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Matrix Isolation and Photochemical Interconversion of Silacyclopentadienes

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1-Silacyclopenta-2,4-diene **1** has been generated by vacuum pyrolysis of 5-silaspiro[4.4]nona-2,7-diene **5** and by photolysis of matrix-isolated 1,1-diazido-1-silacyclopent-3-ene **6**, and characterized by matrix-isolation IR and UV spectroscopy; reversible interconversion of **1** with 1-silacyclopenta-1,3-diene **2**, 1-silacyclopenta-1,4-diene **3** and 1-silacyclopent-3-ene-1,1-diyl **4** has been observed upon irradiation at various wavelengths; the red-shifted UV absorption of **2** and **3**, together with their low Si=C stretching frequencies, provide evidence for Si=C—C=C π conjugation.

Although heavily substituted 1-silacyclopenta-2,4-dienes (siloles) are stable and have been used as starting materials in synthesis,[1–3] only indirect evidence is available for the parent **1**, such as isolation of its 2+4 dimer,[4] and results of kinetic studies.[5] Direct investigations of simple siloles by physical methods have been limited to a recent MS detection of 1-methylsilole in vacuum pyrolysis.[5]

The isomeric siladienes, 1-silacyclopenta-1,3-diene **2** and 1-silacyclopenta-1,4-diene **3**, contain an Si=C bond and can be expected to dimerize even more readily. Little seems to be known about them, although methyl derivatives of **2** and **3** have been postulated as pyrolytic intermediates.[1,4] Yet another isomer, the silylene 1-silacyclopent-3-ene-1,1-diyl **4**, has been postulated as a reactive intermediate,[4] but again, has not been observed directly. We now report a matrix spectroscopic characterization of isomers **1**–**4** and their photochemical interconversion.

In view of the evidence for a thermal isomerization of **4** to **1** obtained by Gaspar *et al.*,[4] and of the availability of 5-silaspiro[4.4]nona-2,7-diene **5**,[6] recently suggested as a potential thermal source of **4** by Chernyshev *et al.*,[6] we have selected **5** as our starting material.

Vapour of **5** mixed with excess argon was passed at 10^{-4} to 10^{-1} Torr through a quartz tube at 1075 K and deposited on a CsI or sapphire substrate held at 26–28 K. FT IR or UV spectra were then recorded at 12 K. Similar spectra of poorer quality were recorded in the absence of argon. In addition to the expected bands of buta-1,3-diene and those of unreacted **5**, a set of new IR peaks appeared, accompanied by a UV peak at 278 nm. These peaks all disappeared simultaneously upon 308 nm irradiation at 12 K and were attributed to a single species. Fig. 1 shows the UV spectrum and Fig. 2(*c*) shows the IR difference spectrum. The absence of visible absorption makes it highly unlikely that the species is the presumed primary product **4** (*cf.* the visible absorption spectra of alkylsilylenes[7–10] and 1-silacyclopenta-1,1-diyl[8]). Instead, we assign it as the product **1** of the expected [3] further thermal rearrangement of **4**. This assignment is supported by the following evidence. (*i*) After warming of the argon matrix or the neat pyrolysate to room temperature, GC–MS analysis showed a single major peak with a mass spectrum identical with that of an authentic sample of the 2+4 dimer of **1**, kindly provided by Professor Gaspar. (*ii*) The IR spectrum agrees very well with expectations [Fig. 2(*a*)] for **1** based on an HF 6-31G* calculation and, in particular, sp^2 Si—H stretching vibrations are absent in the 2200–2230 cm^{-1} region while two sp^3 Si—H stretches appear at 2175 and 2144 cm^{-1}. (*iii*) The UV spectrum compares well with qualitative expectations for a cyclopentadiene perturbed by hyperconjugation through an SiH_2 group.

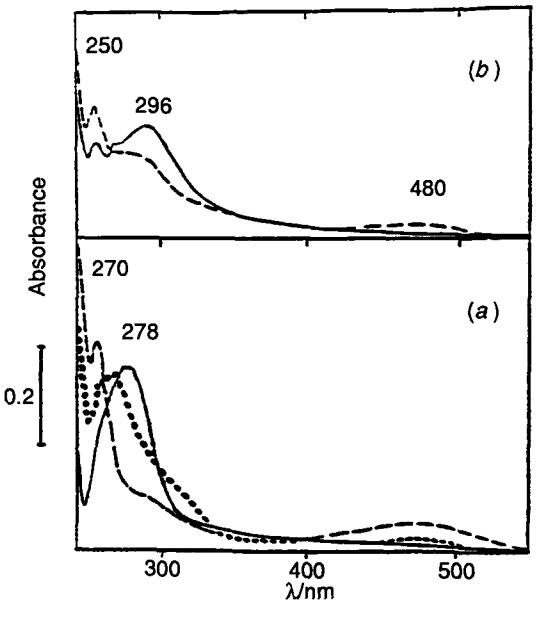


Fig. 1 UV spectra (Ar, 12 K). (*a*) Pyrolysis products of **5** (full line), after 308 nm irradiation (dotted line), and subsequent 260–390 nm irradiation (dashed line); (*b*) after further bleaching by 488 nm light (full line) followed by 308 nm light (dashed line).

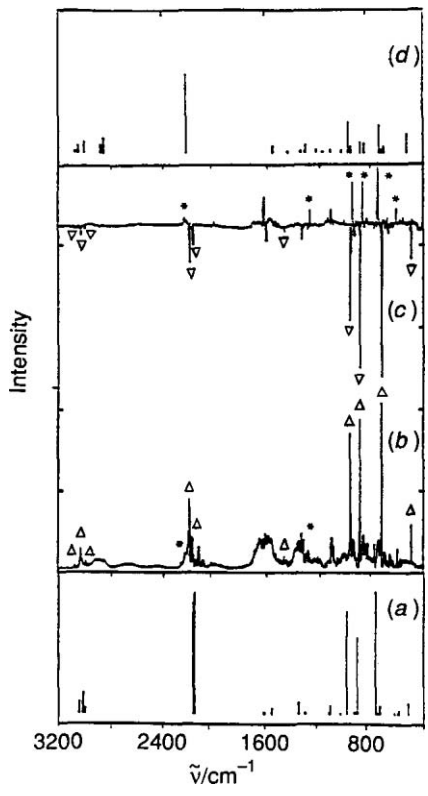


Fig. 2 IR spectra (Ar, 12 K). (*a*) **1**, calculated; (*b*) 248 nm photolysis products of **6**; (△) **1**, (*) **2** and **3**; (*c*) difference of the spectra of pyrolysis products of **5** before (negative) and after (positive) 308 nm light irradiation; (*d*) **3**, calculated.

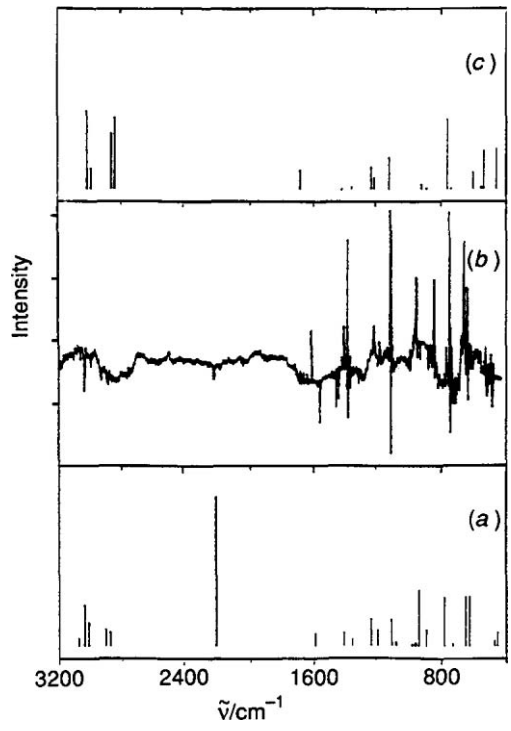


Fig. 3 IR spectra (Ar, 12 K). (*a*) **2**, calculated; (*b*) difference of the spectra of the sample whose UV absorption is shown in Fig. 1(*a*) (dashed line), before (positive) and after (negative) 488 nm irradiation; (*c*) **4**, calculated.

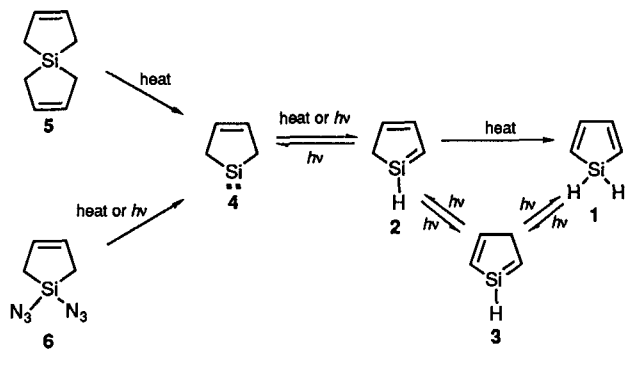
(*iv*) The same product, along with others, is accessible by pyrolysis of the diazide **6** or its irradiation [Fig. 2(*b*)] at 248 or 254 nm in matrix isolation (photochemical loss of geminal azido groups with formation of a silylene is well documented[9,10]). It appears highly likely that the $m/z = 82$ peak observed in a vacuum pyrolysis–MS of **5** should be assigned as a parent ion not from **4**,[6] but, rather, from **1**.

Next, we present evidence that **1** can be reversibly converted to **2**, **3** and **4** by irradiation in argon matrix at 12 K. The interconversions are not clean since the UV absorptions of **1**, **2**, **3** and **4** all overlap. However, the spectra are sufficiently different to permit preferential accumulation of one or another of these species by a suitable choice of irradiation wavelength.

The spectra of **4** are easiest to separate. These are characterized by absorption bands at 250 and 480 nm (Fig. 1) and also by a series of IR peaks. **4** is formed along with traces of **2** and **3** upon irradiation of **1** with broad-band UV light (260–390 nm). Irradiation of **4** at 488 nm, where **1**–**3** cannot be expected to absorb, gradually removes both UV-visible absorption bands and many of the IR peaks, which we therefore also associate with **4** (Fig. 3). The assignment of this photoproduct as **4** is based on its visible absorption band, and also on its mode of formation and the agreement of its IR frequencies with those calculated (HF 6-31G*; note particularly the absence of detectable Si—H stretching bands) [Fig. 3(*c*)]. The short-wavelength absorption peak (250 nm), unprecedented for a simple silylene, clearly belongs to **4**, since (*i*) it disappears in proportion to the 480 nm band upon 488 nm irradiation, and (*ii*) irradiation at 254 nm causes both UV-visible peaks of **4** to be reduced in intensity.

The photochemical conversion of an alkylsilylene to a silene with visible light, reversed by irradiation of the silene with UV light, has been well established for a long time.[7,10] Indeed, the product of bleaching of **4** with either 254 or 488 nm light, characterized by an absorption band at 296 nm (Fig. 1) and a series of IR peaks, is converted back to **4** upon irradiation with 308 nm light. In addition, weak signals due to **1** and **3** also appear. The IR spectrum of the photoproduct from **4** was separated by taking a difference [Fig. 3(*b*)] and contains a single peak at 2210 cm^{-1} in the sp^2 Si—H stretching region. It is compatible with the *ab initio* calculations for structures **2** and **3**. We propose an assignment to **2**, since this is expected to be the primary product of a single H-atom shift in **4**, and the use of 488 nm light in the formation of this material from **4** precludes secondary photochemical processes. The formation of a trace of **1** is intriguing and may be due to the existence of a minor direct photochemical path from **4** to **1**, perhaps initiated by attack of the divalent silicon on the C=C double bond.

Finally, irradiation of matrix-isolated **1** at 308 nm 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 (Fig. 1) and characterized by a series of IR bands [Fig. 2(*c*)], compatible with *ab initio* calculations for **2** and **3** [note particularly a single peak at 2216 cm^{-1} in the sp^2 Si—H stretching region; Fig. 2(*d*)]. By elimination, we propose to assign this as **3**, formed from **1** by a photochemically allowed 1,3-hydrogen shift.



Scheme 1

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The same photochemical interconversions among **1–4** can be observed starting with the product of the pyrolysis or photolysis of **6**. We propose Scheme 1 to account for all these results. An automerizing photochemical 1,3 hydrogen shift in **2** probably also occurs but is not detectable in the absence of labelling.

The calculated geometries of **1–4** contain all heavy atoms in a single plane, and the Si=C bond lengths are unexceptional. The calculations permit an assignment of observed IR peaks. The Si=C stretching frequencies, 929 and 936 cm^{-1} in **2** and **3**, respectively, are lower than those in unconjugated silenes (989 cm^{-1} in 1-methylsilene[10]). These, together with the red-shifted UV absorptions, provide evidence for the presence of Si=C—C=C π conjugation in **2** and **3**.

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