SILENE STEREOCHEMISTRY

IV *. THE CONFIGURATIONAL STABILITY OF 1-PHENYL-1-METHYL-2-NEOPENTYLSILENE UNDER FLASH VACUUM THERMOLYSIS CONDITIONS **

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Summary

When *E*- or *Z*-1-phenyl-1-methyl-2-neopentylsilene is generated by retro Diels–Alder flash vacuum thermolysis of their corresponding cyclopentadiene or anthracene adducts at temperatures between 400 and 650°C and trapped with 2,3-dimethyl-1,3-butadiene, the stereochemical distribution of the products is independent of the stereochemistry of the silene precursor indicating that the silene is not configurationally stable towards *cis-trans* isomerization at these temperatures. Evidence that intermolecular "ene" reaction and the [4 + 2] cycloaddition which occur between silenes and the diene are both concerted reactions is presented.

Introduction

This paper presents the results of our studies of the gas phase stereochemistry of silenes. We recently reported evidence that 1-phenyl-1-methyl-2-neopentylsilene (1), generated in sealed tube thermolyses of its anthracene adduct, 10, is configurationally stable up to temperatures of 300°C [1]. We report herein our studies of the configurational stability of 1, generated under flash vacuum thermolysis conditions at temperatures between 400 and 650°C.

Results and discussion

When 1 is generated by the retro Diels–Alder degradation of isomers of 2-phenyl-2-methyl-3-neopentyl-2-silanorborn-5-ene (2) of known stereochemistry [2] using

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* For Part III see ref. 1.
** Dedicated to Prof. M. Kumada, who, along with his coworkers has made so many contributions to organosilicon chemistry and to our understanding of organosilicon reactive intermediates.

TABLE 1

YIELDS AND PERCENT DECOMPOSITIONS OF VARIOUS TRAPPING REACTIONS OF 1-PHENYL-1-METHYL-2-NEOPENTYLSILENE

| Exp. Substrate	Method[a]	Temperature (°C)	Trap[b]	Ratio[c]	Decomposition (%)	Yield (%)			
						3	4–6	7	8–9
1 E-2a	Inj, NR	550	BD	4.7	38	53	8	2.4	2.9
2 E-2b	Inj, R	550	BD	5.0	93	40	9	2.7	2.5
3 Z-2c 71%	Inj, R	550	BD	10.0	87	26	10	2.2	13.5
4 Z-2c 54%	Evap, NR	550	none		97	22	20	1.3	
5 Z-2c 66%	Inj, R	550	CH	3.5	98	39	11	6.5	
8 E-10a 91%	Inj, NR	650	BD	10.0	28	52	9	tr	27.1

[a] Inj = injection, Evap = evaporation, R = flow restriction between hot zone and trap, NR = no restriction. [b] BD = 2,3-dimethyl-1,3-butadiene, CH = cyclohexane diluent. [c] Mol ratio of trap or diluent to substrate.

(2a) (2b) (2c) (2d)

(E-1) (Z-1)
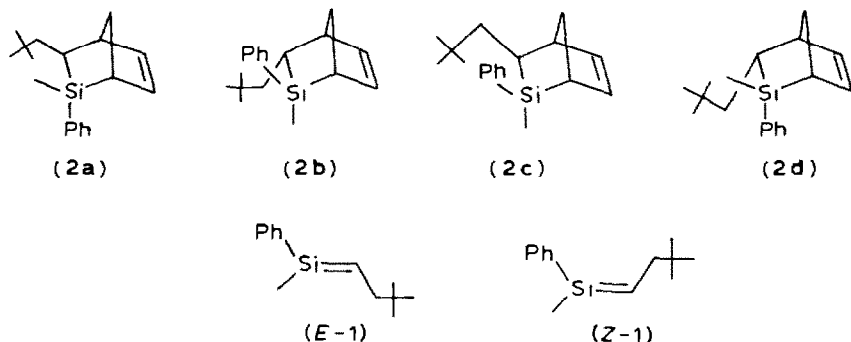
flash vacuum thermolysis the major product in either the presence or absence of a trap is the intramolecular ene product [3], phenylmethylvinylsilane (3). In addition unimolecular silene isomers, tentatively identified as 4–6, and silene dimers, 7a–7e,

Ph—Si
H

(3) (4) (5) (6)

(7a) (7b) (7c) (7d) (7e)
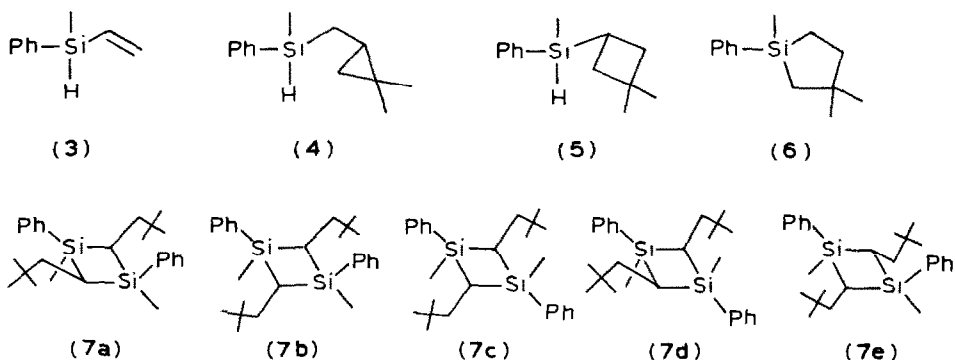
are obtained. In the presence of 2,3-dimethyl-1,3-butadiene as a trapping reagent we obtain 8, the product of the intermolecular ene reaction between 1 and dimethyl-butadiene; and 9a,9b, the *cis*- and *trans*-isomers of 1,3,4-trimethyl-1-phenyl-6-

(8) (9a) (9b)
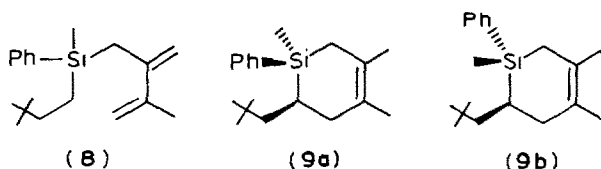
neopentyl-1-silacyclohex-3-ene, formed by the [4 + 2] cycloaddition of the silene with the diene. The preparation and stereochemical characterization of the silanor-bornenes 2 [2]; the silene dimers 7 [4], and 8 and 9 [2] have been reported previously. Typical yields and percent decompositions are given in Table 1. In one experiment (8) 1 was generated by the thermolysis of its anthracene adduct, E-10a.

The results in Table 1 show that decomposition of the silene precursor is not a result of a bimolecular reaction with the trapping agent. When the ratio of butadiene to substrate is doubled (expt. 2 and 3) the percent decomposition decreases. Furthermore the yield of unimolecular silene products 3–6 decreases and the yield of silene trapped by butadiene increases just as one would anticipate. In the flash vacuum thermolysis of 10a (expt. 8) the low percent decomposition even at 650 °C is due to the lack of a flow restrictor forced by the low volatility of the substrate,

resulting in even lower silene concentrations in the reaction zone. In this experiment only traces of silene dimers were observed, and the yield of unimolecular silene products was comparable to expt. 1. In most of the experiments we have accounted for more than 50% of the decomposed substrate as the reported silene products.

The stereochemistry of recovered substrate is compared with that for the starting material in Table 2. The results show that while some of the silene **1** does recombine with cyclopentadiene to form **2**, there is very little, if any stereochemical isomerization of the starting materials. We presume that the Z-**10b** recovered in the thermolysis of pure E-**10a** arises from isomerization of the E-silene to Z-silene followed by recombination with anthracene.

Table 3 gives the isomer distributions for the silene dimers, **7a–7e**, and for the products resulting from silene being trapped by 2,3-dimethyl-1,3-butadiene, (**8**) and **9a–9b**. Control experiments established that these products were stable under the thermolysis conditions. It can be seen that the dimer stereochemistry is essentially independent of the stereochemistry of the silene precursor at 550 °C (expt. 1–5). At 400 °C the dimer stereochemical distribution is again not a function of the silene source with the E-precursor **2b** giving essentially the same mixture of isomers as the Z-precursors, a 74/26 mixture of **2c** and **2d**, respectively. It is intriguing that the formation of the all "*cis*" dimer **7a** is apparently not favored at the lower temperature (expt. 6 and 7). The *cis*-phenyl-*trans*-neopentyl isomer **7b**, is the favored dimer in these experiments. While one might argue that this result is consistent with the formation of the dimers by a stepwise process, such a conclusion seems unwarranted in light of the fact we obtain a distribution of silene dimers similar to that obtained at 550 °C when E-**1** and Z-**1** are generated below room temperature by the reaction of t-butyllithium with vinylmethylphenylchlorosilane in hydrocarbon solvents [4]. We have no good explanation for the unusual dimer-isomer distribution obtained in experiments 6 and 7.

The stereochemistry of the [4 + 2] cycloadducts of **1** with 2,3-dimethyl-1,3-butadiene is also independent of the stereochemistry of the silene source. Thus with either an E- or a Z-silene source the ratio of *cis*- to *trans*-silacyclohexene, **9a** to **9b**, is about 0.71 at 550 °C (expt. 2 and 3), or 0.60 at 400 °C (expt. 6 and 7). Thus, we observe complete stereochemical scrambling for both the silene dimers and for their cycloadducts with the diene.

TABLE 2

STEREOCHEMISTRY OF RECOVERED SUBSTRATE FROM FLASH VACUUM THERMOLYSES

Experiment	Substrate	Temperature (°C)	E-**2a**	E-**2b**	Z-**2c**	Z-**2d**
1	E-**2a**	550	98	2	trace	trace
2	E-**2b**	550	3	97	trace	trace
3	Z-**2c** 71%	550	trace	0	68	32
4	Z-**2c** 54%	550	trace	trace	63	37
5	Z-**2c** 66%	550	trace	trace	72	28
6	E-**2b**	400	1	99	trace	trace
7	Z-**2c** 74%	400	3	1	68	28
			E-**10a**		Z-**10b**	
8	E-**10a** 91%	650	81		19	

Intermolecular "ene" products are frequently observed when silenes react with traps containing allylic hydrogens [2,5,6,7]. It might be suggested that both the "ene" product and the silacyclohexenes both have the same biradical precursor **11** accounting for the scrambling of stereochemistry which we observe.
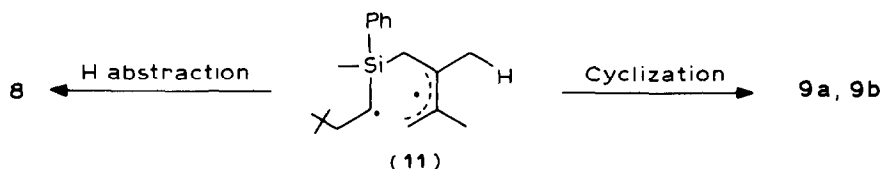
However, the ratio of "ene" products to [4 + 2] cycloadducts for a variety of silenes reacting with 2,3-dimethyl-1,3-butadiene (Table 4) is remarkably constant over a large temperature range. This indicates that the activation energies for the processes leading to the products are similar; and that both **8** and **9** are formed by either a biradical or a concerted pathway. One would anticipate that the hydrogen abstraction required for **11** to give **8** should not compete favorably with ring closure of **11** to give **9** especially for the low temperature reactions. It seems more likely that both the "ene" product and the silacyclohexenes are produced by concerted pathways. If this is the case, the ratio of *cis*-**9a** to *trans*-**9b** obtained is related to the ratio of *Z*-**1** to *E*-**1** present when the silene is trapped. The increasing ratio of *cis*-cycloadduct to *trans*-cycloadduct obtained with increasing temperature (Table 3) is consistent with this suggestion. The *Z*-**1** to *E*-**1** equilibrium is shifted towards the sterically crowded, less stable, *Z*-isomer at higher temperatures.

Overall, our results indicate that 1-phenyl-1-methyl-2-neopentylsilene is not configurationally stable towards *cis-trans* isomerization under flash vacuum thermolysis conditions at temperatures above 400°C. We are in the process of carrying out carefully controlled thermolyses at a series of temperatures between 300 and 400°C aimed at determining the activation energy for the *cis-trans* isomerization of **1**.

Experimental

General

Cyclohexane, which was used as the solvent for some of the thermolyses was dried by distillation from sodium potassium alloy. Reactant and product mixture analyses were accomplished using a Perkin–Elmer Sigma-3 FID gas chromatograph with a 25 m fused silica capillary column containing methylphenylsilicone stationary phase, programmed from 100 to 250°C at 2°C/min. Yields, percent decompositions and isomer distributions were calculated using a Hewlett–Packard 3390A recording integrator programmed with response factors for the compounds determined relative to n-decane as the standard. In determining the response factors it was assumed that all isomers of a given compound had the same response factor. GC/MS analyses of some of the product mixtures were performed at the Southwest Research Institute, San Antonio, Texas.

Samples of the pure stereoisomers used for the thermolyses were purified by preparative GLC collection using a Varian Series 1800 chromatograph with thermal conductivity detection and a 20′ × 3/8″ stainless steel column packed with 10% OV-17 on 80–100 mesh Supelcoport. Because the two Z-norbornene isomers could

TABLE 3

ISOMER DISTRIBUTIONS IN SILENE TRAPPING REACTIONS

Experiment	Substrate	Temperature (°C)	Trap	Ratio	Dimers					Trapped silene		
					7a	7b	7c	7d	7e	8	9a	9b
1	E-2a	550	BD	4.7	9.3	23.9	23.9	25.0	17.8	51.1	21.9	26.9
2	E-2b	550	BD	5.0	11.2	22.4	25.9	21.5	18.9	20.5	32.2	47.3
3	Z-2c 71%	550	BD	10.0	10.9	23.3	23.4	23.4	19.0	20.0	33.8	46.2
4	Z-2c 54%	550	neat		13.1	25.9	23.9	22.0	15.0			
5	Z-2c 66%	550	CH	3.5	17.7	27.6	27.0	25.5	2.1			
6	E-2b	400	BD	10.0	0.2	50.4	17.0	19.1	13.3	21.0	28.8	50.2
7	Z-2c 74%	400	BD	10.0	0.6	43.8	17.8	20.6	17.3	22.0	30.1	47.9
8	E-10a 91%	650	BD	10.0						4.2	42.8	52.0

TABLE 4

COMPARISON OF THE RATIO OF "ENE" TO [4+2] CYCLOADDUCT PRODUCTS FOR A VARIETY OF SILENES TRAPPED WITH 2,3-DIMETHYL-1,3-BUTADIENE

Silene	Generation method	Temperature (°C)	"ene"	[4+2]	Ref.
E- or Z-1	FVP[a]	400	21	79	this work
E- or Z-1	FVP[a]	550	20	80	this work
E- or Z-1	Li-X Elim.	−20	25	75	[2]
Me(H)Si=CH$_2$	FVP[b]	550	18	82	[5]
Me$_2$Si=C(SiMe$_3$)$_2$	FVP[b]	−78	20	80	[6]
Me$_2$Si=C(SiMe$_3$)$_2$	Li-X Elim.	−50	19	81	[6]
Me$_2$Si=C(SiMe$_3$)$_2$	Li-X Elim.	0	20	80	[6]
Me$_2$Si=C(SiMe$_3$)$_2$	Li-X Elim.	150	22	78	[6]

[a] Injection method. [b] Evaporation method.

not be completely resolved, mixtures of 2c and 2d having the compositions given in the tables were used for the thermolyses.

Thermolysis methods

All of the flash vacuum thermolyses were carried out in a horizontal, unpacked, 30 cm quartz tube; 10 mm i.d., at 10^{-4} torr. After heating the reactor to the desired temperature, measured using a chromel-alumel thermocouple, the reactor was treated with 1 to 1.5 ml of hexamethyldisilazane prior to each thermolysis. During the thermolysis the pyrolysate was condensed in a spiral trap, cooled to −196°C with liquid nitrogen, and located immediately following the hot zone. In most of the experiments a brass flow restrictor was placed between the hot zone and the trap which increased the amount of decomposition (Table 1) without altering product distributions significantly (Table 3). Percent decompositions were determined from the mole ratio of cyclopentadiene and dicyclopentadiene (anthracene in expt. 8) to recovered starting material. Percent yields were based on the percent decomposition. Because of loss of cyclopentadiene during work up of the 400°C experiments (expt. 6 and 7) yield and decomposition percentages could not be determined.

For the evaporation method (expt. 4) a mixture containing 54% 2c and 46% 2d was placed in a graduated vial attached to the thermolysis apparatus, and allowed to evaporate into the hot zone.

For the injection method a solution of the pure stereoisomers in 2,3-dimethyl-1,3-butadiene (Aldrich) (cyclohexane in expt. 5) having the composition given in the tables was prepared. Aliquots of these solutions were injected through a septum directly into the hot zone using a gas-tight syringe. Generally, 4 or 5 injections of 50 to 100 μl were used for each run.

Control experiments

The flash vacuum thermolysis of mixtures of the dimer isomers, 7a–7e, at 750°C gave no isomerization or decomposition. Flash vacuum thermolysis of the inter-molecular "ene" product 8 at 550°C gave no reaction. Similarly, flash vacuum thermolysis of pure isomers of 9a or 9b at 650°C gave only unisomerized starting material.

Products

Phenylmethylvinylsilane (**3**) was identified by comparison of its retention time with an authentic sample [8] at 56°C/6.5 torr, prepared by the lithium aluminum hydride reduction of phenylmethylvinylchlorosilane at room temperature in ether.

The silene isomers were tentatively identified as 2-(2,2-dimethylcyclopropyl)-1-phenyl-1-methylsilaethane (**4**), mass spectra: m/z (relative abundance): 204 (18) M^+, 159 (38), 148 (10), 147 (32), 135 (18), 134 (28), 122 (10), 121 (100), 120 (31), 119 (13), 111 (17), 105 (34), 82 (12), 73 (14), 69 (14), 67 (13), 59 (18), 55 (11), 53 (15); (3,3-dimethylcyclobutyl)phenylmethylsilane (**5**), m/z (relative abundance): 204 (25) M^+, 177 (17), 176 (91), 161 (17), 149 (13), 148 (38), 147 (23), 135 (12), 134 (34), 133 (11), 122 (14), 121 (91), 120 (100), 119 (16), 111 (18), 105 (74), 98 (15), 93 (10), 79 (10), 53 (19); and 1,3,3-trimethyl-1-phenylsilacyclopentane (**6**), m/z (relative abundance): 204 (6) M^+, 148 (16), 147 (100), 121 (48), 105 (12). The structure assignments are based solely on the mass spectral fragmentation patterns.

The characterization of the other products has been reported previously [2,4].

Acknowledgement

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