (1000) [13 h]	550	130–133/760	43 (60) (**a**/**b** ≈ 88/12)	C_5H_9SiCl (132.66)	Cl 27.3/26.72
5a, b	Cl	Me	H	**1a, b** 10.3 g (45) isoprene 5 ml (50) benzene 10 ml (112)	550	61–63/40	4.7 (71) (**a**/**b** ≈ 85/15)	$C_6H_{11}SiCl$ (146.69)	Cl 23.9/24.17 C 49.6/49.12 H 8.24/7.57
6a	Cl	Me	Me	**1a, b** 11.2 g (50) CH_2=CMeCMe=CH_2 (50)	550	70–72/30	4.4 (55)	$C_7H_{13}SiCl$ (160.72)	Cl 22.3/22.06
				1a, b 11.4 g (50) CH_2=CMeCMe=CH_2 (33)	400	58–60/19	2.4 (45)		
7a, b	OMe	H	H	**2a, b** 7.8 g (34) butadiene (34)	400	60–62/96 [b]	2.9 (66)$_{\text{corr}}$ (**a**/**b** > 90/10)	$C_6H_{12}OSi$ (128.24)	
8a, b	OMe	Me	H	**2a, b** 9.5 g (45) isoprene 3 ml (30) benzene 10 ml (112)	400	85–87/760	2.2 (52) (**a**/**b** ≈ 87/13)	$C_7H_{14}OSi$ (142.27)	H 9.65/9.92
9a [12]	OMe	Me	Me	**2a, b** 7.7 g (36.6) CH_2=CMeCMe=CH_2 (26)	400	69–72/21	3.2 (79)	$C_8H_{16}OSi$ (156.30)	
10a, b	NMe$_2$	H	H	**3a, b** 3.8 g (14.5) butadiene (excess)	420	94–98/760	1.0 (76) (**a**/**b** > 90/10)	$C_7H_{15}NSi$ (141.29)	N 9.39/9.91 H 10.5/10.70
				3a, b 2.7 g (10) butadiene (10) benzene (22)	400	92–96/760 [c]	0.6 (40)		
11a, b	NMe$_2$	Me	H	**3a, b** 2.6 g (9.9) isoprene 0.7 ml (6.8) benzene 5 ml (56)	420	31–32/50	0.8 (55) (**a**/**b** > 95/5)	$C_8H_{17}NSi$ (155.32)	N 8.52/9.02 H 10.4/10.03
				3a, b 2.6 g (9.9) isoprene (7)	400		0.6 (41)		
					350		0.2 (18)		
12a, b	NMe$_2$	Me	Me	**3a, b** 3.8 g (14.5) CH_2=CMeCMe=CH_2 (10)	400	80–83/28	1.0 (59)	$C_9H_{19}NSi$ (169.34)	N 8.45/8.27

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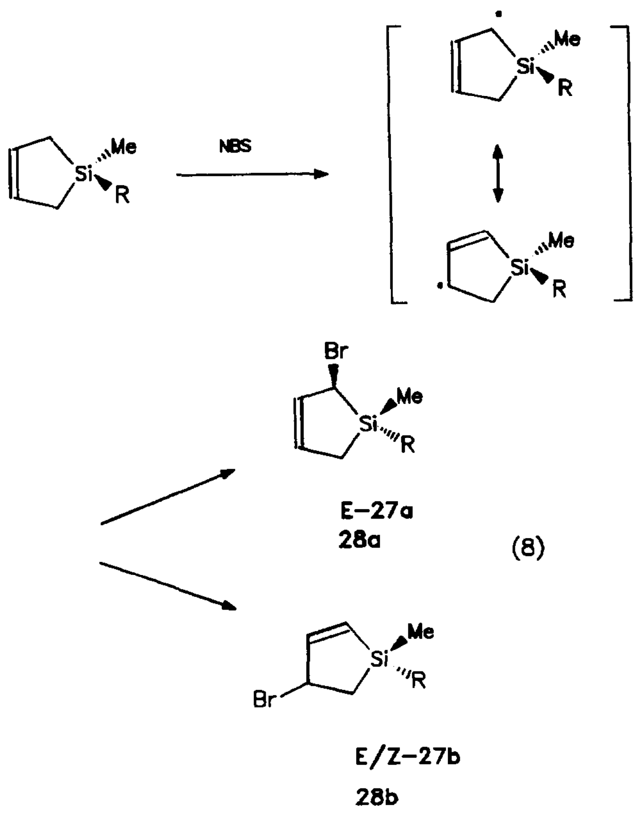
[a] To obtain analytically pure samples rectification through a spinning band column is necessary; the carbon content is often found to be small, probably because of SiC formation and incomplete oxidation.

[b] Contaminated by MeSi(OMe)$_3$.

[c] Contaminated by benzene and MeSi(NMe$_2$)$_3$.

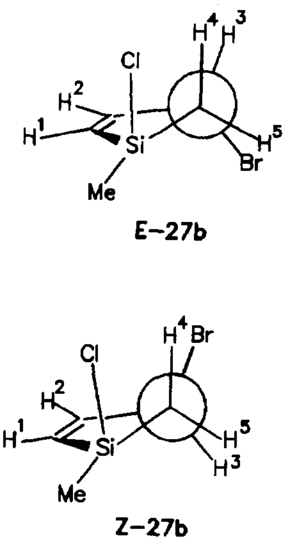


E-27a
28a

(8)

E/Z-27b
28b

cold trap (−65°C) at the bottom of the pyrolyzer and distilled. For silacyclopentenes the results are given in Table 4, with NMR data in Tables 1–3. IR data for silacyclopentenes with X = Cl, OMe, NMe_2 in KBr (cm^{-1}) were as follows: **5a, b** (X = Cl): 3010m, 2960, 2920s, 2890w, 2850m, 1640, 1590 (C=C), 1450, 1435, 1160, 850, 840, 790, 575 (all m), 505s (SiCl); 1390m, 1250s, 1220m, 770s ($SiCH_3$). **8a, b** (X = OMe): 2950s br, 2910w, 2840s, 1600–1650w (C=C), 1460wm, br, 1270s (C–O), 1080s (C–O), 845m; 1255wm, 1190m, br, 795s, 740wm ($SiCH_3$). **11a, b** ($X = NMe_2$): 2960s, 2930w, 2890–2840s, 2790s, 1640br, w (C=C), 1480m, 1460m, 1450w, 1285wm, 1250wm, 1070w, 985s (C–N); 1180s, 900s, br, 795s ($SiCH_3$).



E-27b

Z-27b

Fig. 2. Newman projection of *cis*- and *trans*-**27b** and ^{1}H-NMR data.

3.3. Copyrolyses with heterodi- or tri-enes

3.3.1. 2-Chloro-4,5-diphenyl-3-isopropyl-2-methyl-1,3,2-oxazasiloline-4 (13)

To a solution of 2.4 g (10 mmol) of PhC(=O)–C(=N^iPr)Ph in 2.2 ml (25 mmol) of benzene, was added 3.4 g of **1a, b**. The mixture was immediately introduced dropwise and slowly into the pyrolyzer. The dark viscous oil collected was distilled *in vacuo* (115–117°C/10^{-3} mmHg) to give **13**, contaminated by unchanged PhC(O)C(N^iPr)Ph. Most of the latter crystallized out on standing in a refrigerator, and was filtered off and washed with a little pentane. After removal of pentane 1.4 g (43%) of moisture- and air-sensitive **13** (impure) was obtained. $C_{18}H_{20}ClNOSi$ (329.90); found/calc.: C 65.7/65.53, H 6.53/6.11, N 5.30/4.25, Cl 9.70/10.75%. $\delta^{13}C\{^1H\}$ ($CDCl_3$) (ppm): 1.85 (SiMe), 129.80 (=C–N), 134.95 (=C–O), ^{i}Pr: 44.65 (α-C), 20.22/20.84 (β-C, prochiral), Ph not assigned (123–134).

The corresponding reaction of **1a, b** with PhC(=O)–C(=NMe)Ph did not give a defined product. Copyrolysis of **1a, b** with isoprene in the presence of pyridine gave impure **5a**; no defined product resulting from elimination of HCl and trapping by isoprene could be detected.

3.3.2. 2-Methoxy-2-methyl-5-phenyl-3-styryl-1-oxa-2-silacyclopent-4-ene (14a) and 2-methoxy-2-methyl-3-phenyl-5-styryl-1-oxa-2-silacyclopent-3-ene (14b)

A solution of 9.4 g (40 mmol) of PhCH=CH–CH=CH–CO–Ph and 10.4 g (50 mmol) of **2a, b** in 10 ml (112 mmol) of benzene was pyrolyzed at 400°C, $t_{res} \approx 65$ s to give, on distillation at 128–130°C/0.04 mmHg, 3.7 g (30%) of the diastereoisomer mixtures of **14a** and a little **14b**. $C_{19}H_{20}O_2Si$ (308.45). δ^{13}C-NMR$\{^1H\}$ ($CDCl_3$) (ppm): **14a** C(3) 38.37/40.90, C(4) 102.62/103.00, C(5) 149.34/150.08, SiMe −6.39/−3.62, OMe 50.34/52.01; Ph 126–132 (*ipso* 136.92/137.18, 140.02/140.09); **14b** C(5) 79.7/80.6, SiMe −4.17/−3.16, OMe 50.18/50.51; C(3), C(4) and Ph superimposed and not assigned (the *E*/*Z*-identity of the styryl substituent is the subject of further studies using high-resolution ^{1}H-NMR).

3.3.3. *2,5-Dimethyl-2-methoxy-3-phenyl-1-oxa-2-sila-cyclopent-4-ene (**15a**) / 2,3-dimethyl-2-methoxy-5-phenyl-1-oxa-2-silacyclopent-3-ene (**15b**)*

A solution of 5.8 g (40 mmol) of PhCH=CH–CO–Me and 12.4 g (60 mmol) of **2a**, **b** in 10 ml (112 mmol) of benzene was pyrolyzed at 400°C, $t_{res} \approx 65$ s. Fractionation of the condensate at 85–87°C/2 mmHg gave 5.7 g (65%) of the diastereoisomers of **15a** contaminated by small amounts of the diastereoisomers of **15b**. $C_{12}H_{16}O_2Si$ (220.34). $\delta^{13}C$-NMR{^1H} ($CDCl_3$) (ppm): **15a** C(3) 33.5/34.82, C(4) 102.66/102.89, C(5) 155.87/156.94, SiMe −6.97/−4.50, OMe ≈ 50.6/50.8, CMe 17.89/18.01; Ph ≈ 124.8(*p*), 126.65/126.76(*o*), 128.50/128.56(*m*), 142.02/142.21(*i*); **15b** C(5) 80.51/81.77, SiMe −4.09/−3.82, OMe ≈ 50.9/50.37, CMe 15.4/15.52; C(3), C(4) and C(Ph) partly superimposed and not assigned.

3.3.4. *1,3-Diphenyl-2-methoxy-2-methyl-1,2-azasiloline-4 (**16a**) and 1,5-diphenyl-2-methoxy-2-methyl-1,2-azasiloline-3 (**16b**)*

A solution of 6.2 g (29.9 mmol) of PhCH=CH–CH=NPh and 9.4 g (45 mmol) of **2a**, **b** in 10 ml (112 mmol) of benzene was copyrolyzed at 400°C, $t_{res.} \approx 55$ s. Distillation at 133–135°C/4 mmHg gave 5.9 g (72%) of the mixed diastereoisomers of **16a** (minor components, 25–40%) and of **16b** (major components, 75–60%). $C_{17}H_{19}NOSi$ (281.43); found/calc.: C 71.1/72.55, H 7.0/6.80, N 5.55/4.97%. $\delta^{13}C$-NMR{^1H} ($CDCl_3$) (ppm): **16a** C(3) 35.81/34.14, C(4) 106.03/106.69, C(5) 136.57/137.65, OMe 50.14/50.99. **16b** C(3) 118.08/118.58, C(4) 155.06/155.00, C(5) 67.24/65.57, OMe 50.49/50.69; SiMe of **16a**, **b** −6.59/−3.67/−3.22/−1.75 (I = 18/26/24/32) and phenyl signals not assigned.

3.4. *Substitution reactions of 1-chloro-1-methyl-silacyclopent-3-ene (**4a**)*

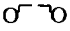
3.4.1. *Alcoholysis or hydrolysis in presence of Et_3N*

A solution of 5 g (38 mmol) of **4a** in 20–30 ml of Et_2O was cooled with ice/water and a solution of ROH and NEt_3 in ether or of H_2O in dioxane was added dropwise with stirring. The mixture was stirred for some time at room temperature, then filtered, the precipitate washed with ether. The solvent was removed from the combined extract and washings and the residue was fractionated. The results are in Table 5 and ^1H-NMR data are in Table 3.

3.4.2. *Alcoholysis in presence of urea*

A mixture of **4a** with an excess (20–25%) of urea was cooled to 0°C and the alcohol was added dropwise. After a further 30 min at 0°C the mixture was stirred at room temperature for 2–9 h. The upper layer was decanted and distilled *in vacuo*. The results are in Table 5.

TABLE 5. Substitution products of 1-chloro-1-methyl-silacyclopentene **4**

	X	products (mmol)	reaction conditions	b.p. (°C/mmHg)	yield g (%)	composition (mol. mass)	found/calc. (%)
7	OMe	**4**, 10 g (75) urea (94), MeOH (113)	0°C, 30 min; 20°C, 2 h	65/105	7.5 (78)	$C_6H_{12}OSi$ (128.25)	C 56.9/56.19 H 8.91/9.43
17	OEt	**4**, 5 g (38) urea (47), EtOH (57)	0°C, 30 min; 20°C, 2 h	75/100	2.8 (51)	$C_7H_{14}OSi$ (142.27)	C 60.8/59.09 H 9.44/9.92
		4, 5 g (38), Et_2O NEt_3 (38), EtOH (38)	0°C, 1 h; 20°C, 30 h		1.7 (32)		
18	OPh	**4**, 5 g (38), Et_2O NEt_3 (45), PhOH (38)	0°C, 30 min; 20°C, 6 h	86–87/20	3.2 (44)	$C_{11}H_{14}OSi$ (190.32)	C 70.5/69.42 H 7.41/7.36
19	O	**4**, 5 g (38), dioxane NEt_3 (40), H_2O (20)	10°C, 30 min; 20°C, 6 h	86–88/20	1.2 (30)	$C_{10}H_{18}OSi_2$ (210.43)	C 57.8/57.07 H 8.41/8.62
20		**4**, 5 g (38), urea (47) $HOCH_2CH_2OH$ (19)	0°C, 30 min; 20°C, 9 h	132–134/8	3.6 (75)	$C_{12}H_{22}O_2Si_2$ (254.47)	C 56.8/56.63 H 9.21/8.71
21	NEt_2	**4**, 5 g (38), Et_2O Et_2NH (80), Et_2O	−30°C, 30 min; 20°C, 2 days	40/3	2.7 (42)	$C_9H_{19}NSi$ (169.35)	C 63.5/63.83 H 11.5/11.31 N 8.55/8.27
22	H	**4**, 5 g (38), Et_2O $LiAlH_4$ (26), Et_2O	−30°C, 1 h; 6 h reflux	92–94/760	1.1 (30)	$C_5H_{10}Si$ (98.22)	C 61.3/61.14 H 9.95/10.26
23	Me	**4**, 22.5 g (169), Et_2O MeMgCl (169), Et_2O	0°C, 2 h; 6 h reflux	101/760	15.7 (83)	$C_6H_{12}Si$ (112.25)	C 63.5/64.19 H 10.6/10.77
24	Ph	**4**, 5 g (38), Et_2O PhMgBr (40), Et_2O	0°C, 30 min; 8 h reflux	100–102/15	4.2 (64)	$C_{11}H_{14}Si$ (174.31)	C 74.9/75.78 H 8.46/8.09
25	*p*-Tol	**4**, 6.4 g (48), Et_2O TolMgBr (50), Et_2O	0°C, 30 min 10 h, reflux	52/4	4.6 (50)	$C_{12}H_{16}Si$ (188.33)	C 75.8/76.52 H 8.58/8.56

3.4.3. Aminolysis

To a cold solution of **4a** in ether (6–10 fold volume) a solution of 2.1 equiv of the amine was added dropwise with stirring. When the reaction was complete, the solution was filtered, the precipitate washed with ether, the solvent removed from the combined filtrate and washings and the residue distilled (data for **21** in Tables 3 and 5).

3.4.4. Reduction with $LiAlH_4$

A solution of 5 g (38 mmol) of **4a** in ether (25 ml) was added dropwise to a suspension of 1 g (26 mmol) of $LiAlH_4$ in 75 ml of ether at −65°C. After 2 h stirring at room temperature and then 6 h under reflux the volatile components were distilled off and then fractionated to give 1.1 g (30%) of 1-methyl-silacyclopent-3-ene (**22**) (Tables 3 and 5).

3.4.5. Reaction with Grignard reagents

The solutions of RMgX were prepared under argon by bubbling in gaseous MeCl or by adding ArBr dropwise to Mg in ether; a 1.1 molar equivalent of RX relative to **4a** and a 20% excess of Mg were used. A solution of **4a** in ether was added dropwise at 0°C and the mixture refluxed for several hours. After hydrolysis with saturated NH_4Cl solution the organic layer was separated and dried over Na_2SO_4, the solvent was distilled off and the residue fractionated. Data for **23–25** are in Tables 3 and 5.

3.4.6. Reaction with sodium

Compound **4a** (6.6 g, 50 mmol) was added dropwise to a boiling suspension of 1.2 g (52 mmol) of Na in 50 ml of toluene to give a deep violet suspension. After 2 h refluxing the solution was filtered, the precipitate washed with ether and the filtrate and washings fractionated to give 1.8 g (37%) of **26**, b.p. 57°C/1 mmHg. $C_{10}H_{18}Si_2$ (194.43); found/calc.: C 60.6/61.77, H 8.72/9.33%.

3.5. Bromination by N-bromosuccinimide (27)

To a boiling solution of 15 g (0.11 mol) of **4a** in 60 ml of CCl_4 19.4 g of dry NBS was added in small portions. The mixture was refluxed for a further 30 min then cooled to *ca.* 0°C, and the succinimide was filtered off, and washed with CCl_4. The combined filtrate and washings were distilled. At 40–41°C/2 mmHg 12.6 g (54%) was obtained of a mixture of three isomers, consisting (according to ^1H- and ^{13}C-NMR data) of *cis/trans*-4-bromo-1-chloro-1-methyl-silacyclopent-2-ene (**27b**) and *trans*-2-bromo-1-chloro-1-methyl-silacyclopent-3-ene (**27a**) (ratio 30 : 57 : 13). $C_5H_8BrClSi$ (211.57); found/calc.: C 28.88/28.39, H 3.78/3.81%. For ^1H-NMR data see Fig. 2, and for ^{13}C-NMR data, Tables 1 and 2.

28: A solution of 15.7 g (0.14 mol) of dimethylsilacyclopent-3-ene (**23a**) in 60 ml of CCl_4 was treated with 24.6 g (0.14 mol) of NBS as above. The succinimide was filtered off and fractionation of the filtrate at 71–72°C/20 mmHg gave 11.6 g (43%) of a mixture of two isomers, 4-bromo-1,1-dimethyl-silacyclopent-2-ene (**28b**) and 2-bromo-1,1-dimethyl-silacyclopent-3-ene (**28a**) in the ratio 66 : 34. $C_6H_{11}BrSi$ (191.14); found/calc.: C 38.33/37.70, H 6.09/5.80%. For ^{13}C-NMR data see Tables 1 and 2.

3.6. Addition of bromine

3.6.1. 1-Chloro-3,4-dibromo-1-methyl-silacyclopentane (29)

A solution of 12 g (76 mmol) of Br_2 in 5 ml of CCl_4 was added dropwise to a solution of 10 g (76 mmol) of **4a** in 20 ml of CCl_4. The mixture was stirred for 30 min and the solvent removed *in vacuo*. Distillation gave 10.4 g (47%) of the *trans*-adduct **29** of b.p. 95–97°C/5 mmHg. $C_5H_9Br_2ClSi$ (292.46); found/calc.: C 21.81/20.53, H 3.60/3.10%. $\delta^{13}C$-NMR{^1H} ($CDCl_3$) (ppm): SiMe 3.25, CH_2 24.14/25.19, CHBr 54.91/56.41 [22*].

3.7. Addition of PhSH

3.7.1. 1,1-Dimethyl-3-phenylthio-silacyclopentane (30)

A mixture of 2 g (18 mmol) of 1,1-dimethylsilacyclopent-3-ene (**23a**) and 4.0 g (36 mmol) of thiophenol under argon was mixed with 1 ml of a cooled 50 wt% solution of diisopropylperdicarbonate in xylene. The vessel was evacuated and then heated for 10 h at 80°C. Distillation gave 1.8 g (46%) of **30**, b.p. 160°C/18 mmHg. $C_{12}H_{18}SSi$ (222.43); found/calc.: C 64.74/64.80, H 7.9/8.15, S 15.3/14.42%. NMR, δ($CDCl_3$) (ppm), ^1H: $SiMe_3$ 0.12/0.17 (2s, 6H), CH_2 0.5–2.1 (m, 6H), CH(S) 3.3–3.4 (m, 1H), Ph 7.1–7.5 (m, 5H); ^{13}C: SiMe −1.19/−1.49, C(2) 21.0, C(3) 48.0, C(4) 33.6, C(5) 11.7, Ph (*i*) 136.3, (*o*) 131.2, (*m*) 128.4, (*p*) 126.1.

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