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Matrix Isolation of Silacyclopentadienes: UV–Vis and IR Spectra and Photochemical Interconversion†

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Abstract: Vacuum pyrolysis of 5-silaspiro[4.4]nona-2,7-diene (**5a**), UV irradiation of matrix-isolated 1,1-diazido-1-silacyclopent-3-ene (**6**), and vacuum pyrolysis of **6** resulted in the formation of 1-silacyclopenta-2,4-diene (**1a**), characterized by its IR and UV–vis spectra. The 3,4-dimethyl analogue **1b** was generated by vacuum pyrolysis of **5b**, the 2,3,7,8-tetramethyl derivative of **5a**. Photoreversible interconversion of **1a** with 1-silacyclopent-3-ene-1,1-diyl (**2a**), 1-silacyclopenta-1,3-diene (**3a**), and 1-silacyclopenta-1,4-diene (**4a**) and the analogous interconversion of **1b** with 3,4-dimethyl-1-silacyclopent-3-ene-1,1-diyl (**2b**), 3,4-dimethyl-1-silacyclopenta-1,3-diene (**3b**), and 3,4-dimethyl-1-silacyclopenta-1,4-diene (**4b**) have been observed upon irradiation at selected wavelengths. Full vibrational assignment in the IR spectra of **1**–**4** has been proposed on the basis of restricted Hartree–Fock calculations for **1a**–**4a** and of literature data on related molecules. The UV–vis spectra are interpreted with help from multireference configuration interaction calculations, but the difference between **3** and **4** is accounted for even at the Hückel level. The significantly lower $\mathrm{Si{=}C}$ stretching frequencies as well as the UV absorption bands of **3** and **4**, red-shifted relative to 1-methyl-1-silene, provide strong experimental evidence for $\mathrm{Si{=}C{-}C{=}C}$ and $\mathrm{C{=}Si{-}C{=}C}$ π-conjugation.

Introduction

1-Silacyclopenta-2,4-dienes (siloles) containing phenyl or methyl substituents on carbon as well as on silicon are stable as monomers at room temperature and have been widely used in synthesis.[2–7] However, chemical isolation of C-unsubstituted siloles presents problems. Initial reports by Goubeau[8] and Nefedov[9] on the preparation of 1,1-dimethylsilole by catalytic dehydrogenation of 1,1-dimethylsilacyclopentane could not be reproduced by Barton[3a] and Laporterie.[4,5] These authors later reported the synthesis of this silole by flash vacuum pyrolysis (FVP) and found that it is stable as a monomer for about 2 hours at room temperature prior to its [2 + 4] dimerization, permitting an NMR characterization.[5]

Si–H bond-containing siloles are even more reactive and less kinetically stable. Although 1-methylsilole has been detected as a monomer by the MS–FVP technique, only its [2 + 4] dimer and its Diels–Alder adduct to maleic anhydride could be isolated.[3a] 3,4-Dimethylsilole was isolated recently.[3b] The synthesis of the parent silole **1a** has been attempted repeatedly without success over a 50-year period.[10,11] In 1974, Gaspar et al.[12] proposed a mechanism of transient silole formation involving a thermal rearrangement of 1-silacyclopent-3-ene-1,1-diyl (**2a**), generated in a gas-phase reaction of high energy $^{31}\mathrm{Si}$ atoms with butadiene or during vacuum pyrolysis of another precursor of the silylene **2a**, 1-methoxy-1-(trimethylsilyl)-1-silacyclopent-3-ene. Once again, only indirect evidence for the parent silole **1a** was obtained, such as isolation of its [2 + 4] dimer[13,14] and kinetic data.[7] Direct physical data for silole **1a** remained unknown. (Structures of the compounds described herein are shown in Chart I.)

The isomeric siladienes 1-silacyclopenta-1,3-diene (**3a**) and 1-silacyclopenta-1,4-diene (**4a**), which contain a $\mathrm{Si{=}C}$ bond in π-conjugation with a $\mathrm{C{=}C}$ bond, can be expected to be even less kinetically stable and to dimerize more readily. No attempts to study them seem to have been reported, and only the methyl derivatives of **3a** and **4a** have been postulated as intermediates in pyrolytic reactions.[13,14] Direct physical data on siladienes are limited to the UV spectrum of 1-mesityl-1-silacyclobutadiene isolated in a 3-methylpentane (3-MP) glass at 77 K.[15] Attempted matrix isolation of 1,1-dimethyl-1-silabuta-1,3-diene, generated by gas-phase pyrolysis, was foiled by the low thermal stability of this species.[16]

The isomeric silylene 1-silacyclopent-3-ene-1,1-diyl (**2a**), postulated as a pyrolytic intermediate, has not been observed directly, either. UV–vis spectra of a few related cyclic silylenes isolated in a 3-MP glass at 77 K are known.[17]

In the present work we provide a full UV–vis and FTIR spectroscopic characterization of the isomeric parent species **1a**–

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† This paper is dedicated to the memory of Andrei K. Maltsev, who was one of the pioneers in matrix isolation spectroscopic studies of molecules with the $\mathrm{Si{=}C}$ double bond, and who would have turned 60 on June 30, 1993.

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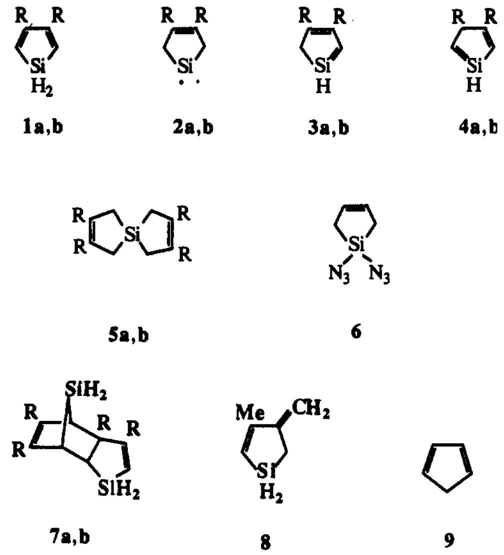
Chart I



a R=H; **b** R=Me

4a, previously reported in a communication,[18] and of their 3,4-dimethyl derivatives: 3,4-dimethylsilole (**1b**), 3,4-dimethyl-1-silacyclopent-3-ene-1,1-diyl (**2b**), 3,4-dimethyl-1-silacyclopenta-1,3-diene (**3b**), and 3,4-dimethyl-1-silacyclopenta-1,4-diene (**4b**). In view of the indirect evidence for thermal isomerization of **2a** to **1a**[13,14] and in view of the availability of 5-silaspiro[4.4]-nonadiene-2,7 (**5a**) and its 2,3,7,8-tetramethyl analogue **5b**, recently suggested as a potential pyrolytic source of the silylenes **2a** and **2b**,[19] we selected **5a** and **5b** as our starting materials. In addition, 1,1-diazido-1-silacyclopent-3-ene (**6**) has been used as an independent photochemical precursor for **2a**. The choice of **6** was based on the well-documented use of diazidosilanes for photochemical generation of silylenes in matrix isolation[20–22] (these precursors are not useful in fluid solution).

Experimental Section and Calculations

General Methods. ^1H and ^{13}C NMR spectra were recorded on a Jeol FX90Q spectrometer. GC–MS analysis of the reaction products was performed on a Finigan MAT 700 ion trap detector mass spectrometer with a Varian gas chromatograph, containing a 20-m × 0.36-mm-i.d. fused silica capillary column coated with 5% phenylsilicone.

Materials. 1,1-Diazido-1-silacyclopent-3-ene (6). To 2.5 g (16 mmol) of 1,1-dichloro-1-silacyclopent-3-ene[23] in 15 mL of dried CH_3CN was added 3 g (46 mmol) of sodium azide. The mixture was stirred at room temperature for 4 h, and then 15 mL of ether was added and the precipitate was filtered. After evaporation of solvent from the filtrate and distillation of the residue at 84 °C/15 Torr, **6** (1 g, 37%) was isolated as a colorless, somewhat moisture-sensitive liquid: ^1H NMR (C_6D_6) δ 1.14 (d, 4H, J = 1.1 Hz), 5.60 (t, 2H, J = 1.1 Hz); ^{13}C NMR (C_6D_6) δ 129.45 (=CH), 14.29 (CH_2); IR (Ar matrix, 12 K) 3039, 2930, 2906, 2896, 2283, 2165, 1608, 1397, 1344, 1330, 1319, 1312, 1260, 1210, 1182, 1143, 1105, 1098, 943, 819, 767, 756, 717, 668, 643, 636, 587, 569, 407 cm^{-1}; UV λ_{max} = 234 nm (ϵ = 75); EIMS m/z (relative intensity) 166 (52), 137 (18), 124 (43), 123 (20), 112 (12), 110 (6), 96 (23), 83 (12), 82 (25), 70 (100), 68 (8), 67 (12), 56 (14), 55 (20), 54 (40); HRMS m/z (calcd for $C_4H_6SiN_6$ 166.0423) 166.0426.

The syntheses of 5-silaspiro[4.4]nona-2,7-diene (**5a**) and its 2,3,7,8-tetramethyl derivative **5b** have been previously described.[19]

Matrix Isolation Spectroscopy. Matrices were deposited on a CsI window cooled with an Air Products CSA-202 Displex closed-cycle helium cryostat. The shroud of the cryostat was fitted with a pair of CsI windows for UV and IR spectroscopic measurements and a Suprasil window for irradiation. In some experiments, matrices were deposited on a sapphire window in a cryostat with a shroud equipped with a pair of Suprasil windows, permitting spectral measurements down to 190 nm. The ratio of argon to sample was approximately 1000:1. Deposition rates were about 0.2–0.5 mmol/min. The argon deposition temperature was 26–28 K to optimize the optical quality of the matrices while still conserving suitable rigidity. Vacuum pyrolysis (800 °C, 10^{-3}–10^{-4} Torr) of precursors **5a** and **5b** was carried out in a quartz furnace mounted on the shroud of the cryostat. During deposition, sample **6** was kept at −25 °C to −35 °C, sample **5a** at −55 °C, and sample **5b** at 35–40 °C.

Experiments in 3-MP glass at 77 K were performed in a 5 × 2 × 0.5-cm Suprasil cell suspended in a liquid nitrogen-filled quartz dewar with Suprasil windows. The diazide **6** was irradiated by a low-pressure mercury lamp (254 nm) or a Lambda Physik EMG 50 excimer laser (KrF, 248 nm). Complete destruction of **6** took 2–4 h of irradiation with the 248-nm laser through a quartz window, depending on the thickness of the matrix. Photobleaching experiments on the primary photolysis or pyrolysis products from **6** and pyrolysis products from **5a** and **5b** used light from a 308-nm excimer laser (XeCl), from 454- and 488-nm Ar^+ lasers, and from a 1000-W high-pressure mercury–xenon lamp equipped with appropriate filters.

IR spectra were recorded using a Nicolet 60SXR FTIR spectrometer at 1-cm^{-1} resolution in the 400–4000-cm^{-1} spectral range, using a MCT detector. UV–vis spectra were measured on a Cary 17 spectrophotometer interfaced to a PDP-11/23 computer.

Calculations. Ground-state *ab initio* calculations on intermediates **1a**–**4a** used the restricted Hartree–Fock (RHF) approximation. The geometries of **1a**, **2a**, **3a**, and **4a** were optimized using a 66–31G* basis set for silicon,[24] 6–31G* for carbon,[25] and 31G* for hydrogen.[26] The harmonic vibrational frequencies were calculated at the same level of theory, using Gaussian 90 programs.[27] As usual for this level of calculation, the calculated frequencies were uniformly scaled by 90% for comparison with the experimental results. They were assigned labels according to the dominant local mode as judged by inspection of the calculated displacements.

The electronic transition energies were computed by multireference second-order configuration interaction (CI) at the above optimized geometries, using the same basis set (20 000–40 000 configurations). The basis orbitals for the CI calculations were generated as the natural orbitals of 4 × 4 complete active space self-consistent field (CAS-SCF) calculations. The active space was limited to the π and π^* orbitals in **1a**, **3a**, and **4a**. In **2a**, the active space was limited to the π, the π^*, the lone pair a_1, and the empty b_1 and b_2 (σ^*_{CSi}) orbitals on Si. In all cases, the weight of the RHF ground configuration in the ground state was over 90%. The excited-state calculations were performed using the GAMESS program.[28]

Results

UV–vis and IR Spectra of Matrix-Isolated Pyrolysis Products from 5a.

In the UV–vis spectrum of 800 °C pyrolysis products from **5a**, frozen at 12 K in an Ar matrix, a single intense band

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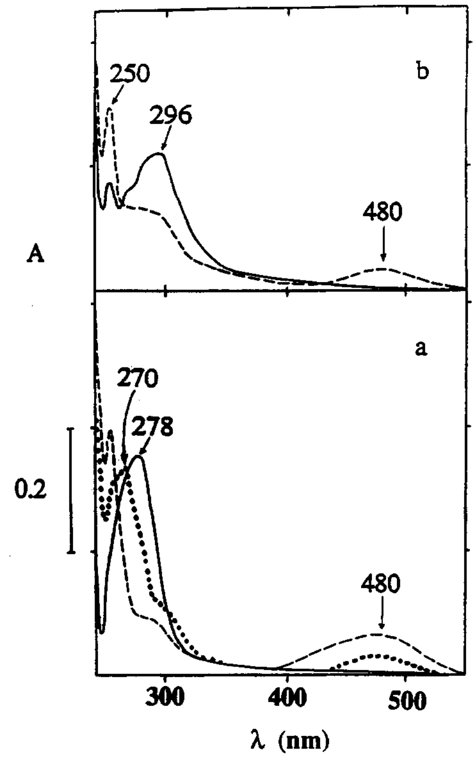

Figure 1. UV spectra (Ar, 12 K). (a) Pyrolysis products of **5a** (—) initially and after 308-nm irradiation (···) and subsequent 260–390-nm irradiation (- - -) and (b) after further bleaching with 488-nm light (—) followed by 308-nm light (- - -).

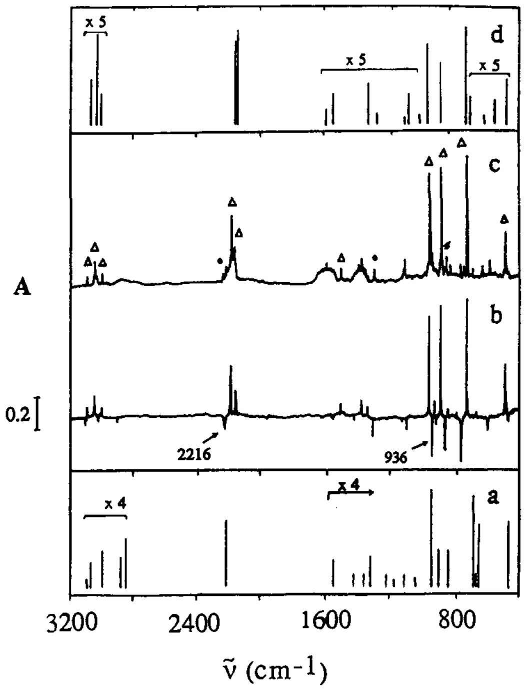

Figure 2. IR spectra (Ar, 12 K). (a) **4a**, calculated. (b) Difference of the spectra of pyrolysis products of **5a** before (positive) and after (negative) 308-nm light irradiation; bands of =Si—H and Si=C stretches in **4a** at 2216 and 936 cm^{-1}, respectively, are highlighted. (c) 248-nm photolysis products of **6**; (Δ) **1a**, (*) **4a**. (d) **1a**, calculated.

at 278 nm is observed (Figure 1a). This UV band is accompanied by a set of new bands in the IR (positive bands in Figure 2b; bands of unreacted **5a** and of 1,3-butadiene have been subtracted). In the IR spectrum, two bands at 2144 and 2174 cm^{-1} occur in the sp^3 Si-H stretching mode region. The same UV and IR bands are observed in the spectra of pyrolysis products frozen at 12 K in the absence of argon. After warmup of the argon matrix or the neat pyrolysate to room temperature, GC-MS analysis shows a single major peak (other than undecomposed **5a**) with a mass spectrum identical with that[14] of an authentic sample of **7a**, the [2 + 4] dimer of silole **1a**.

The new UV and IR peaks disappeared gradually and simultaneously upon 308-nm irradiation at 12 K, proving that they all belong to a single species. The absence of visible absorption makes it highly unlikely that this species is the silylene **2a**, the presumed primary pyrolysis product. This conclusion is based on the known spectral data for dialkylsilylenes[20-22,29] and 1-silacyclopenta-1,1-diyl,[17] all of which absorb in the visible region. Also, bands of sp^2 Si-H stretching vibrations are absent in the 2200–2240-cm^{-1} region of the IR spectrum, suggesting that the siladienes **2a** and **3a** are not present in the matrix.

An increase in pressure in the pyrolysis zone from 10^{-3} to 10^{-1} Torr did not result in any changes in the UV and FTIR spectra of the pyrolysis products. After that observation, we definitely eliminated the possibility that the new UV and IR peaks might belong to the siladienes **2a** and **3a**, since reactive intermediates with a Si=C bond always[30] undergo fast cyclodimerization in the gas phase at pressures higher than 10^{-2} Torr.

High-temperature (980 °C) pyrolysis of **5a** yielded matrices that were completely transparent in the UV–vis and showed strong peaks of acetylene in the IR instead of the bands of the new species obtained at lower pyrolysis temperatures.

We conclude that the UV absorption band at 278 nm and the set of new bands in the IR spectrum, shown in Figure 2b as positive peaks, are due to silole (**1a**), a product of the expected[12] thermal rearrangement of the silylene **2a**. The UV band of **1a** (Table I) is very close to the 285-nm peak observed[6b] for 1,1,3,4-tetramethylsilole, which is stable as a monomer at room temperature. The IR spectrum, shown in Figure 2b, is in good agreement with the calculated RHF 6-31 G* spectrum for **1a** (Figure 2d, Table II). The same product, along with others, has been obtained by vacuum pyrolysis of the diazide **6** or by its irradiation at 248 or 254 nm in a matrix. It appears very likely that the $m/z = 82$ peak observed in mass spectra in the FVP-MS study of **5a**[19] should not be assigned to the molecular ion of **2a**, as proposed there, but rather to the molecular ion of **1a**. Our conclusion has been recently confirmed by the vacuum pyrolysis–mass spectrometric determination[31] of the ionization potential (IP) of the $m/z = 82$ intermediate formed in this reaction. This value appeared to be significantly higher than IPs already measured for some simple silylenes and silenes.

At 800 °C, the pyrolysis caused the disappearance of about 60% of the starting **5a**. The IR band intensities of **1a** and butadiene were comparable. Some elemental silicon coated the walls of the

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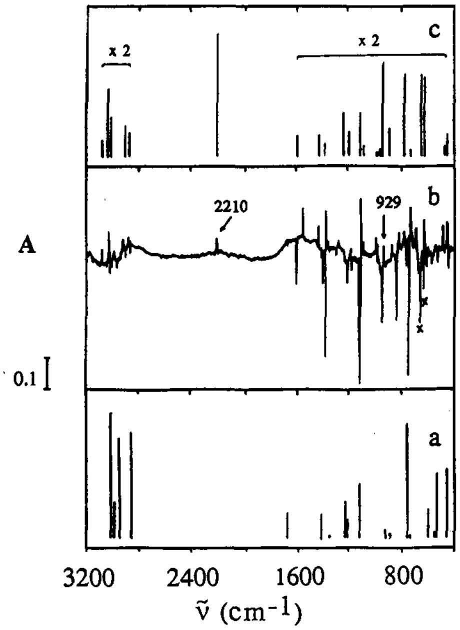

Figure 3. IR spectra (Ar, 12 K). (a) **2a**, calculated. (b) Difference of the spectra of the sample whose UV absorption is shown in Figure 1a, dashed line, before (negative) and after (positive) 488-nm irradiation; (X) **5a**; bands of ═Si—H and Si═C stretches in **3a** at 2210 and 929 cm^{-1}, respectively, are highlighted. (c) **3a**, calculated.

Table I. Calculated and Observed UV–Vis Absorption Spectra of **1–4**

	wavelength[a]		
compd	obsd	calcd	assignment
1a	278	198	$^1B_2\ \pi \rightarrow \pi^*$ (HOMO → LUMO)
		177	$^1A_1\ \pi \rightarrow \pi^*$ ("doubly excited")
1b	280		
2a	480	507	$^1B_1\ n(Si) \rightarrow p(Si)$
	250	220	$^1A_2\ n(Si) \rightarrow \pi^*, \pi^2 n(Si) \rightarrow p(Si)^2\pi^*, \pi n(Si) \rightarrow \pi^* p(Si)$
		183	$^1B_2\ n(Si) \rightarrow \sigma^*_{SiC}$
2b	480 255		
3a	296	251	$^1A'\ \pi \rightarrow \pi^*$ (HOMO → LUMO)
		206	$^1A'\ \pi \rightarrow \pi^*$ (mixed)
3b	312		
4a	270	220	$^1A'\ \pi \rightarrow \pi^*$ (mixed)
		194	$^1A'\ \pi \rightarrow \pi^*$ (mixed)
4b	274		

[a] In nm.

pyrolysis vessel, suggesting that secondary decomposition of **1a** was taking place. Our best estimate is that about two-thirds of **1a** survived intact.

Photochemical Interconversion of 1a–4a. We find that silole (**1a**) can be reversibly converted to the siladienes **3a** and **4a** and to silylene **2a** by irradiation in argon matrix at 12 K. The interconversions are not clean, since the UV absorptions of **1a**, **2a**, **3a**, and **4a** all overlap. However, the spectra differ sufficiently to permit a preferential accumulation of one or another of these species by a suitable choice of irradiation wavelength.

The easiest to separate are the spectra of **2a**, characterized by two UV–vis absorption bands at 250 and 480 nm (Figure 1a), as well as a series of IR peaks. This species is formed along with traces of **3a** and **4a** upon irradiation of **1a** with broad-band UV light (260–390 nm). Irradiation of **2a** at 488 nm (Figure 1a), where **1a**, **3a**, and **4a** cannot be expected to absorb, gradually removes both UV–vis absorption bands and many of the IR peaks (Figure 3), which we therefore associate with **2a** as well (Table III). The assignment of this photoproduct as **2a** is based on its visible absorption band, its IR frequencies, and the agreement of these spectral features with those calculated (Figure 3a).

Table II. Vibrations of Silole (**1a**)

		frequencies[a]		IR intensities		
mode	symmetry	calcd	obsd	calcd[b]	obsd	assignment
1	b_1	248		0.04		
2	a_2	360		0		
3	a_1	480	490	22.2	m	ring vibration
4	b_1	555		7.4		
5	b_2	589		1.8		
6	a_2	658		0		
7	b_2	699	677	15.2	w	asym Si—C stretch
8	a_1	722		2.0		
9	b_1	732	713	227.1	vvs	out-of-plane C—H bend; SiH_2 twist
10	a_2	769		0		
11	b_2	875	880	137.6	vs	SiH_2 wagging
12	a_1	897		3.8		
13	a_1	956	955	188.7	s	SiH_2 scissoring
14	a_2	1006		0		
15	b_1	1007		0.02		
16	a_1	1090	1088	15.6	w	in-plane C—H bend
17	b_2	1101		2.0		
18	b_2	1296	1285	2.0	w	in-plane C—H bend
19	a_1	1349	1346	21.7	m	in-plane C—H bend
20	a_1	1552	1478	11.7	w	C═C sym stretch
21	b_2	1606	1608	3.8	m	C═C asym stretch
22	a_1	2137	2144	206.1	m	Si—H sym stretch
23	b_2	2125	2174	237.3	s	Si—H asym stretch
24	b_2	3002	3001	11.3	vw	C—H stretch
25	a_1	3016		39.4		
26	b_2	3047	3038	22.8	w	C—H stretch
27	a_1	3049		5.9		

[a] In cm^{-1}. [b] In km/mol.

Particularly, the absence of detectable Si–H stretching bands in the IR spectrum (Figure 3b) should be noted. The short-wavelength absorption peak (250 nm, Figure 1), unprecedented in dimethylsilylene[29] or 1-silacyclopenta-1,1-diyl,[17] clearly belongs to **2a** since it disappears in proportion to the 480-nm band upon 488-nm irradiation and since irradiation at 254 nm causes both UV–vis peaks of **2a** (250 and 480 nm) to be reduced in intensity.

The photochemical conversion of a dialkylsilylene to a silene with visible light, reversed by the irradiation of the silene with UV light, has been well established for a long time.[20-22,29] Indeed, after bleaching of **2a** with either 254- or 488-nm light, a new product appears, characterized by an absorption band at 296 nm (Figure 1) and a series of IR peaks (Figure 3). This product is converted back to **2a** upon irradiation with 308-nm light. In addition, weak signals due to **1a** and **4a** have also been noted. The IR spectrum of the photoproduct from **2a** was separated by taking a difference (Figure 3b) and contains a single peak at 2210 cm^{-1} in the sp^2 Si–H stretching region (Table IV). Upon comparison of this spectrum with *ab initio* calculated ones for the structures **3a** and **4a**, we propose an assignment to **3a**, since this is expected to be the primary product of a single hydrogen shift in **2a** and the use of 488-nm light in the formation of this material from **2a** precludes secondary photochemical processes. The formation of a trace amount of **1a** is intriguing and may be due to the existence of a minor direct photochemical path from **2a** to **1a**, perhaps initiated by attack of the divalent silicon on the C═C double bond.

Finally, irradiation of matrix-isolated **1a** with 308-nm light causes a reduction of its UV and IR bands and the appearance of yet another species, absorbing at 270 nm but not at 308 nm (Figure 1a). This species is also characterized by a series of IR bands, compatible with *ab initio* calculations for **3a** and **4a**, and has a single peak at 2216 cm^{-1} in the sp^2 Si–H stretching region (Table V). Further bleaching of this species by 260–390-nm broad-band UV light finally converts it to the silylene **2a**. By elimination, we propose to assign these newly appeared UV and IR bands to siladiene **4a**, formed from silole (**1a**) by a photochemically allowed 1,3-hydrogen shift. Thus, while we believe the evidence for **1a** and **2a** to be unequivocal, the structural

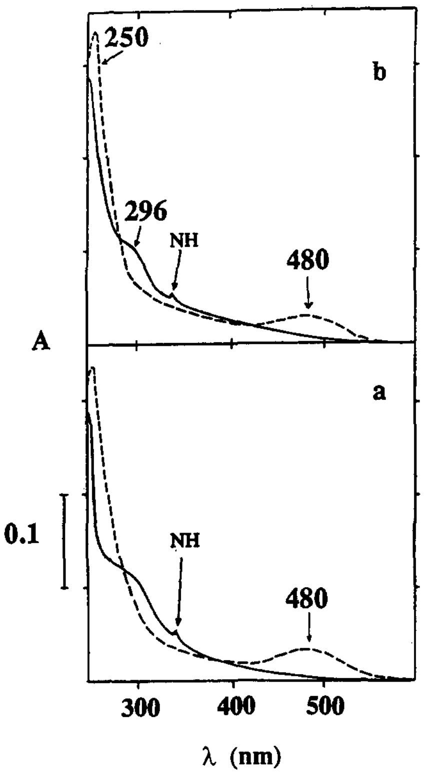

Figure 4. UV spectra (Ar, 12 K). (a) 248-nm photolysis products of **6** (—) initially and after subsequent 308-nm irradiation (- - -) and (b) after further bleaching by 488-nm light (—) followed by irradiation with 308-nm light (- - -).

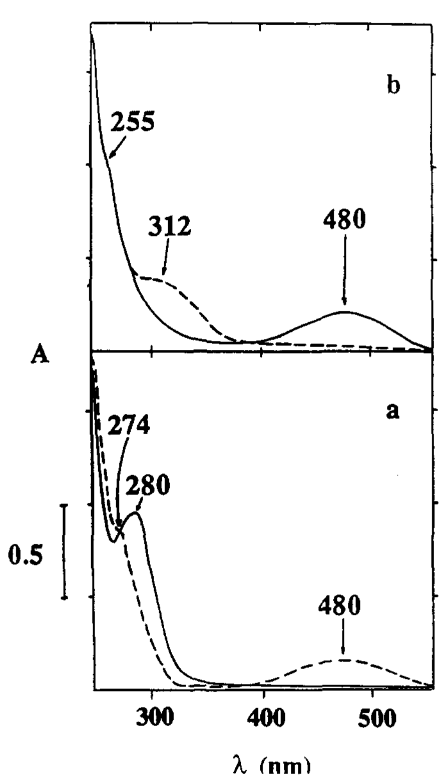

Figure 5. UV spectra (Ar, 12 K). (a) Pyrolysis products of **5b** (—) initially and after subsequent 308-nm irradiation (- - -) and (b) after further 260–390-nm irradiation (—) followed by irradiation with 488-nm light (- - -).

assignment within the **3a**,**4a** pair is less secure and rests on a mechanistic assumption. As we shall see below, this assignment receives additional support from a comparison of the observed with the calculated UV excitation energies.

Decomposition of the Diazide 6. In the Ar matrix IR spectrum (Figure 2c) of the photodecomposition products from **6** we have detected a set of bands that match the IR spectrum of silole (**1a**), already obtained by pyrolysis of **5a** (Figure 2b). Also, a few of the most intense bands of the siladienes **3a** and **4a** are present in this spectrum. A broad band in the 260–350-nm spectral range, with a maximum centered around 278 nm, was observed in the matrix UV–vis spectrum of the photoproducts of **6** (Figure 4a). Irradiation of **6** in 3-methylpentane glass at 77 K produces a broad absorption band at 262 nm. There is little doubt that UV absorptions of the intermediates **1a**, **3a**, and **4a**, as well as that of the NH molecules (337 nm) formed from traces of HN_3, contribute to this band. No UV–vis bands of silylene **2a** were observed in these spectra.

Matrix IR and UV spectra of vacuum pyrolysis products of **6**, taken after subtraction of the absorbance of undecomposed **6**, look similar to those shown in Figures 1c and 4a. Clearly, both matrix photolysis and vacuum pyrolysis of **6** produce silole (**1a**) along with minor amounts of **3a** and **4a**.

The matrix-isolated silole (**1a**) obtained from **6** behaves entirely as the silole obtained from **5a**. Thus, the bleaching of the photoproducts from **6** by broad-band UV light at 260–390 nm significantly reduces the absorption bands of **1a**, **3a**, and **4a** and leads to the gradual growth of the bands of the silylene **2a** at 250 and 480 nm in the matrix UV spectrum (Figure 4a). As expected, these bands are bleached with 248- or 488-nm light, and a 296-nm absorption band of the siladiene **4a** grows in (Figure 4b). Irradiation at 308 nm reverses the process. The matrix IR spectra show the expected corresponding changes.

These results give us additional evidence for the reversible character of the photorearrangement of **2a** to **4a** and also allow us to confirm the assignment of the UV–vis and IR bands of the intermediates **1a**–**4a**.

Matrix UV–Vis and IR Spectra of the Pyrolysis Products from 5b. Vacuum pyrolysis of the tetramethyl-substituted spiro compound **5b** and phototransformations of the intermediates formed have been studied for comparison with the pyrolysis of the unsubstituted parent **5a**. In the Ar matrix UV spectrum of the pyrolysis products from **5b** (Figure 5a), one absorption band at 280 nm is observed. This band is accompanied by a set of new bands in the matrix IR spectrum, shown by positive peaks in the difference spectrum in Figure 6a. No bands in the sp^2 Si–H stretch spectral range are apparent in this spectrum. The same UV and IR bands are observed in the spectra of the pyrolysis products of **5b**, frozen without argon at 12 K. After the pyrolysate was warmed up to room temperature and the products were collected in a trap at 77 K, GC–MS analysis of the condensate revealed the presence of the [2 + 4] cyclodimer **7b**. The fragmentation pattern of this dimer under electron impact is similar to that of the silole dimer **7a**, after taking into account the mass increase due to the presence of four methyl substituents in **7b**.[32]

Irradiation of the pyrolysis products isolated in an Ar matrix with 308-nm light leads to a decrease in the intensities of both UV and all the new IR bands, proving that they belong to a single species, which we assign as the silole **1b** by analogy to the case of the parent **1a**. We did not observe any characteristic spectral features of the possible isomer **8**, such as an IR band due to an exocyclic C=C stretch or a UV band analogous to those observed earlier[6b] for the 1,1-dimethyl-substituted analogue of **8**, at 1615 cm^{-1} and 242 nm, respectively.

The same UV and IR peaks are observed in the spectra when pyrolysis is performed in a reactor loosely packed with quartz wool. Raising the pyrolysis temperature from 800 °C to 950 °C causes complete disappearance of these bands in the matrix spectra. Bands of methylacetylene and allene are observed instead.

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[32] MS of **7b**: *m/z* (relative intensity) 220 [M^+] (72), 219 [M – H] (12), 205 [M – Me] (10), 192 [M – 28] (19), 191 [M – H – 28] (100), 190 [M – 30] (12), 164 [M – 56] (14), 149 (40), 123 (23), 111 (32), 110 (34), 109 (50), 95 (45), 81 (41), 67 (44).

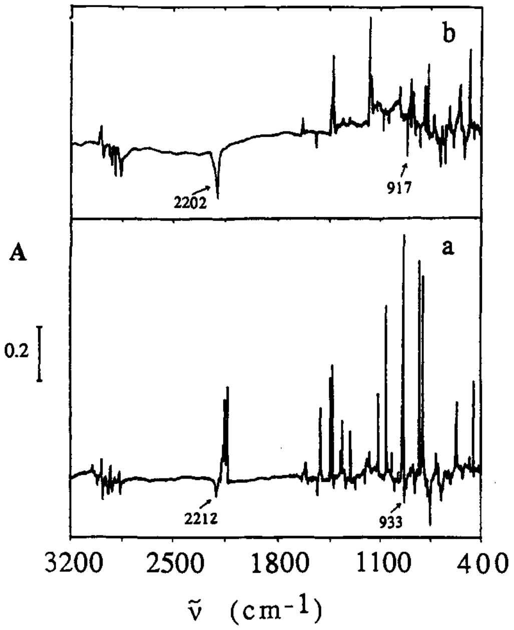

Figure 6. IR spectra (Ar, 12 K). (a) Difference of the spectra of pyrolysis products of **5b** before (positive) and after (negative) 308-nm light irradiation; bands of =Si—H and Si=C stretches in **4b** at 2212 and 933 cm^{-1}, respectively, are highlighted. (b) Baseline corrected difference of the spectra of the sample whose UV absorption is shown in Figure 5b, full line, before (positive) and after (negative) 488-nm irradiation; bands of =Si—H and Si=C stretches in **3b** at 2202 and 917 cm^{-1}, respectively, are highlighted.

Photochemical Transformations of 1b–4b. In the difference IR spectrum (Figure 6a), negative peaks belong to species formed after irradiation of silole **1b** with 308-nm light. The appearance of the band at 2212 cm^{-1} in the sp^2 Si–H stretching range in the IR spectrum and of the absorption band at 274 nm in the UV spectrum (Figure 5a) suggests a phototransformation of the silole **1b** into the siladiene **4b**. The observation of an additional new band at 480 nm in the UV spectrum might be explained by a further rearrangement of either **4b** or **1b** into the silylene **2b**, proceeding as a minor pathway. Further bleaching of this matrix by broad-band light at 260–390 nm completely removes the UV bands at 274 and 280 nm, while new bands appear at 255 and 480 nm (Figure 5b). After irradiation by 254- or 488-nm light, both bands vanish simultaneously with the growth of a broad band at 312 nm (Figure 5b). Under these conditions, the set of IR bands shown in the difference spectrum on Figure 6b as positive peaks is replaced by a set of new peaks, negative in this spectrum, which shows a single band at 2202 cm^{-1} in the sp^2 Si–H stretching range.

Bleaching the matrix by 308-nm light converts the UV spectrum back into the spectrum with two bands at 255 and 480 nm (Figure 5b) and changes the IR spectrum from the one shown by the negative peaks in Figure 6b to the one shown by the positive peaks. These reversible transformations were repeated several times, always reproducing the UV and IR spectra shown in Figures 5b and 6b. The most likely interpretation of these results is the assignment of the UV bands at 255 and 480 nm to the silylene **2b**, which after bleaching by either 254- or 488-nm light rearranges into the siladiene **3b**, absorbing at 312 nm in the Ar matrix UV spectrum. Bleaching this band by 308-nm light converts **3b** back to **2b** along with traces of **1b** and **4b**.

Discussion

Mechanistic Aspects. Scheme I summarizes all reactions and transformations that we believe to have observed in the present work. Both the pyrolysis of the spiro compound **5a** and the pyrolysis or photolysis of the diazide **6** are believed to proceed *via* a common initial intermediate, the cyclic silylene **2a**. Under vacuum pyrolysis conditions, **2a** rearranges rapidly to the most stable isomer, silole (**1a**), the only thermally generated reactive intermediate we could isolate in a matrix in the absence of trapping agents.

In case of the matrix photolysis of **6**, we might have expected **2a** to be the only photoproduct detected in the matrix UV and IR spectra. In fact, a mixture of silole (**1a**) and minor amounts of the siladienes **3a** and **4a** was formed. Since **2a** posesses an absorption at 250 nm and since the photodecomposition of diazide **6** required irradiation with 248- or 254-nm light, it is very likely that silole and the siladienes are secondary products.

A. Siloles 1a,b. Molecular Geometry. Our calculations predict a planar C_{2v} structure for the ring of the parent silole (**1a**), similar to the structure of 1,3-cyclopentadiene (**9**).[25] The C=C (1.33 Å) and C—C (1.49 Å) bond lengths in **1a** are calculated to be very close to those in **9** (1.32 and 1.44 Å, respectively[33]), while the optimized C–Si–C bond angle (~92°) is smaller than the experimentally determined C–C–C bond angle (102°) in **9**. The Si–C bond length in **1a** is calculated to be 1.88 Å and lies within the normal range of values for the Si–C bond (Figure 7).

UV Spectra. The π–π^* transitions in the UV spectra of siloles normally lie at lower energies than those in **9** (257 nm),[34] probably due to increased cyclic hyperconjugation. The intense absorption band at 278 nm in the UV spectrum of silole (**1a**) is attributed to a π–π^* transition (HOMO–LUMO, similar to 1,3-butadiene), based on our multireference CI calculations (Table I). The calculated transition energy is too high, as expected for a relatively small CI and a basis set of valence orbitals only. We believe, however, that the calculation still provides a reasonable qualitative guide to trends within our group of isomers and to the nature of the excited states. In the UV spectrum of **1b**, the band of the HOMO–LUMO transition is slightly bathochromically shifted to 280 nm. This is reasonable upon comparison with the UV band at 285 nm found for the even more highly substituted isolable 1,1,3,4-tetramethylsilole in cyclohexane solution.[6b]

IR Spectra. A full assignment of the experimental bands in the IR spectrum of **1a** has been suggested by comparison with the IR spectra of **9**,[35] silacyclopentane,[36] and 1,1,3,4-tetramethylsilole[6b] and with the *ab initio* calculated vibrational spectrum of **1a**. The molecule has 27 normal vibrational modes; four of these have a_2 symmetry and are forbidden in the IR spectrum. One of the ring skeleton vibrations, calculated to lie below 400 cm^{-1}, could not be observed in our experiments. We have found 14 out of the 22 expected fundamentals in the 400–4000-cm^{-1} spectral region.

Two bands lying above 3000 cm^{-1} in the IR spectrum of **1a** and one band found for **1b** in the same spectral range obviously belong to C–H stretching vibrations. This agrees well with calculations (Table II) and with literature data for **9**[35] and 1,1,3,4-tetramethylsilole.[6b] The intense bands at 2144 and 2174 cm^{-1} in the spectrum of **1a** and those at 2132 and 2152 cm^{-1} observed for **1b** are assigned to symmetric and antisymmetric Si–H stretches, respectively. They are observed in the spectrum of silacyclopentane[36] at about 2150 cm^{-1}.

The bands of symmetric and antisymmetric C=C stretches have been found in the 1480–1580-cm^{-1} region of the IR spectrum of matrix-isolated **9**,[35] while in the spectrum of a liquid film of 1,1,3,4-tetramethylsilole, only one band at 1520 cm^{-1} has been observed.[6b] It is reasonable to assign the bands at 1478 and 1608 cm^{-1} in the IR spectrum of **1a** and those at 1521 and 1608 cm^{-1} observed for **1b** to symmetric and antisymmetric C=C stretches, respectively.

The in-plane C–H bending vibrational frequencies are located in the 1240–1385-cm^{-1} region for **9** and show weak or medium

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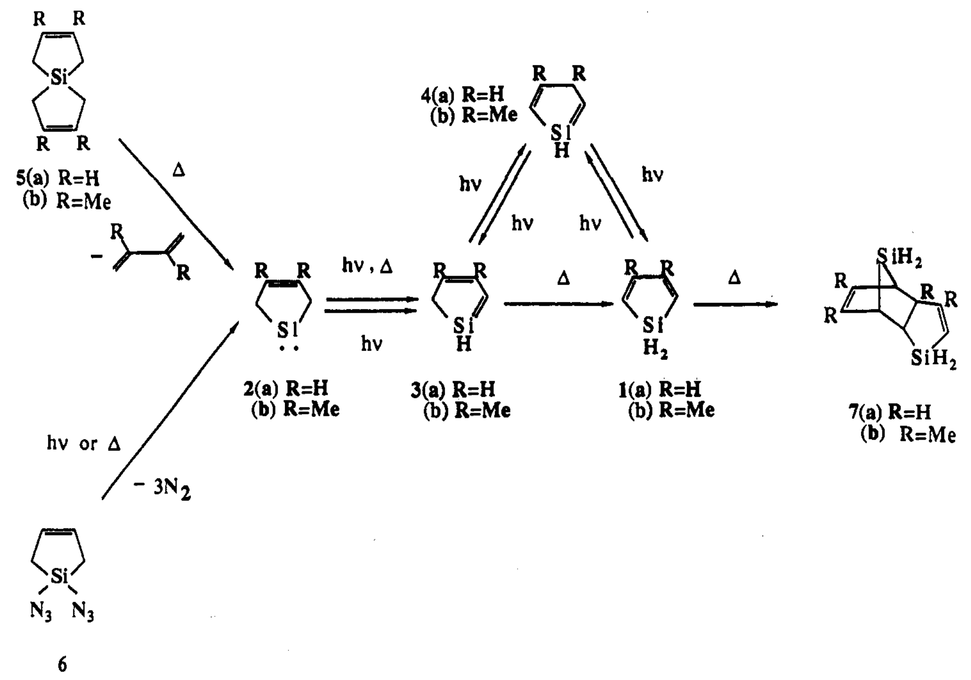
Scheme I



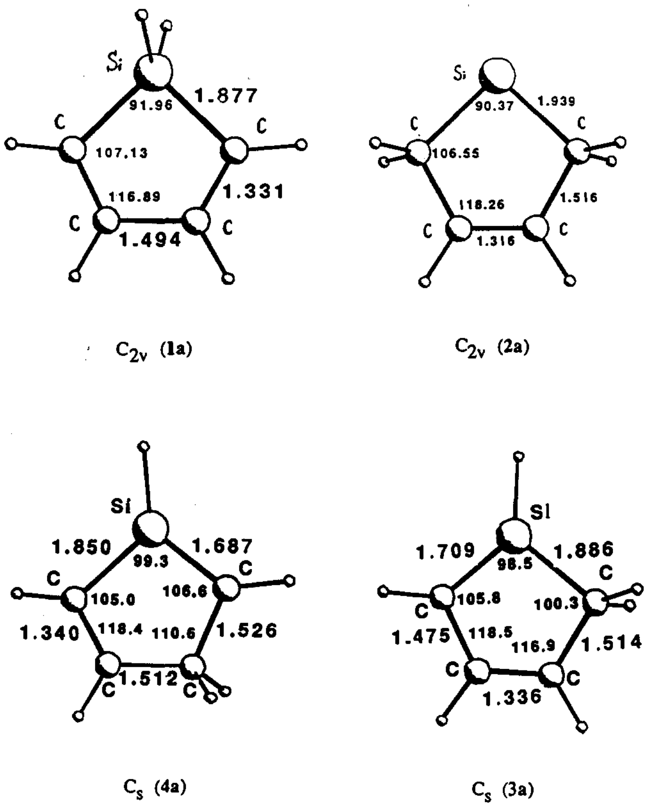


Figure 7. Calculated equilibrium geometries of **1a**–**4a**. Symmetry, bond lengths (Å), and valence angles (deg) are indicated.

band intensities in the IR spectra.[35] In this region of the IR spectrum of **1a** we found two bands at 1285 and 1346 cm^{-1}, in good agreement with the frequencies calculated at 1296 and 1349 cm^{-1}. Because of the expected strong coupling of bending and ring vibrations with deformations of the CH_3 groups in the 3,4-dimethyl-substituted silole **1b**, we do not attempt to suggest an assignment for the bands observed below 1400 cm^{-1} in the absence of spectral calculations done for this very molecule.

A mixed character is suggested for the band at 1088 cm^{-1} in the spectrum of **1a** by its close agreement with the frequency 1089 cm^{-1} calculated for a C–H bending mode coupled with ring vibrations (Table II).

The following ranges for SiH_2 bending motions are reported in the literature:[36] 980–940 (SiH_2 scissors), 955–875 (SiH_2 wagging), 740–630 (SiH_2 twisting), and 520–460 cm^{-1} (SiH_2 rocking). The scissoring mode in the IR spectrum of silacyclopentane[36] has been observed at 959 cm^{-1}. For **1a**, calculations predict the value of 956 cm^{-1}, very close to an intense band observed at 954 cm^{-1}. Another intense band at 879 cm^{-1} in the spectrum of **1a** is assigned to the SiH_2 wagging mode because it agrees very well with both the calculated frequency at 874 cm^{-1} and the assignment of the band at 890 cm^{-1} to this vibration in the spectrum of silacyclopentane.[36]

In accordance with calculations, the most intense band in the spectrum of **1a** at 712 cm^{-1} belongs to the out-of-plane C–H bending mode with some contribution from the SiH_2 twisting mode. The weak band at 677 cm^{-1} is assigned to the antisymmetric Si–C stretch, both because it is close to the calculated frequency at 698 cm^{-1} and because it falls into the 550–760-cm^{-1} region typical for Si–C stretches in dialkylsilanes[37] and for the antisymmetric Si–C motion at 665 cm^{-1} in silacyclopentane.[36] The assignment of the last band at 489 cm^{-1} to a_1 ring deformation is based on calculations, which predict a value of 479 cm^{-1}.

B. Silylenes 2a,b. Molecular Geometry. For the singlet ground state of **2a**, calculations yield an optimized C_{2v} planar ring structure with a C–Si bond length of 1.94 Å, the same as calculated earlier for singlet di-*tert*-butylsilylene,[22] a C═C bond length of 1.32 Å, and a C–Si–C bond angle of 90.4° (Figure 7). The C–Si–C bond angle is not significantly different from the 91.6° angle we calculated at the same level for the saturated analogue, tetramethylenesilylene.

UV–vis Spectra. The broad visible absorption bands at 480 nm for **2a** and **2b** are consistent with those observed for other dialkylsilylenes and cyclic tetramethylenesilylene[17] and are attributed to $n(\mathrm{Si}) \rightarrow p(\mathrm{Si})$ transitions in accordance with our CI calculation on **2a** (Table I). The excellent agreement between experiment and theory is not surprising, since the inclusion of diffuse functions in the basis set is not very important for this type of transition. The absorption bands of this transition in **2a** and **2b** are considerably red-shifted compared to that of tetramethylenesilylene (436 nm[17]). This difference cannot be attributed to a change in the C–Si–C bond angle, which is very

Table III. Vibrations of 1-Silacyclopent-3-ene-1,1-diyl (**2a**)

		frequencies[a]		IR intensities		
mode	symmetry	calcd	obsd	calcd[b]	obsd	assignment
1	b_1	72		4.4		
2	a_2	315		0		
3	a_1	460	463	30.6	w	ring vibration
4	b_2	540	528	29.5	w	ring vibration
5	b_1	554		1.6		
6	a_1	605	616	12.8	m	Si—C sym stretch
7	a_2	619		0		
8	b_2	740	741	0.05	s	Si—C asym stretch
9	b_1	763	770	53.7	m	=CH wag
10	a_1	888	881	0.1	m	C—C ring deform
11	b_2	920	944	3.6	w	C—C ring deform
12	a_2	985		0		
13	a_1	1115	1108	24.3	s	CH_2 rocking
14	b_1	1116		0.6		
15	a_2	1117		0		
16	b_2	1207	1174	8.4	w	CH_2 twisting
17	a_1	1227	1208	17.0	w	=CH sym rock
18	b_2	1352	1307	1.3	w	CH_2 wag
19	b_2	1411	1397	11.7	s	=CH asym rock
20	a_1	1414	1406	0.1	m	CH_2 scissors
21	a_1	1691	1624	14.2	s	C=C stretch
22	b_2	2840	2854	55.2	vw	CH_2 stretch
23	a_1	2841	2876	4.0	vw	CH_2 stretch
24	a_2	2959		0		
25	b_1	2962	2962	42.7	vw	CH_2 stretch
26	b_2	2988	3002	15.6	vw	=C—H stretch
27	a_1	3014	3028	60.4	vw	=C—H stretch

[a] In cm^{-1}. [b] km/mol.

small. It may be due to an involvement of the C=C exocyclic bond. This shift is reproduced very well by the calculations, which yield a value of 391 nm for tetramethylenesilylene. Inspection of the intermediate results provided no obvious clue to the origin of the shift in terms of orbital energies.

Both silylenes **2a** and **2b** show second absorption bands in the UV region (250 and 255 nm, respectively). Such bands have not been observed for saturated silylenes, and it appears that they are due to an interaction of the silicon center with the double bond. The calculations support the existence of such an interaction but do not provide a definitive assignment of the UV band. They place the second excited singlet state ($^1A_2$) at 220 nm, close to the observed value. This excited state corresponds to a mixture of the $n(Si) \rightarrow \pi^*$ configuration with a highly excited configuration in which a $n(Si) \rightarrow p(Si)$ excitation is combined with a $\pi^2 \rightarrow p(Si)\pi^*$ promotion and with a doubly excited configuration in which the $n(Si) \rightarrow p(Si)$ excitation is combined with a $\pi \rightarrow \pi^*$ promotion. This $^1A_2$ state has no counterpart in tetramethylenesilylene, in which the lowest $^1A_2$ state is computed only below 140 nm. The difficulty with the assignment of the band observed at 250 nm to this $^1A_2$ state is its relatively high intensity, since a $^1A_1 \rightarrow {}^1A_2$ transition is symmetry forbidden. It is hard to believe that vibronic intensity borrowing could be so efficient.

The next allowed transition is computed only at 183 nm, and the excited state $^1B_2$ is well described by a promotion from the $n(Si)$ lone pair orbital to the σ^*_{SiC} antibonding orbital. This state has an analogue at 165 nm in tetramethylenesilylene. The computed energy is uncomfortably high for assignment to the experimental 250-nm band. Clearly, higher level calculations are needed to resolve this issue.

IR Spectra. Five out of the 27 vibrations in **2a** are forbidden in the IR spectra. Two others lie below 400 cm^{-1} and could not be detected in our experiments. We found 17 bands in the IR spectrum of **2a** (Table III). Full assignment of these bands was based on the calculated vibrational spectrum of **2a** and comparison with the IR spectra of cyclopentene,[37] silacyclopentane,[36] and di-*tert*-butylsilylene.[22]

The =C—H stretches in spectra of cis-substituted olefins RCH=CHR appear in the 3040–2995 cm^{-1} region. Therefore we assigned the bands at 3028 and 3002 cm^{-1} to the symmetric and antisymmetric =C—H stretching modes, in agreement with the calculated frequencies of 3014 and 2988 cm^{-1}.

Three bands, observed at 2962, 2876, and 2854 cm^{-1} in the spectrum of **2a**, should be attributed to ring CH_2 stretches since they are close to those in the IR spectra of silacyclopentane, which appear in the 2910–2960- and 2860–2880-cm^{-1} regions.[36] This assignment agrees well with the calculations.

The band at 1624 cm^{-1} is assigned to the C=C stretch in **2a**. It is shifted to a higher frequency, 1660 cm^{-1}, in the spectrum of the dimethyl derivative **2b**. This agrees with the location of the C=C stretches in the spectra of cyclopentene at 1611–1617 cm^{-1} and also its shift to 1671–1686 cm^{-1} in derivatives doubly alkylated at the C=C bond.[36]

Our calculations predict that the a_1 CH_2 scissoring mode in **2a** should appear at 1414 cm^{-1}. In the IR spectra of silacyclopentane these modes are observed at 1418–1457 cm^{-1} as bands of medium or high intensity.[36] The closest to this region in the spectrum of **2a** is a medium-intense band at 1406 cm^{-1}, which is most likely attributable to CH_2 scissors.

A strong band at 1397 cm^{-1} is assigned to an in-plane =C—H asymmetric rocking mode of a_2 symmetry. For this mode, calculations predict the value of 1411 cm^{-1}. In the spectra of *cis*-dialkylethylenes RCH=CHR, it appears near 1404 cm^{-1}.[37]

In *cis*-dialkylethylenes, the CH=CH symmetric rocking mode is located at 1250–1270 cm^{-1}. Calculations predict a value of 1227 cm^{-1} for this a_1 mode and also its coupling with an in-phase CH_2 wag of the same symmetry. The closest spectral feature matching this is a weak band at 1208 cm^{-1} (Table III).

A weak band at 1302 cm^{-1} is assigned to an out-of-phase CH_2 wagging mode of b_2 symmetry, which appears at 1309 cm^{-1} in the spectrum of silacyclopentane.[36]

The CH_2 twisting mode ("*b*" type) was found at 1150 cm^{-1} in silacyclopentane.[36] Calculations predict that this b_1 motion will appear at 1206 cm^{-1} in **2a**. It therefore appears safe to assign a weak band at 1174 cm^{-1} to this mode. The assignment of the strongest band at 1108 cm^{-1} to the rocking CH_2 motion in **2a** was based both on the knowledge that this motion appears at 1104 cm^{-1} in cyclopentane and at 1081 cm^{-1} in silacyclopentane and on the calculated frequency of the a_1 mode.

Ring deformations involving C–C stretches are normally observed in cyclopentane within the 1100–800-cm^{-1} range. A weak band at 944 cm^{-1} falls into this spectral region and matches well a calculated C–C mode of b_2 type at 920 cm^{-1}. A medium-intense band at 881 cm^{-1} might be assigned to an a_1 C–C ring deformation, which appears at 852 cm^{-1} in silacyclopentane. A band at 770 cm^{-1} could be attributed to an antisymmetric out-of-plane b_1 =C—H bending mode, which should show a high intensity band in the IR spectrum as calculated. The symmetric and antisymmetric C–Si stretches in di-*tert*-butylsilylene were observed at 586 and 778 cm^{-1}, respectively.[22] For the silylene **2a,** calculations predict these frequencies to lie at 605 (a_1) and 740 cm^{-1} (b_2). This agrees well with the observed bands of **2a** at 616 and 741 cm^{-1} and with bands at 626 and 775 cm^{-1} in the spectrum of the silylene **2b**. The bands observed for **2a** at 528 and 463 cm^{-1} very likely belong to ring deformations in accordance with calculations and literature data on silacyclopentane.[36]

C. Siladienes 3a,b and 4a,b. Molecular Geometry. The calculations yielded planar C_s optimized geometries for 3a and 4a (Figure 7). The Si=C bond lengths, 1.709 Å in **3a** and 1.687 Å in **4a**, are very close to the Si=C bond length, 1.692 Å, calculated earlier for the $H_2Si{=}CH_2$ molecule in the RHF approximation.[38] The central C—C bond in the Si=C—C=C fragment in **3a**, calculated to be 1.475 Å long, is slightly shorter

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(38) Ohta, K.; Davidson, E. R.; Norokuma, K. *J. Am. Chem. Soc.* **1985**, *107*, 3446.

than the other C—C bond in **3a**, 1.514 Å, and **4a**, 1.512 and 1.526 Å. This undoubtedly primarily reflects differences in hybridization but is compatible with a degree of conjugation of the two π bonds in **3a** similar to that in ordinary 1,3-dienes. A similar conclusion can be reached in the case of **4a**, where the central Si—C bond, calculated to be 1.850 Å long in the C=Si—C=C fragment, is somewhat shorter than an ordinary Si—C bond, 1.886 Å, in **3a**.

UV Spectra. The UV absorption bands of the siladienes **3a,b** and **4a,b** (Table I), attributed to π–π^* transitions on the basis of our multireference CI calculations, are considerably red-shifted in comparison with the absorptions of the parent silene at 258 nm[39] and 1-methyl-1-silene at 260 nm[29,39] and suggest that π-conjugation is significant. The excited state in **3a** is calculated to be predominantly of HOMO → LUMO nature, whereas that in **4a** has only about one-third HOMO → LUMO character and many other $\pi \rightarrow \pi^*$ configurations contribute. The experimental findings are compatible with the red-shifted UV absorption bands (3-MP glass, 77 K) of the silene $Me_2Si{=}C(OSiMe_3)C(OEt){=}O$ at 288 nm[40] and 1-mesityl-1-silacyclobutadiene at 278 nm.[15] The red shift is much larger in **3a,b** than in **4a,b**. This agrees well with the relative values calculated for **3a** and **4a** (Table I) and supports the structural assignment of these two isomers made above on the basis of mechanistic arguments, even though the absolute values of the computed excitation energies are again too high, as expected for $\pi \rightarrow \pi^*$ transitions at this level of calculation.

The large difference in the first $\pi \rightarrow \pi^*$ excitation energy of **3a** (λ_{max} = 296 nm) and **4a** (λ_{max} = 270 nm) can be understood at the simple Hückel level as well. *s-cis*-1,3-Butadiene is an alternant hydrocarbon, and the change in electronegativity introduced by a replacement of a carbon by a silicon atom should have no first-order effect, neither in the terminal (**3a**) nor in the internal (**4a**) position. However, the reduction in the value of the SiC resonance integral relative to the CC resonance integral will have a first-order effect. With the Si atom in the terminal position, only the C_3–C_4 bond is affected. At this bond, the HOMO is bonding and the LUMO antibonding; hence the reduction of the resonance integral reduces the HOMO–LUMO gap. With the Si atom in the internal position, the effect of the reduction of the resonance integral across the C_2–C_3 bond needs to be added. At this bond, the HOMO is antibonding and the LUMO bonding; hence the effect on the HOMO–LUMO gap is just the opposite, cancelling much of the effect that originates from the C_3–C_4 bond.

The wavelengths of the absorption maxima in the 1,3-siladiene **3a** are more sensitive to 3,4-dimethyl substitution than in the case of the 1,4-siladiene **4a**. This is shown by the significant change from **3a** (296 nm) to **3b** (312 nm), compared with the much smaller difference in the absorption maxima of **4a** (270 nm) and **4b** (274 nm).

IR Spectra. The calculated and observed frequencies of **3a** and **4a** are given in Tables IV and V. Those observed for the dimethyl substituted molecules **3b** and **4b** are summarized in Table VI. The assignment of the three bands above 3000 cm^{-1} in the spectra of **3a** and **4a** to =C—H stretches appears certain and agrees well with calculations. No =C—H stretch was found in this spectral range for **3b**, probably due to very low intensity of this IR band. In contrast, **4b** has a medium-intense band attributed to the =C—H stretch at 3018 cm^{-1}. Another pair of bands at 2930 and 2865 cm^{-1} in the spectrum of **3a** may clearly be attributed to the antisymmetric and symmetric CH_2 stretches. In the structure of the dimethyl derivative **3b**, these modes most likely appear at 2933 and 2858 cm^{-1}, respectively. The band at 2904 cm^{-1}, found in the spectrum of **4a**, has been assigned to a CH_2 antisymmetric stretching mode, because in the IR spectrum of matrix-isolated **9** this mode appears at 2906 cm^{-1}.[35] Assignment of the bands at 2971 and 2870 cm^{-1} in **3b** as well as the bands at 2961 and 2854 cm^{-1} in **4b** to antisymmetric and symmetric modes, respectively, is based on the knowledge that these bands are very characteristic in the spectra of alkanes and cycloalkanes.[37]

It is already well documented that the bands in the 2200–2240 cm^{-1} range in the spectra of silenes belong to sp^2 Si–H stretching modes.[22,29,39] Therefore, our assignments of the bands at 2210

Table IV. Vibrations of 1-Silacyclopenta-1,3-diene (**3a**)

		frequencies[a]		IR intensities		
mode	symmetry	calcd	obsd	calcd[b]	obsd	assignment
1	*a''*	181		0.3		
2	*a''*	378		3.0		
3	*a''*	455	466	10.3	w	ring vibration
4	*a'*	473	488	4.0	m	ring vibration
5	*a'*	630		0.7		
6	*a''*	631	637	38.2	m	=Si—H out-of-plane bend
7	*a'*	655	680	37.6	w	=Si—H in-plane bend
8	*a''*	733	736	1.8	m	CH_2 rock
9	*a''*	785	790	37.1	w	=C—H bend
10	*a'*	787	819	18.1	w	C—C ring
11	*a'*	891	852	12.6	w	C—C ring
12	*a'*	936	929	42.7	m	Si=C stretch
13	*a'*	957	961	2.0	m	=C—H bend
14	*a''*	977	974	0.4	m	=C—H bend
15	*a''*	1073		2.7		
16	*a'*	1103	1092	20.2	s	CH_2 wag
17	*a'*	1188	1181	11.7	w	=C—H bend
18	*a'*	1231	1282	20.5	w	=C—H bend; CH_2 wag
19	*a'*	1352	1354	4.8	m	=C—H bend
20	*a'*	1406	1406	9.9	m	CH_2 scissors
21	*a'*	1592	1551	9.6	m	C=C stretch
22	*a'*	2201	2210	116.0	m	Si—H stretch
23	*a'*	2876	2865	10.8	m	CH_2 stretch
24	*a'*	2906	2939	12.7	m	CH_2 stretch
25	*a'*	3013	2994	17.9	w	=C—H stretch
26	*a'*	3040	3038	31.6	s	=C—H stretch
27	*a'*	3076	3066	5.9	m	=C—H stretch

[a] In cm^{-1}. [b] km/mol.

Table V. Vibrations of 1-Silacyclopenta-1,4-diene (**4a**)

		frequencies[a]		IR intensities		
mode	symmetry	calcd	obsd	calcd[b]	obsd	assignment
1	*a''*	272		11.2		
2	*a''*	386		1.2		
3	*a''*	443		0.01		
4	*a'*	474	470	36.7	w	ring vibration
5	*a'*	641		11.9		
6	*a''*	651	597	34.9	m	=Si—H out-of-plane bend
7	*a'*	672		7.1		
8	*a''*	689	742	53.6	s	=C—H out-of-plane bend
9	*a'*	804		18.0		
10	*a'*	838	859	20.9	s	CH_2 rock
11	*a''*	910	913	12.0	m	=C—H bend
12	*a'*	930	936	59.7	s	Si=C stretch
13	*a'*	985	985	4.6	w	=C—H bend
14	*a''*	986		0.07		
15	*a'*	1075	1103	5.6	m	=C—H bend
16	*a''*	1140	1135	1.7	w	CH_2 wag
17	*a'*	1196	1149	6.0	w	=C—H bend
18	*a'*	1283	1278	15.1	w	=C—H bend
19	*a'*	1325		3.6		
20	*a'*	1427	1426	3.1	w	CH_2 scissors
21	*a'*	1538	1543	13.3	m	C=C stretch
22	*a'*	2193	2216	152.1	m	Si—H stretch
23	*a'*	2860		28.3		
24	*a''*	2883	2904	16.2	w	CH_2 stretch
25	*a'*	3010	3025	21.2	w	=C—H stretch
26	*a'*	3057	3061	14.7	w	=C—H stretch
27	*a'*	3080	3095	4.6	w	=C—H stretch

[a] In cm^{-1}. [b] In km/mol.

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Table VI. IR Bands of **1b**–**4b**

molecule	frequencies (cm^{-1})
1b	459, 489, 575, 716, 809, 835, 878, 943, 1025, 1062, 1118, 1180, 1194, 1313, 1360, 1437, 1451, 1521 (C═C sym stretch), 1608 (C═C stretch asym), 2132 (Si—H stretch sym), 2152 (Si—H stretch asym), 2864, 2990, 3050 (═C—H stretch)
2b	486, 556, 576, 626, 675, 775, 797, 879, 902, 975, 1134, 1165, 1179, 1432, 1660 (C═C stretch), 2985, 2993
3b	519, 596, 658, 688, 829, 864, 888, 917 (Si═C stretch), 1012, 1079, 1547 (C═C stretch), 2202 (═Si—H stretch), 2858, 2870, 2933, 2971
4b	449, 533, 613, 680, 758, 864, 920, 933 (Si═C stretch), 1004, 1210, 1276, 1341, 1419, 1541 (C═C stretch), 2212 (═Si—H stretch), 2854, 2909, 2932, 2961, 3018

cm^{-1} in **3a**, 2216 cm^{-1} in **4a**, 2202 cm^{-1} in **3b**, and 2212 cm^{-1} in **4b**, in fairly good agreement with calculations (Tables IV and V), are reasonable.

Calculations also predict an appearance of the C═C stretching mode in **3a** and **4a** below 1600 cm^{-1} as a result of strong π-conjugation. This agrees well with the assignment of the observed bands at 1551 cm^{-1} in the spectrum of **3a** and 1547 cm^{-1} in **3b**, as well as 1543 cm^{-1} in **4a** and 1541 cm^{-1} in **4b**, to this vibrational mode.

The IR bands of the CH_2 scissoring mode are usually very characteristic in the spectra of cycloalkanes,[37] and we assign the band at 1426 cm^{-1} in **4a** to this motion. A medium-intense band at 1354 cm^{-1} and weak bands at 1282 and 1181 cm^{-1} are assigned to the in-plane ═C—H bending modes in the spectrum of **3a** in accordance with calculations (Table IV). In the spectrum of **4a**, weak bands at 1278, 1149, and 1103 cm^{-1} are also likely to be attributed to the in-plane ═C—H bending modes, in fairly good agreement with the calculations.

The CH_2 wagging mode in **9** appears in the IR spectrum at 1091 cm^{-1}. Calculations predict this mode at 1103 cm^{-1} in the spectrum of **3a** and at 1140 cm^{-1} in the spectrum of **4a**. This agrees well with the observed bands in the spectra of **3a** (1092 cm^{-1}) and **4a** (1135 cm^{-1}).

The most interesting matter is the location of the Si═C stretching mode in the spectra of the π-conjugated silenes **3a**,**b** and **4a**,**b**. As was established earlier, this band appears at 1003 cm^{-1} in the spectrum of 1,1-dimethyl-1-silene[30] and at 989 cm^{-1} in that of 1-methyl-1-silene[20,29] and is very sensitive to the electronic and steric nature of the substituents.[41] Normally, π-conjugation of a C═C bond with another double bond results in a considerable shift to lower frequencies in the vibrational spectra, e.g., the C═C stretching mode in cyclopentene is found at 1617 cm^{-1} and in **9** at 1572 cm^{-1}, i.e., 45 cm^{-1} lower. We could thus expect the Si═C stretch in siladienes to appear at about 940 cm^{-1}. The values predicted by our calculations are very close to this estimate: 936 cm^{-1} for **3a** and 930 cm^{-1} for **4a**. This gave strong support to an assignment of the bands at 929 cm^{-1} in **3a** and at 936 cm^{-1} in **4a** to the Si═C stretching mode. We believe that in 3,4-dimethyl-substituted siladienes this mode is shifted to lower frequencies, 917 cm^{-1} in **3b** and 933 cm^{-1} in **4b**.

The out-of-plane ═C—H bending modes are associated with the bands at 974, 961, and 790 cm^{-1} in **3a**, as well as those at 985, 913, and 742 cm^{-1} in **4a**, in agreement with calculations and literature data[35] on **9**.

We believe that the CH_2 rocking mode appears in the spectrum of **3a** at 736 cm^{-1} and in that of **4a** at 859 cm^{-1}. These assignments are based on comparison with the calculations (Tables IV and V).

A weak band at 680 cm^{-1} and a medium intense band at 637 cm^{-1} in the spectrum of **3a** are assigned to the in-plane and out-of-plane ═Si—H bending modes, in agreement with calculations and with the previous assignment of the bands at 678 and 614 cm^{-1} in the spectrum of 1-methyl-1-silene to these modes.[20] We could not observe the ═Si—H in-plane bending mode in the spectrum of **4a**, probably because of its low intensity. The band at 597 cm^{-1} might be assigned to the out-of-plane ═Si—H bending mode. The other observed bands at 852, 819, 488, and 466 cm^{-1} in the spectrum of **3a** and at 470 cm^{-1} in the spectrum of **4a** probably belong to ring vibrations, as suggested by the calculations.

The remaining bands observed in the spectra of **3b** and **4b** are difficult to assign to specific vibrational modes in the absence of calculations for these very molecules.

Conclusion

Our matrix isolation–vacuum pyrolysis studies of the silaspirodienes **5a**,**b** and diazidosilacyclopentene **6**, as well as matrix photolysis of **6**, have clearly demonstrated that these compounds are highly selective precursors for the reactive siloles **1a**,**b** both in the gas phase and in condensed media. It is proposed that the siloles **1a**,**b** undergo photoinduced rearrangement to the 1,4-siladienes **4a**,**b**, which in their turn can be photochemically converted into the 1,3-siladienes **3a**,**b** and then reversibly transformed into the silylenes **2a**,**b**. The structural assignments of **1a**,**b** and **2a**,**b** are firm, whereas the structural attribution within the pairs **3a**,**4a** and **3b**,**4b** rests on a mechanistic argument and comparison with *ab initio* calculations.

The calculated geometries of **1a**–**4a** contain all the heavy atoms in a single plane, and the Si═C bond lengths in **3a** and **4a** are found to correspond to expectations. The calculations permitted an assignment of observed IR peaks in the spectra of **1a**–**4a** and suggested an attribution of vibrational modes in the dimethyl-substituted molecules **1b**–**4b**. As expected, the Si═C stretching frequencies, 929, 936, 917, and 933 cm^{-1} in **3a**, **4a**, **3b**, and **4b**, respectively, are significantly lower than those in unconjugated silenes (989 cm^{-1} in 1-methylsilene[20,29] and 1003 cm^{-1} in 1,1-dimethylsilene[30]). These data, together with the red-shifted UV absorptions, provide evidence for strong Si═C—C═C and C═Si—C═C π-conjugation in the siladienes **3a**,**4a** and **3b**,**4b**, respectively.

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