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FLASH VACUUM THERMOLYSIS AND MASS SPECTROSCOPY OF 9,10-DIHYDRO-9-SILAANTHRACENES

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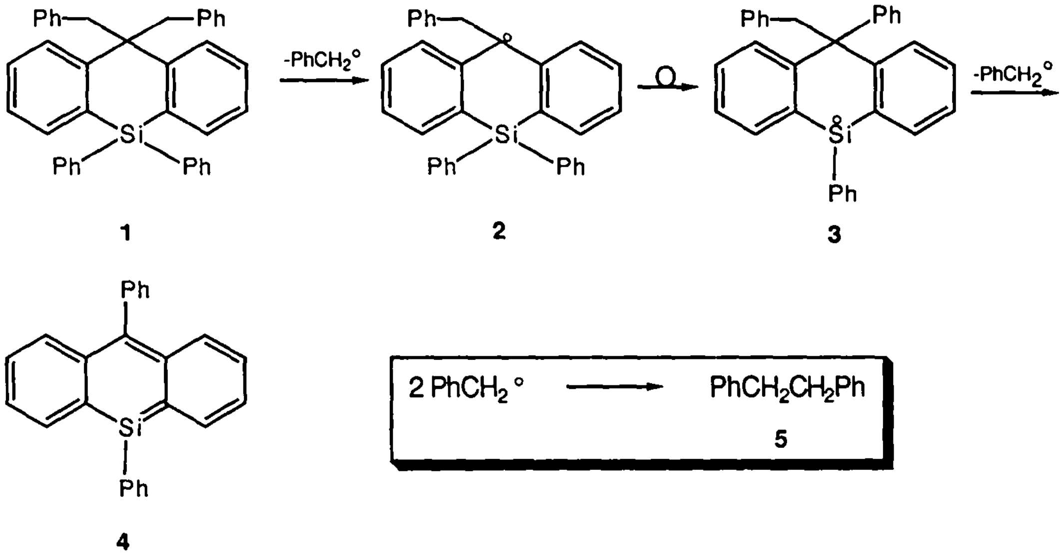
Abstract - The synthesis of 9,10-dibenzyl-9,10-diphenyl-9,10-dihydro-9-silaanthracene (**8**), and of some similarly substituted 9,10-dihydro-9-silaanthracenes is reported. Compound **8** was prepared with the aim of converting it by Flash Vacuum Thermolysis (FVT) into 9,10-diphenyl-9-silaanthracene (**4**), with 1,2-diphenylethane (**5**) as the expected byproduct. At lower temperatures, a surprisingly stable, dark green organic radical was formed, which was investigated by ESR and ENDOR spectroscopy and tentativily assigned the triphenylmethyl type structure **9**. Both benzyl groups of **8** were efficiently cleaved off, presumably to give **4**, and the yield of **5** was about 70% at higher temperatures. However, no direct information on the existence of **4** was obtained, and it was concluded that it polymerizes under the conditions of reaction. Parallel to FVT experiments, the formation of ionized 9-silaanthracenes in the EI mass spectra of **8** and of analogues was investigated. Fragmentation leading to the ionized 9-silaanthracenes was found to be favoured by the presence of one or two phenyl groups at silicon and in the precursor ion of a benzyl group and a hydrogen at the 10-carbon position.

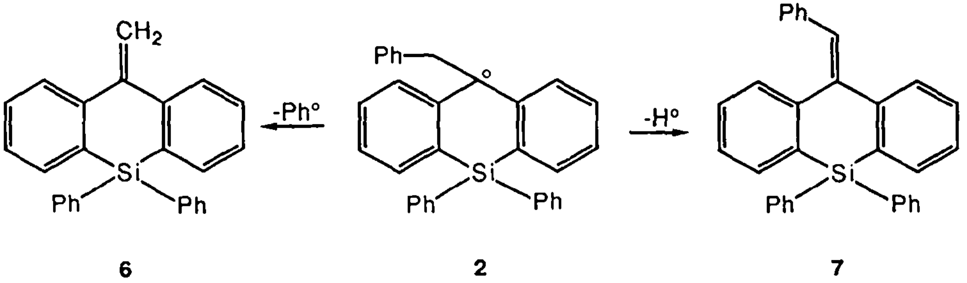
INTRODUCTION

Recently, we reported[1] an attempt to convert 9,9-diphenyl-10,10-dibenzyl-9,10-dihydro- 9-silaanthracene (**1**) thermally into a derivative of 9-silaanthracene. In analogy to successful approaches in the phospha- and arsaanthracene series[1,2] **1** was expected to be a precursor for the sterically protected 9,10-diphenyl-9-silaanthracene (**4**) formed via **2** and **3** by the radical mechanism depicted in Scheme 1.



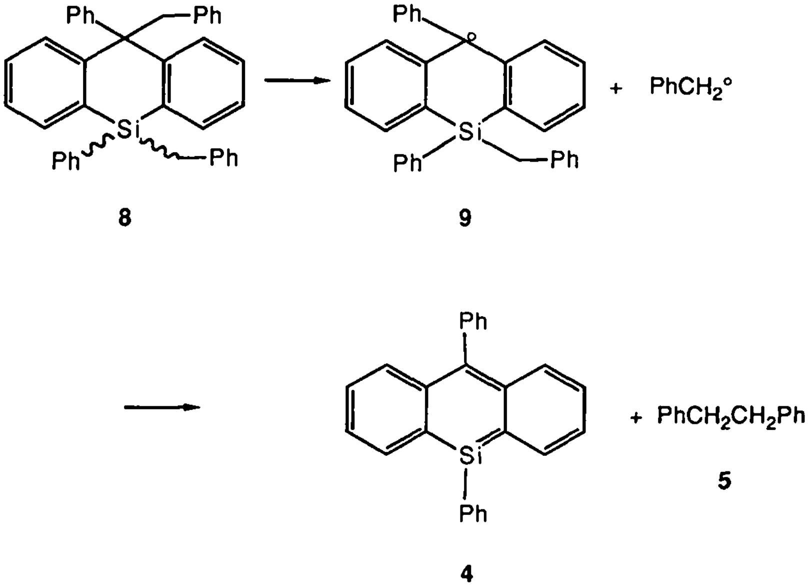
Scheme 1

However, instead of **4** the escape products **6** and **7** were obtained. It was concluded that only one of the two benzyl groups present in **1** was efficiently cleaved off to form the radical **2**. But **2** did not transfer its phenyl group by a 1,4-migration from silicon to the 10-position to yield **3**, which is in marked contrast to analogous radical intermediates in the phosphorus and arsenic series. Instead, **2** underwent rapid β-cleavage reactions: either a phenyl radical was cleaved off to give **6**, or a hydrogen atom was lost to give **7** (Scheme 2). Apart from steric factors, the difference in stability between the carbon centered radical **2** and the silicon centered radical **3** may be responsible for the deviant behavior, in that **2** is a tertiary and resonance stabilized radical of the diphenylmethyl-type, whereas **3** is not strongly stabilized by resonance delocalization of the unpaired electron into the aromatic rings.



Scheme 2

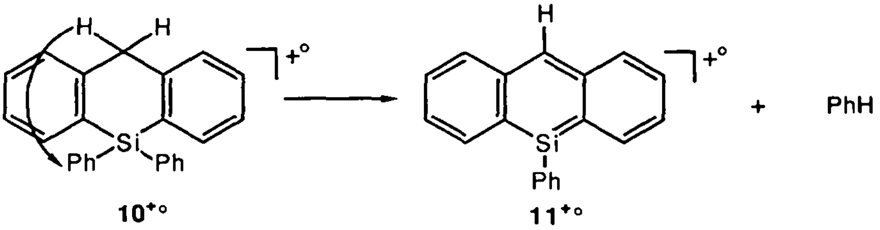
We therefore decided to investigate a route which does not involve a 1,4-phenyl migration: 9,10-dibenzyl-9,10-diphenyl-9,10-dihydro-9-silaanthracene (**8**), an isomer of compound **1**, appeared to be a good precursor for **4**. The formation of **4** was expected to proceed by an initial cleavage of the benzyl group from the 10-carbon position to yield the triphenylmethyl type radical **9**, and by the subsequent aromatization under the extrusion of the second benzyl radical (Scheme 3). The two benzyl radicals were expected to combine afterwards to give 1,2-diphenylethane (**5**).



Scheme 3

As discussed previously[1], it was anticipated that **4** may have insufficient stability under the pyrolysis conditions. Nevertheless, even in this case the experiment would furnish valuable information, because the formation of 1,2-diphenylethane and hopefully of dimers or polymers of **4** would indicate the essential validity of this approach. Without such encouraging indication, further synthetic endeavours directed towards a more stable derivative of **4** would appear too risky as they would involve rather lengthy and laborious routes.

In parallel to the findings on the thermal conversion of 9,9-diphenyl-9,10-dihydro-9-silaanthracene (**10**) and 10,10-dibenzyl-9,9-diphenyl-9,10-dihydro-9-silaanthracene (**1**) we reported on the EI mass spectrometric fragmentation of substituted 9,10-dihydro- 9-silaanthracenes[1,3]. The mass spectrum of **1** shows only a minor signal for ionized **4**, which may be formed either by a concerted transannular mechanism or by the stepwize loss of two benzyl radicals. The formation of ionized 9-phenyl-9-silaanthracene, **11**$^{+\circ}$, is responsible for the most abundant signal in the mass spectrum of **10**; it was confirmed by D-labelling that **11**$^{+\circ}$ is formed by a 1,4-elimination of benzene from the molecular ion of **10** (Scheme 4).



Scheme 4

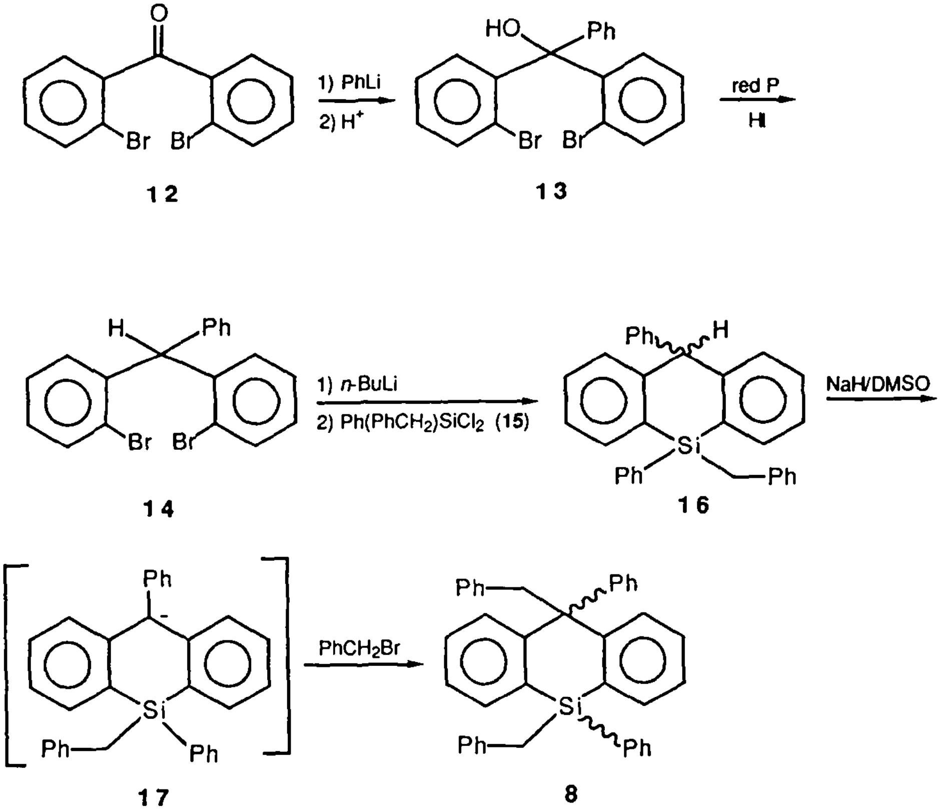
Following these findings we decided to further pursue investigations on the occurence of ionized (substituted) 9-silaanthracenes in the mass spectra of (substituted) 9,10-dihydro-9-silaanthracenes, especially since mass spectrometric and thermolytic behaviour often show interesting analogies.

RESULTS AND DISCUSSION

Synthesis of starting materials

The synthesis of **8** is outlined in Scheme 5. The starting benzophenone (**12**) and its conversion to **13** via **14** have been described previously[4]. By changing the work-up procedure (i.e. purification by column chromatography, instead of sublimation) the overall yield of **14** was increased from 24% to 36%; this yield is still low, presumably due to substitution reactions at the halogen position as observed in the reaction of of 2-bromobenzophenone with Grignard reagents[5].

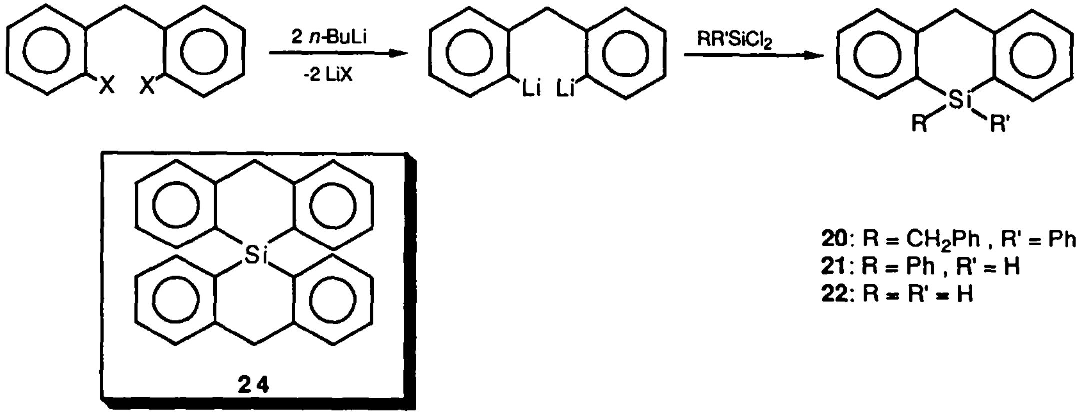
Compound **14** was converted to its dilithio derivative with *n*-butyllithium in hexane, and treated with benzyldichlorophenylsilane (**15**) to give **16** as a 1:1 mixture of the two possible stereoisomers **16'** and **16"**. The ^{1}H NMR signals of the methylene and the methine protons of both isomers could be observed separately (see Experimental); when subjected to GCMS, the retention times of the stereoisomers were found to be slightly different. One of the isomers was obtained in a diastereomeric excess of > 90% (^{1}H NMR; yield 20%) by crystallization of the mixture from diethyl ether. The other isomer was obtained in a diastereomeric excess of about 50% from the mother liquors (^{1}H NMR; yield 25%). Finally, treatment of either of the isomers with dimsylsodium furnished presumably the same intermediate anion (**17**)(Scheme 5) which with benzyl bromide gave **8** in 74% yield. Due to the extremely low solubility of **8**, its ^{1}H-NMR spectrum could not be measured, and therefore the ratio of the two possible stereoisomers is not known.



Scheme 5

For the purpose of further mass spectrometric experiments, 9-benzyl-9-phenyl-9,10-dihydro- 9-silaanthracene (**20**), 9-phenyl-9,10-dihydro-9-silaanthracene (**21**), 9,10-dihydro-9-silaanthracene (**22**), and 10-benzyl-9,9-diphenyl- 9,10-dihydro-9-silaanthracene (**23**) were synthesized. The synthesis of **20**, **21**, and **22** is outlined in Scheme 6.

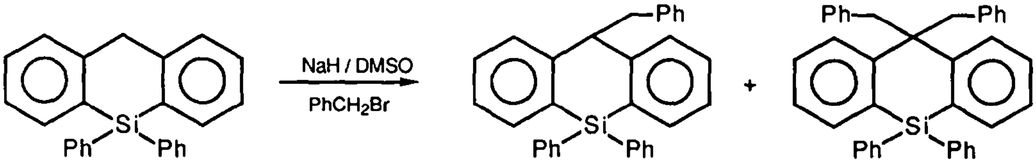
The route outlined here turned out to be successful for compounds **20** and **21** (see Experimental); they could be isolated in pure form in 45% and 34% yield, respectively. For **22**, however, this shortcut from the literature route[6] was found to be inefficient, in that the major product obtained by crystallization from the reaction mixture was the spiro compound **24**. In the mother liquors, **24** (20%) and **22** (30%) were the only identified products (GCMS). For the synthesis of **23**, we followed the route outlined in Scheme 7.



24

20: R = CH$_2$Ph , R' = Ph
21: R = Ph , R' = H
22: R = R' = H

Scheme 6



10 **23** **1**

Scheme 7

Unfortunately the major product obtained in the attempted synthesis of **23** was the disubstituted compound **1**[1] and much of the starting material was recovered. Although we did not succeed in any purification, sufficient **23** was formed to allow for EI and MI mass spectrometric experiments.

Flash vacuum thermolysis of 8

Flash vacuum thermolysis (FVT) of **8** was performed at 10^{-6} mbar (pump pressure) in the temperature range of 500-700°C. A coloured deposit formed directly behind the hot zone; the deposit was green at a pyrolysis temperature of 500°C and yellow at 600 and 700°C. The more volatile material was collected in a cold trap (liquid nitrogen). The total recovery ranged from 85 to 95% and the yield of 1,2-diphenylethane (**5**) increased with increasing temperature (Table I).

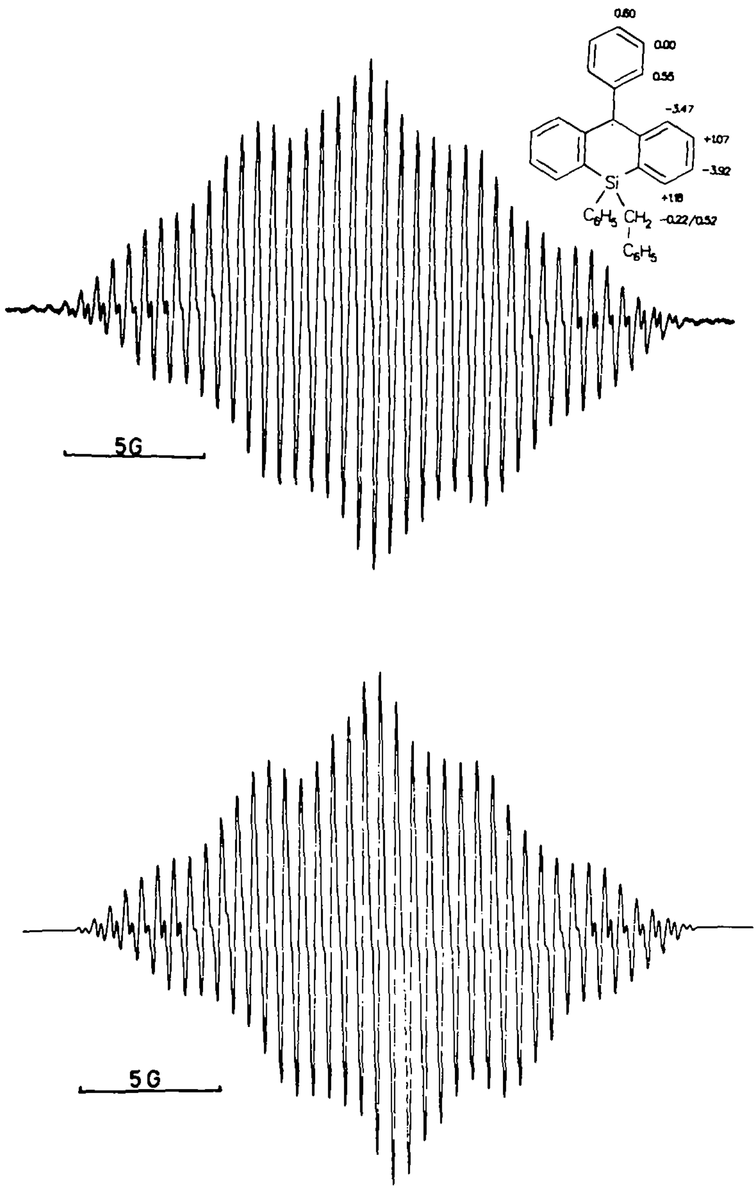


Fig. 1. ESR-Spectrum of the radical tentatively assigned to **9** at 293 K in n-Heptan. top: experiment; bottom: simulation

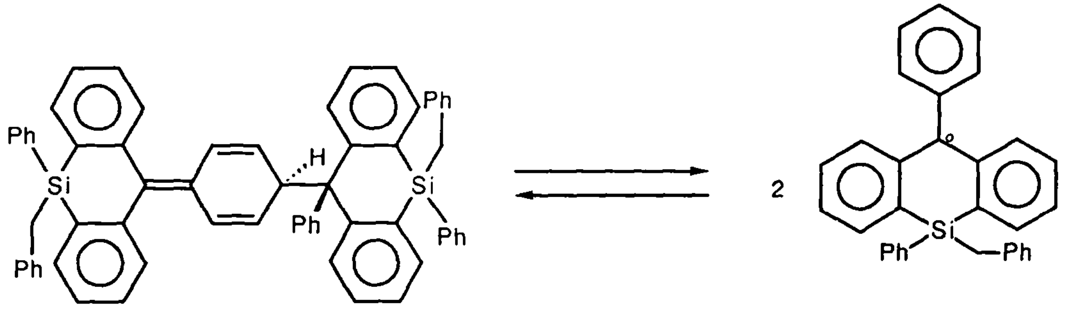
Table 1. Yield of 1,2-diphenylethane (**5**) on FVT of **8**.

T(°C)	run I	run II
500	22%	23%
600	51%	63%
700	68%	78%

In no instance the desired **4** or its dimer could be detected, not even by subjecting the total pyrolysate to direct inlet mass spectrometry (under EI conditions). From the observation that the yield of **5** was higher than 50% at higher temperatures, one may conclude that, to a considerable degree, both benzyl groups of **8** were cleaved off. In line with this cleavage of two benzyl groups we propose that a corresponding product in the gas phase is the highly reactive **4**, which apparently polymerizes. It is noted that, to date, silaaromatic compounds have only been observed in the gas phase or in a matrix[9] and that no silaaromatics have been isolated in pure form nor detected in solution.

From Table 1. it is seen that at 500°C only (less than) one benzyl radical cleaves off; this corresponds with the abovementioned formation of a green deposit. The suspected formation of radical material under these conditions was confirmed by ESR measurements; the ESR spectrum of the "solid" compound showed only one line, with a width of 10 G and a g-factor of 2.0036. The relative intensity of this sole signal increased 14 times by raising the temperature from 0°C to 180°C; this increase in intensity was reversible. From this change in intensity a ΔH_{Diss}(dimer) of 3.5 kcal mol^{-1} was estimated; note that the for the dimer of triphenylmethyl radicals a ΔH_{Diss} of 10.7 ± 0.2 kcal mol^{-1} was found. The ENDOR-spectrum of the pure, solid compound revealed the following proton couplings: 4.4 G, 1,8 G, 1,2 G. More information concerning the radical structure can be obtained by investigation of a solution in *n*-heptane. The ESR spectra at 293 K consist of numerous hyperfine components (see Fig 1) and can hardly be interpreted. However, from ENDOR- and TRIPLE-experiments a set of proton coupling constants and their relative signs could be obtained. A refinement of these values was done by spectra simulation. A negative sign for the larger coupling constants was assumed. The numbers which fit the experimental spectrum and a tentatively assignment to distinct molecule positions of the radical proposed are given in Fig. 1.

In view of the results derived from the ESR experiments, considering the possible reaction pathways in the present study and in analogy with the wellknown behavior of the triphenylmethyl radical[7], we propose a monomer/dimer equilibrium involving **9** and **25** as shown in Scheme 8.



25

9

Scheme 8

In order to obtain confirmation for the identity of the proposed radical, several further experiments would be necessary, e.g. trapping experiments or labelling of different positions of the starting material. These experiments are beyond the scope of the present investigation.

Mass spectrometry of (substituted) 9,10-dihydro-9-silaanthracenes

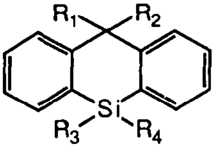
In marked contrast to the observation that the thermolysis of (substituted) 9,10-dihydro- 9-silaanthracenes does not produce directly observable (substituted) 9-silaanthracenes, ionized 9-silaanthracenes have been observed in the electron ionization (EI) mass spectra of various (substituted) 9,10-dihydro-9-silaanthracenes. The molecular ion of 9-phenyl-9-silaanthracene (**11**), is the base peak in the mass spectrum of **10**[1,3]. Analogous observations were reported for the formation of ionized 9-halo- and 9-methyl-substituted 9-silaanthracenes from the appropriately substituted analogues of **10**[3,8]. The presence of a metastable ion signal for the formation of ionized (substituted) silaanthracenes from the molecular ions of the halosubstituted compounds was also reported[3]. Therefore, it may be concluded that the odd electron 'molecular' ions of substituted 9-silaanthracenes are formed by fragmentation following ionization.

The observation of fragment ions which correspond to the molecular ions of substituted silaanthracenes prompted us to investigate the fragmentation processes of (substituted) ionized 9,10-dihydro-9-silaanthracenes **1**, **8**, **10**, **16**, **20**, **21**, **22**, and **23**.

Partial EI mass spectra of **1**, **8**, **10**, **16**, **20**, **21**, **22**, and **23**, corrected for isotope contributions, are given in Table 2. Spectra of compound **16** were obtained for two mixtures containing different ratios of the two diastereomers (ratio of 20:1 and 1:3, as shown by NMR), but the mixtures did not produce significantly different mass spectra. The diastereomers of **8** could not be separated and the spectrum reported here was obtained from a mixture with an unknown ratio of the diastereomers.

Table 2. Partial EI mass spectra of 9,10-dihydro-9-silaanthracenes.

COMPOUND	**22**	**21**	**10**	**20**	**23**	**16**	**1**	**8**
ION[a]				INTENSITY[b,c]				
$M^{+\circ}$	100	13	2	9	0.1	8	1	0.3
$(M\text{-}H)^+$	87	22	1	-	-	-	-	2
$(M\text{-}H_2)^{+\circ}$	$\underline{20}$	$\underline{6}$	-	-	-	-	-	-
$(M\text{-}H_2\text{-}H)^+$	32	3	-	-	-	-	-	-
$(M\text{-}Ph)^+$	1	9	58	1	-	-	-	-
$(M\text{-}PhH)^{+\circ}$	3	$\underline{100}$	$\underline{100}$	-	-	$\underline{1}$	-	-
$(M\text{-}PhH\text{-}H)^+$	1	30	5	-	-	-	-	1
$(M\text{-}PhH\text{-}Ph)^+$	-	-	7	-	-	-	-	-
$(M\text{-}Bz)^+$	-	-	-	100	4	100	82	100
$(M\text{-}Bz\text{-}H)^{+\circ}$	-	-	-	$\underline{5}$	-	$\underline{1}$	-	$\underline{1}$
$(M\text{-}Bz\text{-}H_2)^+$	-	-	-	2	-	3	-	-
$(M\text{-}Bz\text{-}Ph)^{+\circ}$	-	-	-	1	$\underline{100}$	6	-	4
$(M\text{-}Bz\text{-}PhH)^+$	-	-	-	7	4	14	100	43
$(M\text{-}Bz\text{-}PhH\text{-}H_2)^+$	-	-	-	1	3	11	5	1
$(M\text{-}Bz\text{-}Bz)^{+\circ}$	-	-	-	-	-	-	$\underline{14}$	$\underline{33}$
$(M\text{-}C_{20}H_{18})^{+\circ}$ (270)	-	-	-	-	-	-	24	10
$C_{13}H_9^+$ (165)	62	13	9	8	4	6	22	5
$C_6H_5Si^+$ (105)	9	7	11	9	6	5	85	40
Bz^+	-	-	1	6	1	6	24	8
$PhH^{+\circ}$	-	2	1	-	1	-	-	-
Ph^+	1	1	1	1	1	-	-	1



compound	R_1	R_2	R_3	R_4
22	H	H	H	H
21	H	H	H	Ph
10	H	H	Ph	Ph
20	H	H	Ph	Bz
23	H	Bz	Ph	Ph
16	H	Ph	Ph	Bz
1	Bz	Bz	Ph	Ph
8	Ph	Bz	Ph	Bz

a) M = molecule, Ph = phenyl radical, Bz = benzyl radical; b) Intensities (in % of the base peak) are reported for ions which contain exclusively $^{12}C^{28}Si$ *isotopes (corrected if necessary); c) The intensities of ionized 9-silaanthracenes are underlined.*

From the underlined entries in Table 2 it is seen that (substituted) ionized 9-silaanthracenes occur in the mass spectra of all compounds, albeit with abundances ranging from 1% to 100%. Ionized 9-silaanthracene, *m/z* 194, is present in the mass spectra of **21** (100%) and **22** (20%). Ionized 9-phenyl-9-silaanthracene, *m/z* 270, dominates the mass spectra of **10** (100%) and **23** (100%) and produces only a minor signal in the mass spectrum of **20** (5%). A signal corresponding to ionized 9,10-diphenyl-9-silaanthracene, $4^{+\circ}$ *m/z* 346, is present in the mass spectra of **8** (33%) and **16** (1%). Some compounds favour the loss of only one radical, to produce closed shell fragment ions, whereas others favour the loss of a molecule or of two radicals, to produce the open shell fragment ions. The loss of a benzyl radical by direct bond cleavage at a silicon atom which is bound to a phenyl group (**16** and **20** and probably **8**) is highly favoured. The loss of a benzyl radical from the 10-carbon position is less favourable, although becoming more intense with increasing substitution at the 9- and 10-position (**1** and **23**). The tendency to lose two radicals in a subsequent reaction to produce a substituted 9-silaanthracene ion is especially favoured in the case of ionized **23**, where the benzyl radical loss is followed by a loss of phenyl; that the radicals are indeed lost by subsequent steps was confirmed by the MI mass spectra of the molecular and product ions. The EI mass spectra also show that the loss of a benzene molecule (from **10** and **21**, 100%) is favoured over any radical loss, i.e. loss of Ph° and H°, if no benzyl moiety is present in the molecule at all. Note that the loss of benzene and of a hydrogen molecule (from **21**, 6%, and **22**, 20%) requires a transannular elimination reaction. In conclusion, the abundance of ionized 9-silaanthracene type ions in the EI mass spectra of 9,10-dihydro-9-silaanthracenes is strongly dependent upon the substitution pattern of these compounds.

The major fragmentation processes of the molecular ions and their primary daughter ions were further studied by metastable ion (MI) mass spectrometry (except for **8**, for which the molecular ion is of too low intensity). For compounds **1**, **10**, **16**, **20**, **21** and **23**, the only peaks observed in the MI mass spectra of the molecular ions correspond to the losses of a hydrogen radical, a benzyl radical, or a benzene molecule. Hydrogen loss from the metastable ions is not considered in the discussion, because the intensities and peak shapes suffer from metastable ion and isotopic interferences (^{13}C, ^{29}Si) in most cases; the contribution of isotopic interferences in the other metastable ion signals was found to be of no importance. The behaviour of metastable **22**$^{+\circ}$ deviates notably from that of all other molecular ions in the present study. Metastable ion fragmentation by loss of H_2 (100%, kinetic energy release at half height, $T_{0.5}$ = 350 ± 10 meV) is observed, in agreement with the findings of Chernyshev et al.[6]. In addition we found that metastable 22 ions rearrange to lose $^\circ SiH_3$ (75%, $T_{0.5}$ = 33 ± 3 meV), $^\circ CH_3$ (6%, $T_{0.5}$ = 47 ± 3 meV) and C_6H_6 (1%, $T_{0.5}$ = 33 ± 3 meV). The relative MI peak intensities and the kinetic energy releases for the loss of benzene and of benzyl are given in Table 3.

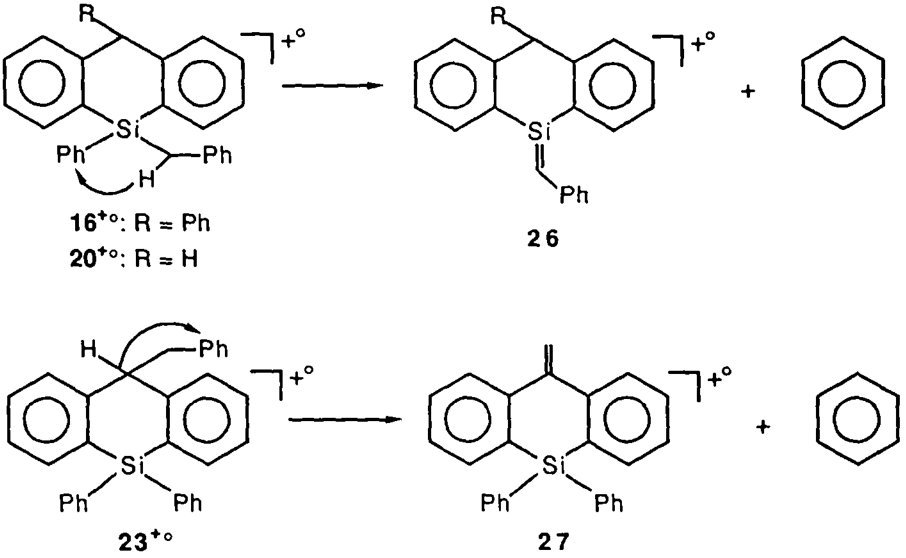
Table 3. Metastable ion benzyl and phenyl loss in the molecular ions of 9,10-dihydro-9-silaanthracenes.

MOLECULAR ION	$22^{+\circ b}$	$21^{+\circ}$	$10^{+\circ}$	$20^{+\circ}$	$23^{+\circ}$	$16^{+\circ}$	$1^{+\circ}$
neutral lost			relative intensity^a/ kinetic energy release^b				
C_6H_6	100	100	100	2	7	9	18
$T_{0.5}$ (± 3 meV)	33	15	42	77	70	89	79
$C_7H_7^\circ$	-	-	-	100	100	100	100
$T_{0.5}$ (±3 meV)	-	-	-	41	28	37	36

a) Intensities are reported relative to the highest intensity of the peaks in this table, other fragmentations may be more intense, see text. b) All peaks have a Gaussian peak shape.

It is seen from Table 3 that benzene is lost from all metastable molecular ions. This shows that benzene is not necessarily lost by a transannular elimination, as such a process cannot occur from ionized **1** nor from ionized **22**. Note that the loss of benzene from ionized 22, involving the migration of two hydrogen radicals, must proceed via a ring opening.

Such a ring opening, accompanied by H-migration, suffers competition from a 1,4-hydrogen migration with the subsequent loss of a silyl- or a methylradical ($^{\circ}SiH_3$, $^{\circ}CH_3$)(*vide supra*) to produce the resonance stabilized fluorenyl ($C_{13}H_9^+$) or silafluorenyl ($C_{12}H_9Si^+$) cations respectively. Further, the loss of benzene observed in the MI mass spectra of ionized **1**, **20**, and **23** is absent in the corresponding EI mass spectra. Here and in ionized **16**, the loss of benzene may occur by the formation of a ionized silene (**26**) or 1,1-diphenylethene (**27**) type ion (Scheme 9); ionized **16** and **20** may alternatively undergo a transannular elimination reaction as depicted for **10** in Scheme 4.



Scheme 9

In contrast to ionized **1**, **16**, **20**, and **23**, ionized **10** (and **21**) can only lose a benzene molecule via a transannular elimination reaction (Scheme 4). The possibility of two mechanisms for the loss of benzene is suggested to account for the observed differences in the kinetic energy release: fragmentation via a transannular elimination produces a small kinetic energy release, whereas fragmentation by a formal 1,3-hydrogen migration produces a much larger kinetic energy release (Table 2). The possible simultaneous occurrence of both fragmentation processes at the time, for **16** and **20**, which would result in two different amounts of kinetic energy release, may remain hidden in the metastable ion peak shape.

If at least one benzyl group is present in the molecule, the loss of a benzyl radical from substituted 9,10-dihydro-9-silaanthracene ions dominates the metastable fragmentation of the molecular ion. The required direct bond cleavage is accompanied by a kinetic energy release ranging from 28 to 41 meV, quite common for direct bond cleavages in general. The source generated product ions of benzyl loss from **1**, **8**, **16**, **20**, and **23** were also subjected to MI experiments. Except for **23**, the product ions predominantly lose a benzene molecule generating a secondary, closed shell product ion. In the case of **23**, the benzyl loss is followed by the loss of a phenyl radical, to produce the odd electron m/z 270 ion: ionized 9-phenyl-9-silaanthracene. In the product ions from **1**, **8**, **16**, and **20**, such a resonance stabilization by aromatization can only be obtained by the loss of H° (instead of a larger radical) which does not take place.

CONCLUSION

Two benzyl radicals are cleaved off from **8** by flash vacuum thermolysis at higher temperatures, presumably generating **4**, a derivative of 9-silaanthracene which is highly unstable. No direct evidence for the generation of **4** was obtained but it is likely that, under the conditions of the reaction, **4** immediately polymerized. Polymerization may be prevented in precursors with bulkier substituents around the sensitive central ring of the silaanthracene system, but the synthesis of such compounds will require a considerable synthetic effort.

The formation of 9-silaanthracene type molecular ions in the EI mass spectra of 9,10-dihydro- 9-silaanthracenes is favoured by the simultaneous presence of a phenyl group on the 9-silicon atom and a hydrogen atom on the 10-carbon atom. The phenyl group may either prevent the cleavage of the bond to Si in the precursor ion or act as a leaving group in a transanular elimination reaction, together with the hydrogen on 10-carbon. The presence of a benzyl group on the 10-carbon atom also favours the formation of a 9-silaanthracene type ion, because the benzyl radical is easily lost from the 10-carbon position to produce an even electron product ion which may subsequently lose a radical to form a still more stabilized 9-silaanthracene type radical cation. If analogous arguments apply to the behavior of 9,10-dihydro-9-silaanthracenes under the conditions of flash vacuum thermolysis, compounds **10**, **21**, and **23** are good candidates for the formation of 9-silaanthracenes. As stated above, the thermolysis of these compounds leads to polymerization, presumably via the 9-silaanthracenes as primary. However, substitution at the outer rings of the 9,10-dihydro-9-silaanthracene may prevent such a polymerization. Further investigations to explore possibilities to generate (stable) 9-silaanthracenes are under way.

EXPERIMENTAL

All reactions with air sensitive materials were carried out in glassware flamed out under a nitrogen atmosphere. Diethyl ether and *n*-pentane were distilled from $LiAlH_4$. DMSO was distilled from CaH. All products were purified by crystallization, by distillation or by column chromatography. The reported melting points are uncorrected. Elemental analyses were performed by the Mikroanalytisches Labor Pascher, Remagen-Bandorf, Germany. The NMR spectra were measured in $CDCl_3$ on a Bruker WH-90 NMR spectrometer at 90 MHz (^1H) and on a Bruker WM 250 NMR spectrometer at 62.89 MHz (^{13}C) or 49.69 MHz (^{29}Si). Chemical shifts were measured relative to external Me_4Si or 85% H_3PO_4. The ESR, ENDOR and TRIPLE spectra were recorded on a Varian E-Line spectrometer equipped with a Bruker ENDOR ER 810 unit and a Bruker ER 140 data system. The *g* values were determined by comparison with the siganal of 4-*tert*-butoxy-2,6-di-*tert*-butylphenoxyl ($g = 2.004627$) in a double resonator. All products were checked for their purity by GCMS on a 5070 Hewlett-Packard Mass Selective Detector connected to a HP 5890 gas chromatograph equipped with a 25 m CPsil 5 CB capillary column and using a column head pressure of 12 psi. LR and HR EI mass spectra and MI mass spectra were obtained on a Finnigan MAT 90 magnetic sector instrument of reversed geometry (Finnigan MAT, San José, USA), operating at 70 eV electron energy, ion source temperature 200°C and 5 kV accelerating voltage. In addition to HRMS, the exact masses of all molecular ions ($[M-H]^+$ in **8**) and of some fragment ions were checked by peak-matching against an appropriate reference signal. MI mass spectra were recorded at an energy resolution of the electrostatic analyzer of ca. 5 eV, as to allow a determination of the kinetic energy release for the metastable ion fragmentation reactions. All compounds were introduced via a direct insertion probe with probe temperatures ranging from 40°C (for the unsubstituted compound) to 120°C (for the tetrasubstituted compounds).

2,2'-Dibromotriphenylmethane (13)[3]

A solution of phenyllithium (0.041 mol) in diethyl ether (200 ml) was added in 0.5 h to a solution of 2,2'-dibromobenzophenone (**12**)[3] (13.6 g, 0.04 mol) in diethyl ether (50 ml) at room temperature. After the addition was completed, the reaction mixture was stirred for 14 h at room temperature and then poured into 100 ml of water. The organic layer was separated, washed three times with water and then dried over $MgSO_4$. After filtration and evaporation of the solvent from the filtrate, the residue (crude benzhydrol **13**, a viscous yellow oil) was directly treated with red phosphorus (53 g) and hydroiodic acid (57%, 53 ml) for 19 h at 140°C. After cooling to room temperature, the reaction mixture was poured into a mixture of water (100 ml) and chloroform (100 ml). The reaction vessel was washed with another 50 ml of chloroform. The combined phases were filtered, the organic layer was separated and washed until neutral with water and subsequently with aqueous NaS_2O_3 and was then dried over $MgSO_4$. After filtration and evaporation of the filtrate, the residue was purified by column chromatography (silica gel/*n*-pentane) and yielded **14** (5.8 g, 36%) as a colourless powder (m.p. 128°C). ^1H NMR : δ 6.76-7.77 (m, 13H, aryl H), 6.18 (s, 1H, methine H); mass spectrum (relative intensity) *m/z* : 402(26) $M^{+\circ}$, 321(24) $[M\text{-}Br]^+$, 242(48) $[M\text{-}Br\text{-}Br]^{+\cdot}$, 165(100) $[M\text{-}Br\text{-}Br\text{-}Ph]^+$.

Benzyldichlorophenylsilane (15)

A solution of benzylmagnesium chloride (0.217 mol) in diethyl ether (230 ml) was added, at room temperature, to a solution of freshly distilled phenyltrichlorosilane (45.9 g, 0.217 mol) in diethyl ether (250 ml). After stirring overnight, the solvent was evaporated and *n*-pentane was added. After filtration from the magnesium salts and evaporation of the filtrate, the residue was distilled in vacuum and yielded **15** (40 g, 70%) as a colourless liquid (b.p. 102°C/0.5 mm Hg). ^1H NMR: δ 7.12-7.68 (m, 10H, aryl H), 2.87 (s, 2H, CH_2-). ^{13}C NMR : δ 30.3 (t, ^1J(CH) = 123.7 Hz), 125.8 (d, ^1J(CH) = 161.3 Hz), 128.2 (d, ^1J(CH) = 161.7 Hz), 128.4 (d, ^1J(CH) = 152.3 Hz), 129.2 (d, ^1J(CH) = 157.7 Hz), 131.6 (s), 131.6 (d, ^1J(CH) = 175 Hz), 133.7 (d, ^1J(CH) = 161 Hz), 133.8 (s). ^{29}Si NMR : δ 13.8 ppm. Mass spectrum *m/z* (relative intensity): 266(25) $M^{+\circ}$, 175(100) $[M\text{-}CH_2Ph]^+$, 91(29) $[PhCH_2]^+$, 77(30) $[Ph]^+$. HRMS: found 266.009; calcd. $C_{13}H_{12}{}^{35}Cl_2Si$: 266.0085.

9-Benzyl-9,10-diphenyl-9,10-dihydro-9-silaanthracene (16)

A solution of *n*-butyllithium (0.069 mol) in hexane (43 ml) was added to a solution of **14** (11 g, 0.027 mol) in diethyl ether (500 ml) at room temperature. After the addition was completed, a small sample from the reaction mixture was quenched with D_2O to give triphenylmethane with more than 99% D_2 incorporation (GCMS). Then, subsequently, pure **15** (7.3 g, 0.027 mol) was added and, after stirring overnight, the reaction mixture was poured into water and worked up in the usual way. The residue contained a 1:1 mixture of two isomers **16'** and **16"** (GC and ^1H NMR). By crystalization of the mixture from diethyl ether, one of the isomers (**16'**) was obtained (2.4 g, 20%) in a diastereomeric excess >90% as a colourless powder (m.p. 153-154°C). ^1H NMR : δ 6.80-7.62 (m, 23H, aryl H), 5.51 (s, 1H, methine H), 2.36 (s, 2H, -CH_2-). ^{13}C NMR : δ 22.5 (t, ^1J(CH) = 122.0 Hz), 56.3 (d, ^1J(CH) = 126.9 Hz), 124.3 (d, ^1J(CH) = 159.9 Hz), 125.7 (d, ^1J(CH) = 160.8 Hz), 125.9 (d, ^1J(CH) = 160.1 Hz), 127.8 (d, ^1J(CH) = 166.7 Hz), 127.9 (d, ^1J(CH) = 167.9 Hz), 128.2 (d, ^1J(CH) = 185.0 Hz), 128.4, 129.1, 129.4, 129.5, 129.5, 130.2, 132.1, 134.7, 135.8 (d, ^1J(CH) = 159 Hz), 136.2 (d, ^1J(CH) = 158.7 Hz), 138.3 (s), 146.7 (s), 149.3 (s) (the signals were so close that not all expected signals and coupling constants could be distinguished). ^{29}Si NMR : δ -24.1 ppm. The other isomer (**16"**) was obtained in a diastereomeric excess of about 50% (3 g, 25%). ^1H NMR: δ 6.80-7.62 (m, 23H, aryl H), 5.30 (s, 1H, methine), 2.91 (s, 2H, CH_2). HRMS: found 438.180; calcd. $C_{32}H_{26}Si$: 438.1804.

9-Benzyl-9-phenyl-9,10-dihydro-9-silaanthracene (20)

This compound was synthesized the same way as compound **16**; instead of **14**, 2,2'-dibromodiphenylmethane (**18a**) (5.0 g, 15 mmol) was used. The crude reaction product was crystallized from *i*-PrOH, yielding **20** (2.5 g, 45%) as colourless cristals (m.p. 79-82°C). ^1H NMR: δ 7.62 - 6.69 (m, 18 H, aryl-H), 3.78 - 3.33 (AA'BB' system, J_{AB}=18 Hz, 2 H), 2.82 (s, 2H, -CH_2Ph). ^{13}C NMR : δ 23.4 (t, $^1J(CH)$ = 119.3 Hz), 41.2 (t, $^1J(CH)$ = 126.5 Hz), 124.3 (d, $^1J(CH)$ = 160.0 Hz), 125.5 (d, $^1J(CH)$ = 167.4 Hz), 127.8 (d, $^1J(CH)$ = 157.0 Hz), 127.9 (d, $^1J(CH)$ = 156.5 Hz), 127.9 (d, $^1J(CH)$ = 157 Hz), 128.8 (d, $^1J(CH)$ = 158.4 Hz), 129.4 (d, $^1J(CH)$ = 159.1 Hz), 129.8 (d, $^1J(CH)$ = 159.6 Hz), 131.8 (s), 134.1 (s), 134.7 (d, $^1J(CH)$ = 158.7 Hz), 135.6 (d, $^1J(CH)$ = 159.2 Hz), 138.1 (s), 146.9 (s). ^{29}Si NMR: δ -23.32 ppm. HRMS: found 362.147; calcd. $C_{26}H_{22}Si$: 362.1491.

9-Phenyl-9,10-dihydro-9-silaanthracene (21)

This compound was synthesized the same way as compound **20**, using dichlorophenylsilane and 2,2'-diiododiphenylmethane (**18b**) instead of **15** and 2,2'-dibromodiphenylmethane (**18a**) respectively. After the usual work up procedure, **21** was obtained as a crude viscousm oil, which can be purified by column chromatography, using Al_2O_3 (70-230 mesh ASTM) with *n*-pentane as eluent to yield **21**. (0.92 g, 34%) as a colourless oil. ^1H NMR: δ 7.72 - 6.17 (m, 13 H, aryl-H), 5.42 (s, ^1H, Si-H), 4.20 (s, ^1H, methine-H). ^{13}C NMR : δ 41.8(t, $^1J(CH)$ = 126.1 Hz), 125.8 (d, $^1J(CH)$ = 157.0 Hz), 128.1 (d, $^1J(CH)$ = 155.0 Hz), 128.1 (d, $^1J(CH)$ = 160.0 Hz), 129.7 (d, $^1J(CH)$ = 151.8 Hz), 130.1 (d, $^1J(CH)$ = 159.4 Hz), 131.0 (s), 132.3 (s), 135.0 (d, $^1J(CH)$ = 156.2 Hz), 135.9 (d, $^1J(CH)$ = 159.2 Hz), 146.4 (s). ^{29}Si NMR: δ -33.6 (d, $^1J(SiH)$ = 193.0 Hz). HRMS: found 272.098; calcd $C_{19}H_{16}Si$: 272.1021.

9,10-Dihydro-9-silaanthracene (22)

Dichlorosilane (2.5 g, 25 mmol) was condensed in a three necked flask, containing diethyl ether (10 ml) at -72°C. At this temperature a yellow coloured solution of the dilithio compound (**19**)(11 mmol) in diethyl ether (25 ml), (prepared as described for **16**) was added. Immediate decolourization was observed. After the addition was completed, the reaction mixture was allowed to warm to room temperature in one hour. After stirring over night it was worked up in the usual way. The crude reaction mixture was crystallized from CH_2Cl_2/*n*-pentane, yielding suprisinghly spiro compound **24** as colourless cristals. (0.6 g, 1.7 mmol) slightly (10%) contaminated with the desired **22**. Actions to obtain the (known[6]) pure **22** from the mother liquor were unsuccessful, so ^1H, ^{13}C, ^{29}Si NMR spectra could not be recorded. ^1H NMR: δ 7.50 - 7.11 (m, 16H, aryl-H), 4.42 (s, 4H, methine H), HRMS: found 196.068; calcd. $C_{13}H_{12}Si$: 196.0708 (**22**). HRMS: found 360.138; calcd.$C_{26}H_{20}Si$: 360.138 (**24**).

10-Benzyl-9,9-diphenyl-9,10-dihydro-9-silaanthracene (23)

This compound was synthesized in the same way as **1** using only one equivalent of dimsylsodium and benzylbromide[1]. After the usual work up procedure, the amount of desired product turned out to be very small. The main product appeared to be the disubstituted **1**. Despite this unexpected outcome, mass spectrometry experiments could be performed on the crude reaction product (*vide infra*). However, purification did not yield enough pure compound for any additional identification (i.e. ^1H, ^{13}C, and ^{29}Si NMR). HRMS: found 438.191; calcd. $C_{32}H_{26}Si$: 438.1804.

9,10-Dibenzyl-9,10-diphenyl-9,10-dihydro-9-silaanthracene (8)

A solution of **16** (1 : 1 mixture of **16'** and **16"**, 5.0 g, 10.9 mol) in DMSO (10 ml) was added at room temperature to a solution of dimsyl sodium, prepared from NaH (0.48 g of a 55% dispersion in mineral oil, 11 mmol) in DMSO) (5.7 ml). To the red-brown solution, pure benzyl bromide (1.36 ml, 11 mmol) was slowly added. After the addition was complete, the almost colourless reaction mixture was poured into water. The water layer was extracted several times with chloroform. The combined organic phases were washed twice with water. After the organic layer was separated, **8** precipitated on standing. After filtration, the precipitate was washed with acetone, yielding **8** (4.3 g, 74%) as a colourless powder (m.p. 225°C). HRMS: found 527.220; calcd. $C_{39}H_{31}Si$ $[(M-H)^+]$ 527.2195. Anal. Calcd. for $C_{39}H_{32}Si$: C, 88.59; H, 6.10; Si, 5.31. Found: C, 87.83, H, 6.02, Si, 5.20. Compound **8** was too insoluble to measure the ^1H-NMR spectrum.

Flash vacuum thermolyses (FVT).

The FVT apparatus has been described earlier[11]. In our experiments, a 28 cm quartz heating tube was used (inner diameter 17 mm) at a pump pressure of 10^{-6} mbar. In a typical run, **8** was heated to 230°C and sublimed into the hot zone at a rate of about 8 mg.h^{-1}, using a sublimation furnace (Büchi, GKR-50) to heat the sample bulb. The pyrolysate partly polymerized directly behind the hot zone and was partly trapped in a finger cooled with liquid nitrogen. After the FVT, the trap was allowed to warm to room temperature and the pyrolysate was washed with $CDCl_3$ into a NMR tube sealed onto the apparatus; then a known amount of cyclopentane (as internal standard) was added by distillation and the NMR tube was disconnected. The amount of 1,2-diphenylethane was determined by ^{1}H NMR spectroscopy (CH_2 signals), using cyclopentane as internal standard. No other identifiable products could be detected not even by GCMS or by subjecting the residue to direct inlet mass spectroscopy. After evaporating the $CDCl_3$ at reduced pressure, the total recovery was about 90%.

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