Reviews

Interconversions of the silylene-to-silene and germylene-to-germene types: direct spectroscopic studies and calculations*

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The recent advances in spectroscopic and quantum-chemical studies of carbene-to-olefin isomerization of carbene analogs of Group 14 elements are discussed. Primary attention is devoted to the use of matrix isolation spectroscopy, whose successful combination with modern calculation techniques has resulted in the first spectroscopic characterization of a number of novel short-lived silylenes and germylenes and their structural isomers with unsaturated Si=C, Ge=C, and Si=O bonds.

Key words: carbene analogs, silylene-to-silene isomerization, germylene-to-germene isomerization, infrared spectroscopy, ultraviolet spectroscopy, pyrolysis, photochemistry, matrix isolation, quantum-chemical calculations, unsaturated silicon—carbon bond, unsaturated germanium—carbon bond, metal atom reactions, silacyclopentadienes, germacyclopentadienes, germenes, silanones.

Introduction

Carbene-to-olefin isomerization, which is accompanied by 1,2-migration of H atoms and alkyl or other groups to the carbene center, is fairly well known.[1] In the case of silyl-substituted carbenes, this isomerization affords silaalkenes (silenes), unstable under ordinary conditions.[2,3] This route was used more than 20 years ago by Chapman[4] and Chedekel,[5] later by us,[6] and most recently by Sander[7] to generate and stabilize 1,1,2-trimethyl-1-silene in a low-temperature matrix and to detect it directly by spectroscopy.

$$Me_3SiCHN_2 \xrightarrow[-N_2]{i} Me_3Si\ddot{C}H \longrightarrow Me_2Si{=}CHMe$$

i. Δ or *hν*, in an Ar matrix, 8—12 K

Silenes are also formed in the thermal and photochemical isomerization of silylenes. Direct spectroscopic

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evidence for this type of transformation was first obtained in studies[8—10] of isomerization of dimethylsilylene into 1-methyl-1-silene.

$$Me_2Si: \xrightarrow{i} Me(H)Si{=}CH_2$$

i. Δ or *h*ν, in an Ar matrix, 12 K

Isomerization of dimethylsilylene and other alkylsilylenes into the corresponding silenes has also been studied by Maier *et al*,[11—13] who employed matrix UV and IR spectroscopy.

Conversely, the possibility of similar isomerization of germanium analogs of carbenes (germylenes) into molecules with the Ge=C double bond (germenes)[14] has until recently not been experimentally proven. The attempt to monitor the photoisomerization of matrix-isolated dimethylgermylene into 1-methyl-1-germene by spectroscopy made by Barrau *et al.*[15] was unsuccessful.

$$Me_2Ge: \overset{\text{Ar, 12 K, }h\nu}{\nrightarrow} Me(H)Ge{=}CH_2 .$$

This negative result can probably be explained by the data of theoretical calculations,[16—18] which predict a higher thermodynamic stability of alkylgermylenes compared to the isomeric germenes, whereas the isomerization of alkylsilylenes to the corresponding silenes is virtually neutral from the thermodynamic viewpoint.[18,19]

We obtained the first direct spectroscopic evidence for germylene-to-germene isomerization, studied silylene-to-silene transformations of cyclic silylenes and silacyclopentadienes, and demonstrated the possibility of photoisomerization of alkoxysilylenes into alkylsilanones for new substrates. The results of these studies, carried out in 1990—1998 within the framework of cooperation of our scientific centers, are presented below.

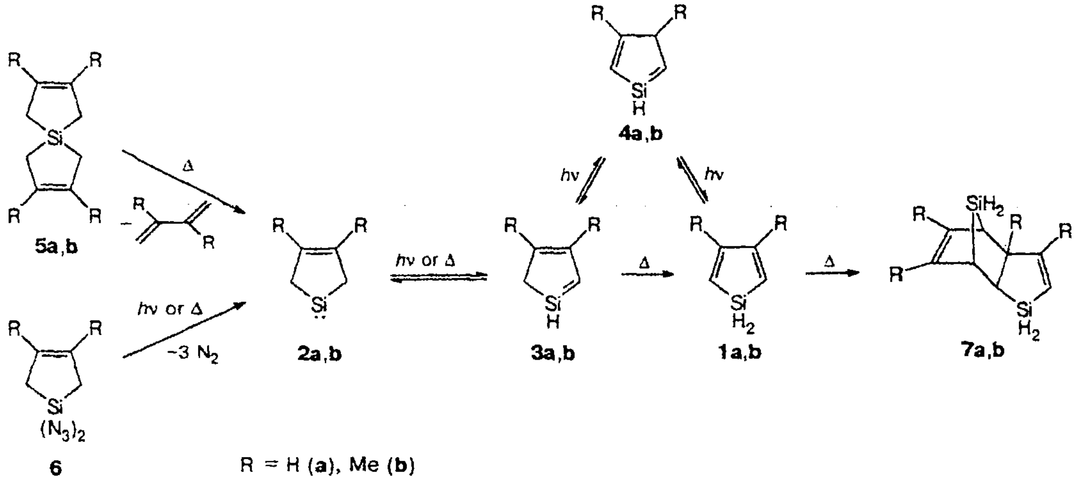
Generation and direct spectroscopic study of cyclic silylenes and isomeric silacyclopentadienes

The intermediate formation of 1-silacyclopenta-2,4-diene (silole) (**1a**) in the thermal isomerization of a cyclic silylene, 1-silacyclopent-3-ene-1,1-diyl (**2a**), has been assumed based on the detection of the stable [2+4]-dimer[20,21] and kinetic data.[22] The intermediate participation of other structural isomers of **2a**, 1-silacyclopenta-1,3-diene (**3a**) and 1-silacyclopenta-1,4-diene (**4a**), which are kinetically even more labile than silole **1a**, was also postulated for these processes. In view of these data, we chose spirononadienes **5a,b** as the precursors for generation of cyclic silylene **2a** and its 3,4-dimethyl derivative (**2b**).[23] 1,1-Diazido-1-silacyclopent-3-ene (**6**) was used as an alternative source for pyrolytic and photochemical generation of silylene **2a**.

The products of decomposition of compounds **5a,b** and **6** (Scheme 1) were studied[24—28] by low-temperature matrix spectroscopy using an optical cryostat with CsI external windows and a CsI substrate, which allowed recording of the IR and UV spectra for the same deposited matrix. Photolysis and the subsequent irradiation of the matrices have been performed using eximer and argon lasers and a mercury or xenon lamp.[24—28]

The matrix UV spectrum of the products of pyrolysis of spirononadiene (Fig. 1, *a*, curve *1*) exhibits only one band at 278 nm. The IR spectrum of the same matrix was found to contain a set of new bands (they are shown as positive peaks in Fig. 2, *b*); two of them occur in the range of the Si(sp^3)—H stretching vibrations. The same UV and IR bands were detected in the spectra of pyrolysis products frozen without argon at 12 K. After matrices have been warmed up to room temperature, the GC/MS analysis of the products showed the pres-

Scheme 1



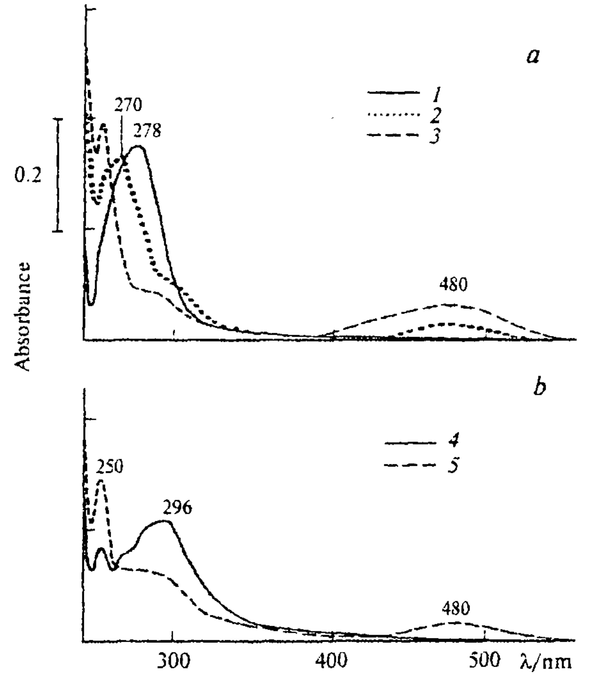


Fig. 1. UV spectra (Ar, 12 K) of the products of pyrolysis of **5a** before (*1*) and after (*2*—*5*) successive exposure to light with various wavelengths/nm: 308 (*2*) and 260—390 (*3*); 488 (*4*) and 308 (*5*).

ence of the [2+4]-dimer of silole **1a** (**7a**), in conformity with the data published previously.[20,21]

When the Ar matrix containing the products of pyrolysis of spirononadiene is exposed to light with a wavelength of 308 nm, the above-mentioned new UV and IR bands gradually and simultaneously disappear, indicating that they belong to the same single species. This species does not absorb in the visible region of the spectrum and does not exhibit bands for Si(sp^2)—H stretching vibrations in the 2200—2240 cm^{-1} region, as would be expected for siladienes.[29] Therefore, the new UV band at 278 nm was assigned to silole **1a**. The IR bands ascribed to this molecule are in good agreement with the vibrational spectrum of silole **1a** calculated by the Hartree—Fock method (Fig. 2, *d*). The same bands were observed in the spectrum of the products of pyrolysis or photolysis of another precursor of silole **1a**, 1,1-diazido-1-silacyclopent-3-ene (**6**) (Fig. 2, *c*).[26] Finally, the conclusion about the generation and detection of the silole **1a** was confirmed[30] by a study of vacuum pyrolysis of its precursor **5a**, 1-silaspiro-[4.4]nona-3,7-diene, by pyrolytic mass spectrometry. Determination of the ionization potential (IP), comparison with the calculated IP for isomeric silacyclopentadienes with *m/z* 82, and calculation of the heats of their formation have shown[30,31] that silole **1a** is formed as the thermodynamically most stable intermediate in the gas phase.

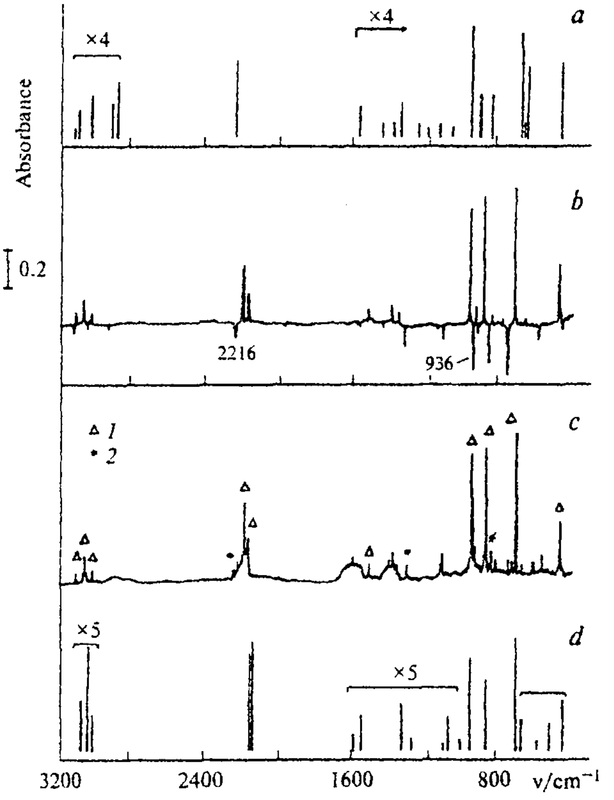


Fig. 2. IR spectra (Ar, 12 K): (*a*) the spectrum of **1a** calculated by the Hartree—Fock method; (*b*) the difference between the spectra of the products of pyrolysis of **5a** before (positive peaks) and after (negative peaks) exposure to light at 308 nm; (*c*) the spectra of the products of photolysis (248 nm) of diazide **6**: **4a** (*1*), **3a** (*2*); (*d*) the spectrum of **4a** calculated by the Hartree—Fock method.

It was found that on exposure to light with a wavelength of 308 nm, silole **1a** isomerizes *via* 1,3-H-shift to silacyclopenta-1,4-diene (**4a**), which absorbs at 270 nm in the UV region (Fig. 1, *a*, curve *2*) and is responsible for a set of IR bands, which are shown as negative peaks in Fig. 2, *b*. This spectrum has a single peak at 2216 cm^{-1}, in the region of "olefinic" Si(sp^2)—H stretching vibrations, which is consistent with the theoretical spectrum of siladiene **4a** (Fig. 2, *a*). Irradiation of **4a** by the light of a Hg lamp at 260—390 nm results in appearance of new bands in the UV and visible regions of the spectrum, at 250 and 480 nm (Fig. 1, *a*, curve *3*). The subsequent exposure to light with a wavelength of 254 or 488 nm induces a proportional decrease in the intensities of both the two UV/VIS peaks (Fig. 1, *b*) and the IR bands (Fig. 3). Based on these data, the product absorbing at 250 and 480 nm was identified as cyclic silylene **2a**. This assignment is consistent with the calculations of the electron transition energies[26] and the IR spectrum of this intermediate (Fig. 3, *a*). When the matrix is irradiated with light at a

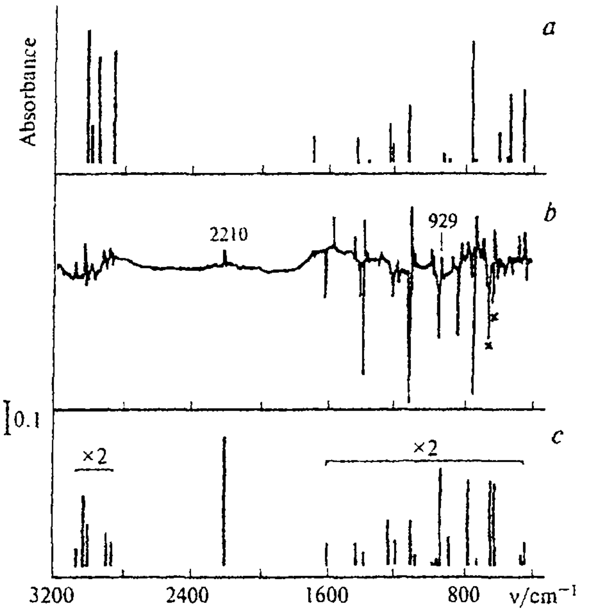


Fig. 3. IR spectra (Ar, 12 K): (*a*) the spectrum of **2a** calculated by the Hartree—Fock method; (*b*) the difference between the spectra of the matrix whose UV absorption is shown in Fig. 1, *a* (curve *3*) before (negative peaks) and after (positive peaks) exposure to light at 488 nm; (*c*) spectrum of **3a** calculated by the Hartree—Fock method.

wavelength of 254 or 488 nm, silylene **2a** isomerizes into silacyclopenta-1,3-diene (**3a**), which absorbs at 296 nm and undergoes reverse isomerization on irradiation with light at 308 nm to give silylene **2a** again (Fig. 1, *b*). The detected IR bands of siladiene **3a**, which are shown as positive peaks in Fig. 3, *b*, are in good agreement with the simulated spectra of this molecule in the visible, UV, and IR regions (Fig. 3, *c*).[26]

The matrix UV spectra of the products of pyrolysis or photolysis of 1,1-diazido-1-silacyclopent-3-ene (**6**) exhibit only a peak of silole **1a** at 278 nm; on further irradiation, this compound undergoes a series of similar photoselective transformations to give isomeric silacyclopentadienes **3a** and **4a** and silylene **2a**, thus confirming once again the identification of these compounds.

3,4-Dimethylsilole (**1b**) was generated by vacuum pyrolysis of tetramethyl-substituted silaspirononadiene **5b**, isolated in an argon matrix and characterized by UV and IR spectra. By analogy with unsubstituted silole **1a**, compound **1b** was converted into dimer **7b** by warming the matrix to room temperature, and isomerized into siladienes **3b** and **4b** and the corresponding silylene **2b** on exposure to light with the same wavelengths (see Scheme 1). The IR and UV absorption bands of these compounds shift regularly upon the dimethyl substitution in relation to the spectral bands of unsubstituted analogs[26,31].

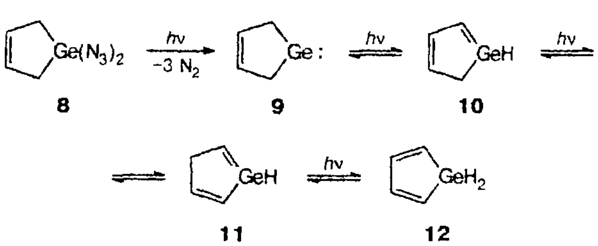
The bands at 480 nm in the spectra of silylenes **2a,b** were assigned to the n(Si)—p(Si) transitions in agreement with the calculations.[26] The observed bathochromic shift of these bands with respect to the absorptions of alkylsilylenes (for example, 454 nm for Me_2Si in the argon matrix)[10] and cyclic silylene, 1-silacyclopenta-1,1-diyl (436 nm in the matrix of 3-methylpentane)[32] is, apparently, due to interaction of the C=C bond with the silicon atom in the excited state, resulting in a lower energy of this transition. The calculations of excited states by the method of configurational interactions[26] indicate that this interaction is possible. The presence of the second UV absorption bands in the spectra of silylenes **2a,b** was explained by the substantial contribution of the n—π^* configuration to the mixed transitions at 250 and 255 nm.

The UV absorption bands occurring at 296, 312, 270, and 274 nm in the spectra of new isomeric siladienes **3a,b** and **4a,b** and assigned, based on the calculations, to π—π^* transitions[26,31] exhibit substantial bathochromic shifts relative to those observed for simple silenes, $H_2Si{=}CH_2$ (258 nm)[11,12] and $Me(H)Si{=}CH_2$ (260 nm).[8—12] The occurrence of these shifts was confirmed by the absorption at 312 nm observed recently[33] for 1,1-dimethyl-1-silabuta-1,3-diene, generated in the liquid phase by laser flash photolysis. The bathochromic shifts are indicative of a considerable π-conjugation in siladienes **3a,b** and **4a,b**, which also leads to a significant decrease in the Si=C stretching frequencies (929 cm^{-1} in **3a** and 936 cm^{-1} in **4a**; 917 cm^{-1} in **3b** and 933 cm^{-1} in **4b**) as compared with those for silenes: $Me_2Si{=}CH_2$ (1003.5 cm^{-1})[34—40] and $Me(H)Si{=}CH_2$ (989 cm^{-1}).[10] The presence of π-conjugation in the siladienes is confirmed by shortening of the central bonds, the C—C bond in the Si=C—C=C moiety of siladiene **3a**, and the Si—C bond in the C=Si—C=C moiety of siladiene **4a**, with respect to the calculated lengths of single C—C and Si—C bonds. Thus, the data of the electronic absorption spectra and infrared spectra and the quantum-chemical calculations provide convincing evidences for the substantial π-conjugation in the Si=C—C=C and C=Si—C=C moieties of siladienes **3a,b** and **4a,b**.

Photochemistry of matrix-isolated germacyclopentadienes and the first experimental evidence for germylene-to-germene isomerization

The successful generation of isomeric silylenes and silacyclopentadienes from 1,1-diazido-1-silacyclopent-3-ene has stimulated investigations[28,30,41—44] of the germanium analogs of these intermediates, which were obtained by decomposition of 1,1-diazido-1-germacyclopent-3-ene (**8**). Cyclic germylene **9** and the corresponding isomeric germacyclopentadienes **10—12** were generated (Scheme 2) by photolysis of matrix-isolated diazide **8**. Since, according to out results,[31,45] the 3,4-dimethyl derivative of germylene **9** is thermally much less stable than its silylene analog, the idea of using vacuum pyrolysis of diazide **8** for the generation of germanium intermediates **9**—**12** has been rejected.

Scheme 2



Conditions: Ar matrix, 12 K.

Photolysis of diazide **8** yielded a pale-yellow-colored matrix, whose electronic absorption spectrum showed a band at 248 nm, a broad band in the 260—320 nm range with a maximum near 272 nm, an absorption band for the NH molecule, and a weak absorption band in the visible region (Fig. 4, *a*). The band at 272 nm was assigned to germole (**12**), which is consistent with the data of comparison of the simulated vibrational spectrum of this intermediate (Fig. 5, *a*) with the observed set of IR bands (Fig. 5, *b*). Amid these bands, the strong band at 2096 cm^{-1} and the two weaker bands observed at wavenumbers higher than 2100 cm^{-1} are missing from the spectrum of the products of photolysis of deuterated diazide **8**-**d**$_6$. All these bands show large isotopic shifts to the 1450—1650 cm^{-1} region (Fig. 5, *b'*). This implies that no intermediate monoazide (or azidogermaimine) is present among the matrix photolysis products.

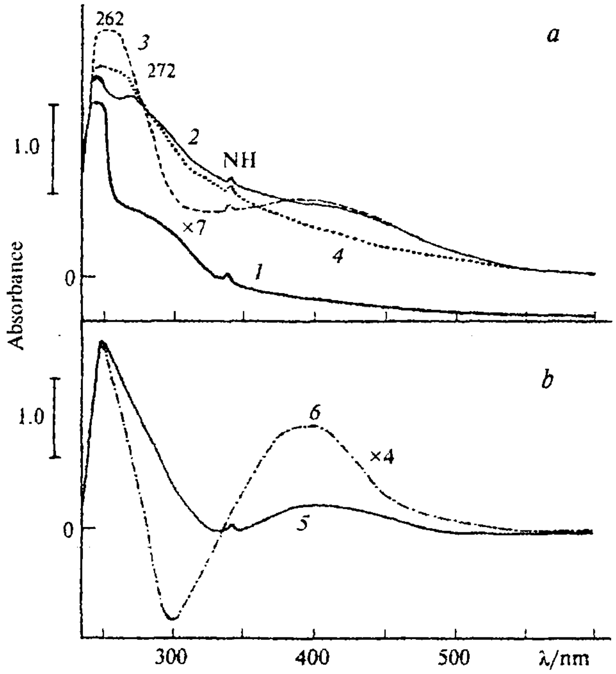


Fig. 4. UV spectra (Ar, 12 K) of the products of photolysis (248 nm) of **6** (*1*) and **8** (*2*—*5*) before (*2*) and after (*3*—*5*) successive exposure to light with different wavelengths/nm: 308 (*3*), 454 or 254 (*4*), and 308 (*5*); and the difference (*6*) between the spectra recorded before (negative peak) and after (positive peaks) irradiation.

The two other new UV/VIS bands (Fig. 5, *a*) disappeared simultaneously on exposure of the matrix to ultraviolet or visible light. The subsequent irradiation with light at a wavelength of 308 nm resulted in the appearance of a UV band at 262 nm and enhancement of the absorption in the visible region of the spectrum, indicating the formation of at least two new products. In the IR spectrum obtained by subtraction of the spectra recorded before and after the above-mentioned irradiation (Fig. 5, *c*), the negative peaks were assigned to germole (**12**). The positive peaks (one of them is an intense peak at 2127 cm^{-1}) should be assigned most reasonably to germacyclopenta-1,4-diene (**11**), which could be formed from germole (**12**), by analogy with photoisomerization of silole to silacyclopenta-1,4-diene on exposure to light with the same wavelength

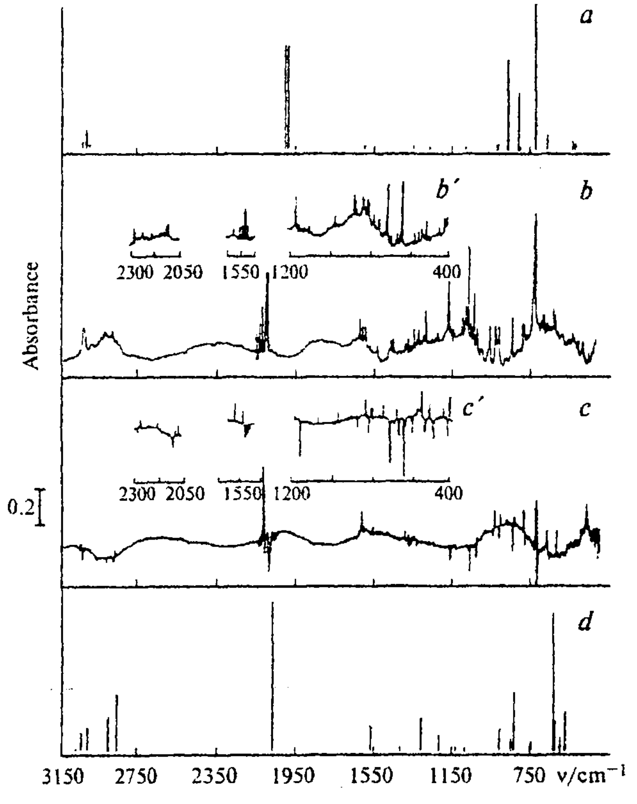


Fig. 5. IR spectra (Ar, 12 K): (*a*) spectrum of **12** calculated by the Hartree—Fock method; (*b*) spectrum of the products of photolysis of **8** (248 nm) and **8**-**d**$_6$ (*b'*), (*c*) differences between the spectra recorded before (positive peaks) and after (negative peaks) subsequent irradiation with light with a wavelength of 308 nm (*c'* is the same for the deuterated sample); (*d*) spectrum of **11** calculated by the Hartree—Fock method.

(308 nm).[24–26] This is consistent with the RHF simulated IR spectrum of germacyclopenta-1,4-diene (Fig. 5, *d*) and the isotopic band shifts observed in the spectrum of its deuterated analog **11-d$_6$** (Fig. 5, *c'*).

The second photoproduct, which absorbs in the visible region, was identified as cyclic germylene **9**. This intermediate disappears on irradiation with light with a wavelength of 454 or 254 nm to give a new product (Fig. 4, *a*, curve *4*). When this product is irradiated with light with a wavelength of 308 nm, the absorption in the visible region is restored (Fig. 4, *b*). Computer subtraction of both the UV and the IR spectra of these matrices makes it possible to distinguish the absorption spectra of individual compounds. As a result of this operation, both positive bands in the UV/VIS spectrum (Fig. 4, *b*, curve *6*) and the corresponding positive peaks in the IR spectrum (Fig. 6, *b*) were assigned to cyclic germylene **9** in accordance with its simulated spectrum (Fig. 6, *c*). The negative peak at 301 nm in the UV/VIS spectrum (Fig. 4, *b*) and the negative peaks in the corresponding IR spectrum (Fig. 6, *b*) were assigned to germacyclopenta-1,3-diene (**10**) based on the fact that their behavior resembles that of peaks for silacyclopenta-1,3-diene produced by similar isomerization of silylene to sila-1,3-diene[24–26] and also on the observation of the IR band of the Ge(sp^2)—H stretching vibration at 2115 cm^{-1} and its isotopic shift to 1536 cm^{-1} (Fig. 6, *b'*) in accord with the simulated spectra of germacyclopenta-1,3-diene (Fig. 6, *a*) and its d$_6$-analog.[28]

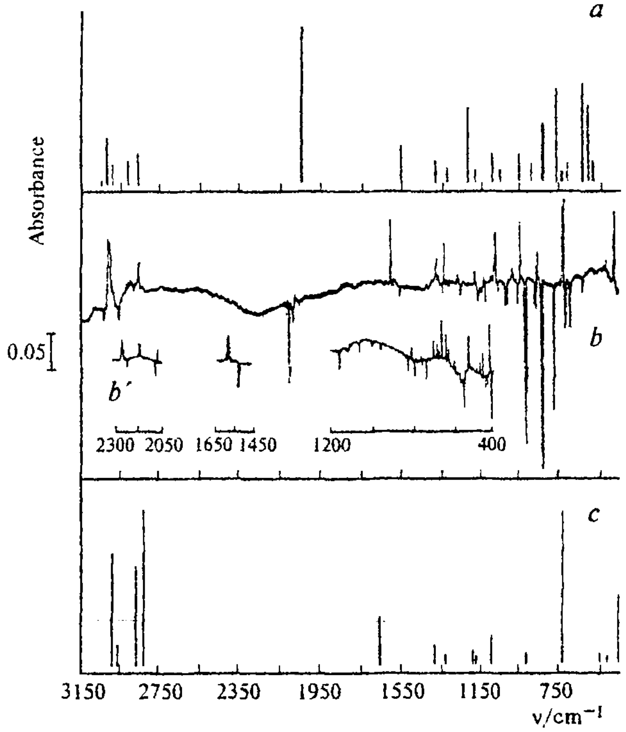


Fig. 6. IR spectra (Ar, 12 K): (*a*) spectrum of **10** calculated by the Hartree—Fock method; (*b*) differences between the spectra recorded before (positive peaks) and after (negative peaks) subsequent irradiation of the matrix, whose spectrum is presented in Fig. 5, *b*, with light with a wavelength of 454 or 254 nm (*b'* is the same for the deuterated sample); (*c*) spectrum of **9** calculated by the Hartree—Fock method.

The identification of the absorption bands in the spectra of the photolyzate of **8** is helpful for suggesting a mechanism for this reaction (see Scheme 2). Diazide **8** absorbs at 232 nm in the UV spectrum and, therefore, it decomposes on exposure to light at 248 or 254 nm. Since intermediates **9—12** also absorb this light to some extent, photolysis of **8** affords initially a mixture of these isomeric products. The product ratio changes under the action of the subsequent selective photoirradiation. According to our RHF/DZ+d calculations, among the four isomers **9—12**, germole (**12**) is thermodynamically the most stable. Germylene **9** is only 2 kcal mol^{-1} less stable than germole (**12**), whereas germadienes **10** and **11** are much less stable (by 25 and 27 kcal mol^{-1}, respectively) than **12**. This particularly means that the direct transformation of 1,3-germadiene (**10**) into germole (**12**) is substantially exothermic and can evidently occur in the ground state *via* a 1,5-H shift immediately after generation of **10** from germylene **9**. Germole (**12**) is also formed from germylene **9** *via* intermediate germadienes **10** and **11** by a 1,5-H shift followed by two photochemically allowed 1,3-H shifts.[28,31]

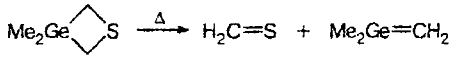
The reversible phototransformation of cyclic germylene **9** into 1-germacyclopenta-1,3-diene (**10**) observed in this study is the first example of germylene-to-germene isomerization studied. The possibility of this process is well substantiated by our DFT-B3LYP/6-311G(d,p) calculations,[42–44] which predict that the barrier for the 1,2-H shift in cyclic germylene **9** should be lower than that in methylgermylene by 18 kcal mol^{-1}, most likely due to an existing π conjugation in germadiene **10**.

Analysis of the optimized geometric parameters and of the experimental IR spectra along with the calculated harmonic vibration frequencies and potential energy distribution (PED) have led us to the conclusion that the effect of π-conjugation in germadienes **10** and **11** is weaker than that in siladienes **3a** and **4a**. This is demonstrated by a substantially smaller degree of contraction of the central Ge—C and C—C bonds in the C=C—Ge=C and C=C—C=Ge moieties, respectively, and by a somewhat lower Ge=C stretching frequency in **10** and **11** than in 1,1-dimethyl-1-germene $Me_2Ge=CH_2$ (**13**).[42–44,46] According to PED data, the Ge=C stretching vibrations both in **10** and in **11** are highly mixed; therefore, it is quite appropriate to compare[46] their frequencies with the frequency of this vibration in germene **13**, occurring at 847.3 cm^{-1} and being also mixed. This comparison shows a slight low-frequency shift of ν(Ge=C), which occurs at 834 cm^{-1} in **11** and at 838 cm^{-1} in **10** in good agreement with the isotope shifts of these bands to 686 cm^{-1} in **11-d$_6$** and to

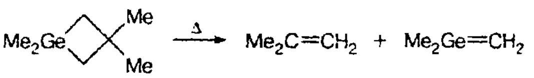
691 cm^{-1} in **10-d**$_6$, observed and predicted[28] by calculations, which are caused by even more pronounced mixing of vibrations in these cyclic molecules.

Spectroscopic evidence for the generation of germylenes in the thermal germene—germylene isomerization and dissociation of 1,1-dimethyl-1-germene

Unexpected transformations were discovered in our study[47] of the products of vacuum pyrolysis of precursors of short-lived 1,1-dimethyl-1-germene (**13**), namely, 1,1-dimethyl-1-germathietane (**14**) and 1,1,3,3-tetramethyl-1-germacyclobutane (**15**), by pyrolytic mass spectrometry and matrix IR spectroscopy. The formation of germene **13** upon [2+2]-decomposition of **14** and **15** was expected to occur according to the following Schemes[14]:



14 **16** **13**



15 **13**

The aim of the mass spectrometric study of the vacuum pyrolysis of 1,1-dimethyl-1-germa-3-thietane (**14**)* was to detect germene **13** directly in the gas phase and optimize the conditions of its generation for subsequent study by matrix Fourier IR spectroscopy. As the temperature increased, the peak of the molecular ion of thioformaldehyde $H_2C=S$ (**16**) (*m/z* 46) in the mass spectra (ionization energy 70 eV) of the pyrolysis products of germathietane **14** (at 100—1100 °C) became more intense with respect to the molecular ion peak of **14** (*m/z* 160); the element composition of these species was determined by precision mass measurements. In addition to these peaks, the peak with *m/z* 114, corresponding to the weight of the molecular ion of germene **13**, whose formation was expected according to the stoichiometry of the [2+2] thermal decomposition of **14**, was also found to increase. The intensity of this peak increases with temperature rise out of proportion to that of the peak for **16** (*m/z* 46), apparently, due to secondary thermal isomerization and dissociation of germene **13** under the conditions studied. This hypothesis is supported by the parallel increase in the intensities of lighter ion peaks with *m/z* 86, 85, 71, 70, 28 (C_2H_4), and 15 (CH_3). The peaks of ions with *m/z* 132 and 102, pointing to the formation of dimethylgermathione $Me_2Ge=S$ and germanium sulfide GeS, were also found to increase; these by-products may have resulted from a parallel unimolecular channel of decomposition of **14** under the conditions of vacuum pyrolysis.

Structures for the germanium-containing products were proposed based on the molecular formulas established by measurements of the exact masses of ions and the observation of the natural Ge-isotopic splitting of peaks in the mass spectrum. The molecular formula determined for the ions with *m/z* 114 is $C_3H_8{}^{70}Ge$, which exactly corresponds to the elemental composition of the molecular ion of germene **13**. Based on the same measurements, the ions with *m/z* 85 were assigned to $[M - H]^+$ fragment ions derived from the ^{70}Ge-isotopomer of methylgermylene MeGeH (**17**), which produces a molecular ion peak with *m/z* 86, and heavier isotopomers with *m/z* 88, 90, 92.

Experiments on matrix IR spectroscopy of the products of pyrolysis of both germathietane **14** and germacyclobutane **15** were carried out in a cryogenic setup, in which 40 to 50 mirror-polished surfaces of a rhodium-coated copper polyhedron were accessible for matrix deposition.[48] The deposition onto each surface was carried out consecutively. The IR spectra were recorded[31,47] after twofold transmission of the beam through the layer of the deposited matrix, according to the optical reflection scheme.

As the temperature in the reaction area gradually increased from 500 to 600—650 °C, in addition to bands due to thioformaldehyde (**16**), new bands *A* and *B* were observed and proportionally intensified in the matrix IR spectrum of the products of vacuum pyrolysis of germathietane **14** (Fig. 7, *c*). However, with further increase in the pyrolysis temperature, the intensities of bands *B* and the ethylene bands have sharply grown with respect to bands *A*, which have simultaneously weakened (Fig. 7, *d*). This indicated the presence of two new products, characterized by the corresponding sets of bands *A* and *B*. The same sets of bands were also observed[31,47] in the matrix IR spectra of the pyrolysis products of another germene precursor, tetramethylgermacyclobutane **15**. Based on these findings, the *A* bands were attributed to 1,1-dimethyl-1-germene (**13**). This assignment is in good agreement with the calculated frequencies and intensities of bands in the IR spectrum of this germene (Fig. 7, *a*). It is most likely that bands *B* belong to methylgermylene (**17**). This assignment is consistent with the spectrum of **17** calculated by the B3LYP method (Fig. 7, *b*) and also by Hartree—Fock and MP2 methods.[31,42—44,47]

Methylgermylene **17** can be formed upon thermal decomposition of germene **13** in accordance with the mechanism shown in Scheme 3.

No similar fragmentation pathway was found[34,39] in the case of 1,1-dimethyl-1-silene (**18**). In order to explain this difference, the relative thermodynamic stabilities of

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* The studies were carried out jointly with J. Tamash *et al.* within the framework of the Program for Cooperation with the Central Chemical Research Institute of the Hungarian Academy of Sciences.

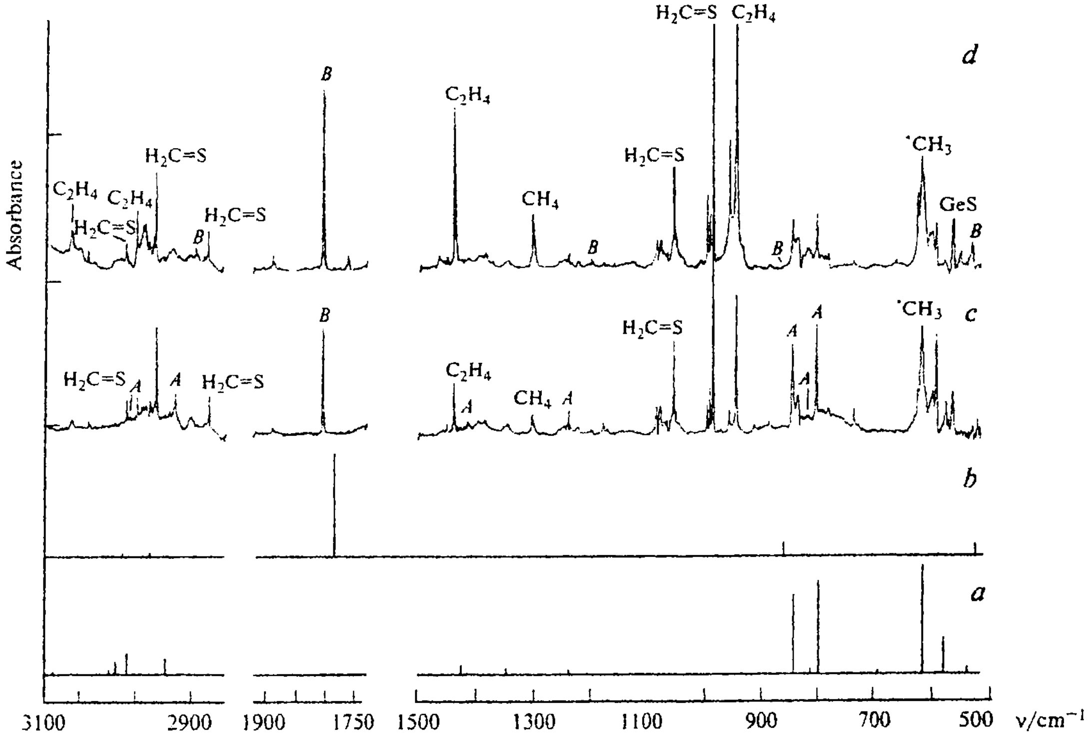
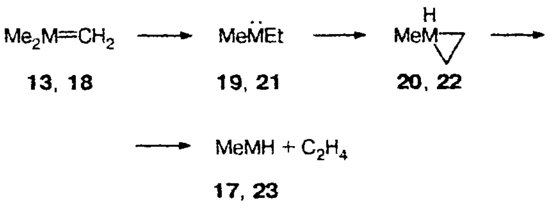


Fig. 7. IR spectra (Ar, 12 K): (*a*) spectrum of **17** calculated by the B3LYP/6-311G(d,p) method; (*b*) spectrum of **13** calculated by the B3LYP/6-311G(d,p) method; (*c*) spectrum of the products of pyrolysis (10^{-4} Torr, 600 °C) of compound **14** after subtraction of the spectrum of **14**; (*d*) spectrum of the products of pyrolysis (10^{-4} Torr, 900 °C) of **14** after subtraction of the spectrum of **14**. The following bands are marked: (*A*) germene (**13**); (*B*) germylene (**17**).

Scheme 3



M = Ge (**13**, **17**, **19**, **20**), Si (**18**, **21**, **22**, **23**)

the germene isomers, methylethylgermylene (**19**) and 1-methyl-1-germirane (**20**), the analogous silene isomers, methylethylsilylene (**21**) and 1-methyl-1-silirane (**22**), and the products of their thermal dissociation (see Scheme 3) were estimated by quantum-chemical MP2 calculations. According to these calculations, the stabilities of 1,1-dimethyl-1-germene and its structural isomers **19** and **20** are rather close, whereas the energy of methylethylsilylene **21** is 14 kcal mol^{-1} higher than that of isomeric silene **18**. The first step of the process shown in Scheme 3, isomerization of 1,1-dimethyl-1-germene into methylethylgermylene, requires overcoming a barrier of 48.7 kcal mol^{-1}; for a similar isomerization of 1,1-dimethyl-1-silene, a higher barrier (56.8 kcal mol^{-1}) was predicted.

Direct experimental evidence for the occurrence of germene-to-germylene thermal isomerization under the conditions of vacuum pyrolysis of precursors **14** and **15** was obtained by observation of the IR bands of methylethylgermylene **19** (528.0, 554.8, and 783.6 cm^{-1}). These bands were recorded in the matrix spectra of the products of pyrolysis of germathietane **14** at temperatures above 800 °C. The fact that the observed bands correspond to the calculated most intense bands in the IR spectrum of germylene **19** in the 500—1000 cm^{-1} range served as the basis for both the identification of **19** and the assignment of vibration frequencies (Table 1). The bands at 528.0 and 554.8 cm^{-1} were assigned to the Ge—C stretching vibrations of the Ge—CH_2 and Ge—Me groups, respectively, whereas the band at 783.6 cm^{-1} was attributed to the rocking vibration of the Me group in **19**. Detection of IR bands in the 2800—2950 cm^{-1} region, which are expected to be rather intense according to calculations, is hampered due to their overlap with more intense peaks corresponding to another pyrolysis product **14**.

According to our B3LYP/6-311G(d,p) calculations, the molecule of germylene **19** is asymmetric (Fig. 8). The dihedral angle θ between the CCGe and CGeC planes is 7.3°. The calculated Ge—C bond lengths in germylene **19**, 2.016 and 2.023 Å, are close to the Ge—C bond length in methylgermylene,[47] and the

Table 1. Calculated (B3LYP/6-311G(d,p)) and experimental vibration frequencies (ν) of methylethylgermylene (**19**) and their assignment

ν/cm^{-1}		Assignment
Calculation	Experiment	
58 (0)[a]		CCGe twisting
80 (0)		Me(Ge) twisting
152 (1)		CGeCC synphase rocking
190 (1)		Me(CH$_2$) twisting
279 (1)		CGeCC antiphase rocking
496 (25)	528.0	Ge—CH$_2$ stretching
521 (28)	554.8	Ge—Me stretching
525 (18)		CH$_2$ rocking
607 (9)		Me rocking
771 (22)	783.6	Me rocking
915 (7)		Me(CH$_2$) rocking
967 (0)		CH$_2$ wagging, Me rocking
1035 (4)		C—C stretching
1219 (2)		CH$_2$ wagging, Me rocking
1243 (13)		CH$_2$ twisting, Me rocking
1249 (1)		Me(Ge) deformation
1417 (5)		CH$_2$ scissoring, Me scissoring
1432 (3)		Me scissoring
1441 (7)		CH$_2$ scissoring, Me scissoring
1460 (11)		Me scissoring
1498 (4)		Me(CH$_2$) scissoring
1508 (8)		Me(CH$_2$) scissoring
2977 (24)		CH$_2$ symmetrical stretching
2992 (10)		Me(Ge) symmetrical stretching
3013 (54)		Me(CH$_2$) symmetrical stretching
3018 (17)		CH$_2$ antisymmetrical stretching
3065 (34)		Me(Ge) antisymmetrical stretching
3067 (20)		Me(CH$_2$) antisymmetrical stretching
3076 (49)		Me(CH$_2$) antisymmetrical stretching
3113 (14)		Me(Ge) antisymmetrical stretching

[a] The intensity is given in parentheses (km mol^{-1}).

C—Ge—C angle (95.9°) is somewhat greater than that in methylgermylene and somewhat smaller than that in dimethylgermylene.[49]

The second step (see Scheme 3) includes intramolecular insertion of the germylene center into a terminal C—H bond of the ethyl substituent of germylene **19** to give 1-methyl-1-germirane (**20**), whose subsequent dissociation, giving methylgermylene (**17**) and ethylene, is endothermic (25.5 kcal mol^{-1}); for comparison, dissociation of silicon analog **21** is even more endothermic (48.3 kcal mol^{-1}). This means that decomposition of **20** is likely to proceed more readily. Our calculations are quite consistent with the experimental data[50—52] obtained for the simplest silirane stable under ambient conditions, hexamethylsilirane, which decomposes with extrusion of dimethylsilylene even at 65—75 °C.

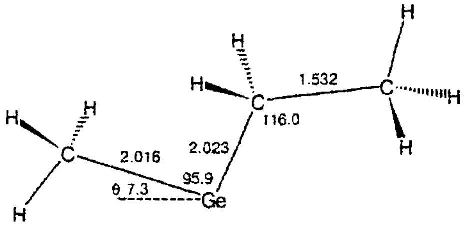


Fig. 8. Geometry of methylethylgermylene **19** optimized by the B3LYP/6-311G(d,p) method. The bond lengths (Å) and angles (deg) are presented.

Direct dissociations of germene and silene into the corresponding singlet dimethylgermylene (**24**) and dimethylsilylene (**25**), and also methylene (Scheme 4), are highly endothermic processes. The calculated thermal effects of these reactions reflect in each case the overall strengths of the s and π components of the Ge=C and Si=C unsaturated bonds, estimated to be 106.6 and 124.2 kcal mol^{-1}, respectively.

Scheme 4

$$\underset{\mathbf{13,\ 18}}{Me_2M{=}CH_2} \longrightarrow \underset{\mathbf{24,\ 25}}{Me_2M(^1A')} + CH_2(^1A')$$

M = Ge (**13**, **24**), Si (**18**, **25**)

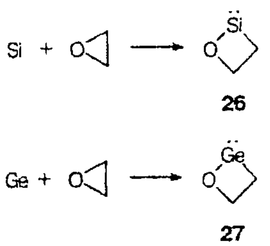
Thus, according to calculations, the proposed isomerization—dissociation mechanism requires altogether less energy in the case of germene **13** than in the case of silene **18** and is thermodynamically more favorable than direct dissociation of these metallaalkenes. This is consistent with the experimental observation of methylgermylene in the thermal decomposition of 1,1-dimethyl-1-germene and no detection of methylsilylene upon pyrolytic generation of 1,1-dimethyl-1-silene at elevated temperatures.

Spectroscopic and theoretical study of photoisomerization of methoxy-substituted silylenes and germylenes as a new method for generation of methylsilanones and germanones

The results obtained recently in low-temperature studies of reactions of atomic silicon or germanium with small and strained organic molecules are briefly surveyed below. It was shown previously[53—55] that the cocondensation reactions of silicon and germanium atoms with simple inorganic molecules (H_2O, HF, H_2) in Ar matrices at 15 K proceed either spontaneously or upon photoinitiation.

In our experiments, in the matrix IR spectra of low-temperature (12—15 K, argon) co-condensates of atomic Si and Ge with ethylene oxide, new bands characterizing the products of insertion into the C—O bond of this strained ring were observed (Scheme 5). These bands were assigned to the endocyclic Si—O (809 cm^{-1}), Si—C (690 cm^{-1}), and Ge—O (658 cm^{-1}) stretching vibrations by comparison with the calculated[56] spectra of new products **26** and **27**.

Scheme 5



Conditions: Ar, 12—15 K.

Scheme 6

$$\mathrm{Si + MeOMe \longrightarrow \underset{\mathbf{28}}{Si...OMe_2} \xrightarrow{h\nu} \underset{\mathbf{29}}{Me_2Si{=}O} + \underset{\mathbf{30}}{MeO\ddot{S}iMe}}$$

Conditions: Ar, 12—15 K.

In the IR spectrum of the argon matrix-isolated co-condensate of an atomic beam of thermally evaporated silicon with dimethyl ether, a set of new bands was also found. The intensities of these new bands repeated those of the matrix-isolated Me_2O; however, they were all respectively shifted to lower frequencies (Fig. 9, *a*). This observation and the data of calculations[57] strongly suggest the formation of a complex of the $Si...OMe_2$ type in a matrix (Scheme 6).

The subsequent irradiation of this matrix with unfiltered light from a mercury lamp results in the complete disappearance of the peaks assigned to complex **28**. They are replaced by several new bands (Fig. 9, *b*), which coincided with the most intense IR bands of dimethylsilanone (**29**)[58—60] (Fig. 9, *c*). In addition to these bands, the spectrum of the photolyzate (Fig. 9, *b*) exhibited a number of weaker peaks, which matched the known IR bands[13] of methyl(methoxy)silylene (**30**) recorded after thermal generation of this intermediate and its subsequent isolation in the matrix. When photoirradiation was applied simultaneously with co-condensation of atomic silicon with dimethyl ether into an argon matrix, the IR spectrum exhibited only the bands of dimethylsilanone (**29**), which is the most photostable reaction product formed under these conditions.

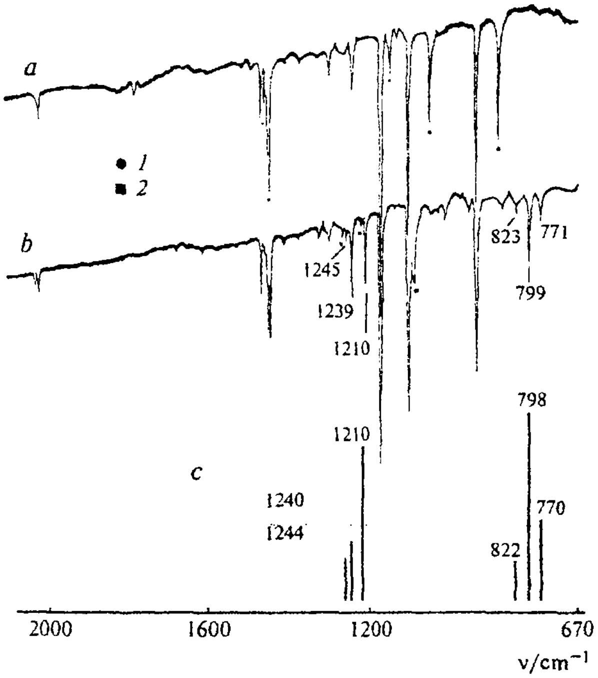


Fig. 9. IR spectra of the co-condensate of atomic Si with MeOMe and Ar at 12 K (*a*); the same matrix after irradiation with light with $\lambda > 200$ nm (*b*); silanone $Me_2Si{=}O$ (*c*).[58—60] The following bands are marked: (*1*) the $Si...OMe_2$ complex; (*2*) silylene MeOSiMe.

The DFT B3LYP/6-311G(d,p) calculation of the energies of the ground and transition states for this reaction predict that the formation of complex **28** in the first reaction step is exothermic by 21.2 kcal mol^{-1}. The next step, namely, insertion of a Si atom into the C—O bond to yield methyl(methoxy)silylene (**30**), is even more exothermic (114.1 kcal mol^{-1}); however, for this step to occur, a barrier of 20.8 kcal mol^{-1} should be overcome (Fig. 10, *a*). This is consistent with the observation of only complex **28** in the experiments carried out without photoexcitation. According to calculations, the energy of dimethylsilanone **29** is 20.7 kcal mol^{-1} lower than that of the isomeric methylmethoxysilylene **30**, which is separated from silanone **29** by a barrier of 54.3 kcal mol^{-1}. These data explain quite well the formation of silanone **29** as the major product after photoirradiation of the low-temperature co-condensate with the full light ($\lambda > 200$ nm) of a mercury lamp.

Our calculations predict that a similar reaction of atomic germanium with dimethyl ether should pass through a higher barrier both for the insertion of Ge into the C—O bond (25.0 kcal mol^{-1}) and for the subsequent isomerization of methyl(methoxy)germylene into dimethylgermanone (66.7 kcal mol^{-1}) (Fig. 10, *b*). The latter, unlike the silicon analog, is predicted to lie 6.2 kcal mol^{-1} higher in energy than the isomeric germylene. Thus, in the case of germanium, the reaction is expected to proceed with somewhat greater difficulty, and in this case, photoinitiation with the full light of a mercury lamp is likely to produce a mixture of methyl(methoxy)germylene and dimethylgermanone with predominance of the former intermediate.

The low-temperature co-condensation of atomic Si with MeOH even in the absence of photoinitiation resulted in recording of a matrix IR spectrum (argon, 12 K) containing strong bands of methoxysilylene (**31**),

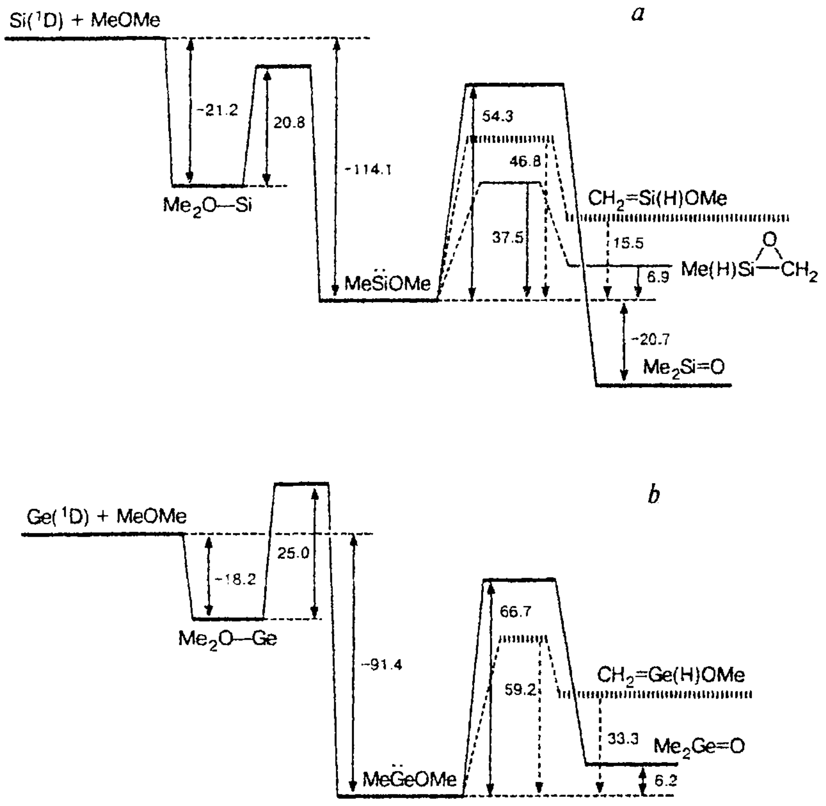
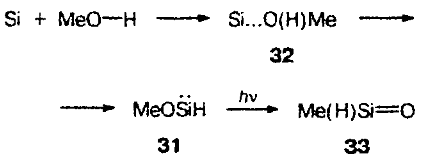


Fig. 10. Energy profiles for the reactions: (*a*) Si (¹D) + MeOMe, (*b*) Ge (¹D) + MeOMe.

which is the product of insertion of silicon into the O—H bond of methanol (Scheme 7). The bands at 749, 859, 1086, and 1925 cm^{-1} were assigned to silylene **31** by comparison with the calculated IR spectrum of this molecule.[57] In this case, the Si...O(H)Me complex (**32**) is converted almost entirely into silylene **31**. These data imply that this reaction proceeds spontaneously and that insertion of the Si atom into the O—H bond is preferred over inserion into the C—O bond.

Scheme 7



$$\mathrm{Si} + \mathrm{MeO{-}H} \longrightarrow \underset{\mathbf{32}}{\mathrm{Si...O(H)Me}} \longrightarrow \underset{\mathbf{31}}{\mathrm{MeO\ddot{S}iH}} \xrightarrow{h\nu} \underset{\mathbf{33}}{\mathrm{Me(H)Si{=}O}}$$

The subsequent exposure of the matrix to the full light ($\lambda > 200$ nm) of a mercury lamp causes complete disappearance of the bands of silylene **31** and appearance of a series of new peaks. The most intense peaks (at 756, 929, 1208, and 1244 cm^{-1}) were assigned to methylsilanone Me(H)Si=O (**33**) based on comparison with published data[61] and simulation of the vibrational spectrum of **33**.[57] This interpretation is consistent with the DFT calculations of the energies of the elementary steps and transition states of this reaction (see Scheme 7) and those for the similar reaction of atomic Ge. The calculations predict low barriers to the insertion into the O—H bond (5.6 kcal mol^{-1} for Si and 8.3 kcal mol^{-1} for Ge) and much higher barriers to the insertion into the C—O bond (26.1 kcal mol^{-1} for Si and 28.8 kcal mol^{-1} for Ge). According to the same calculations, isomerization of methoxysilylene into methylsilanone is an exothermic process (21 kcal mol^{-1}) occurring *via* a barrier of 54.3 kcal mol^{-1}, whereas the analogous isomerization of methoxygermylene MeOGeH into methylgermanone Me(H)Ge=O is, conversely, endothermic (6.4 kcal mol^{-1}) and requires overcoming of a higher barrier (66.6 kcal mol^{-1}).[57] The calculation data apparently envision the necessity of using more rigorous experimental conditions in the case of generation of methylgermanone by isomerization of methoxygermylene.

Thus, the experimental and theoretical results obtained in the studies of the the reactions of atomic silicon and germanium with dimethyl ether and methyl alcohol suggest that these reactions can be considered as a new method for the generation of silanones, germanones, and, probably, for other metallanones of Group 14 elements. The use of this method for the generation of other heteroatom-containing short-lived molecules of the R$_2$M=X type, where M = Si, Ge, Sn, or Pb, and heteroatom X is N, P, S, or Se, also appears quite possible.

Conclusion

During our physicochemical studies of carbene-to-olefin isomerization of Group 14 carbene analogs, generated both in the gas phase and in solid inert matrices at liquid helium temperatures, new short-lived organoelement molecules with Si=C, Ge=C, and Si=O unsaturated bonds and their structural isomers, the corresponding silylenes and germylenes, were stabilized and studied by spectroscopy for the first time. Stabilization of the silole is especially important since the earlier attempts[62,63] to synthesize this reactive compound have failed. The silole molecule is the simplest model of the monomeric unit in polysiloles, which have been extensively studied[64–67] in recent years due to their unique electrooptical properties.

1-Silacyclopenta-1,3- and -1,4-dienes and their germanium analogs, generated by silylene-to-silene and germylene-to-germene isomerization, respectively, and stabilized and characterized by direct spectroscopic methods, are the first simple representatives of metalladienes containing nonaromatic π-conjugated systems of the M=C—C=C and C=M—C=C types (M = Si or Ge). Prior to our studies, the information on metalladienes had been limited to the results of calculations[68,69] and indirect chemical data.[14,29,70]

The first direct experimental observations of photoreversible germylene-to-germene isomerization, made for cyclic germylene, 1-germacyclopent-3-ene-1,1-diyl, and of thermal germene-to-germylene isomerization of 1,1-dimethyl-1-germene were adequately interpreted using the data of quantum-chemical calculations, predicting that the relative thermodynamic and kinetic stabilities of the structural isomers should be substantially affected by electronic factors. This combination of theoretical and experimental approaches based on the enhanced reliability of modern quantum-chemical calculations and the use of refined spectroscopic methods is now being considered as a promising strategy for accomplishing the following fundamentally important task: stabilization and direct spectroscopic observation of molecules with the triple Si$\equiv$C and Ge$\equiv$C bonds (sila- and germaalkynes).

According to calculations,[71] the main obstacles preventing the stabilization of the simplest silaalkyne HSi$\equiv$CH are (i) the exceptionally low barrier separating the silaalkyne from the carbene $H_2Si=C$: (2.7 kcal mol^{-1}) and the silylene $H_2C=Si$: (5.0 kcal mol^{-1}) and (ii) the much higher (by 39.2 kcal mol^{-1}) thermodynamic stability of the silylene isomer with respect to the silaalkyne. A similar situation has been predicted for the germanium analogs. Therefore, only the carbene type isomers, $H_2C=Si$: and $H_2C=Ge$:, have been detected so far by spectroscopy.[72–74] Meanwhile, calculations predict that the substituents R (F, Cl, and OH) at the silicon atom would increase the barrier separating the RSi$\equiv$CH and R(H)C=Si: isomers to 17—25 kcal mol^{-1} and substantially increase the thermodynamic stability of silaalkyl structures,[75] thus enhancing the probability of *direct* detection of these species by spectroscopy. As applied to this goal, low-temperature matrix isolation spectroscopy appears to be the most promising and informative technique among the other instrumental methods, in particular, tandem mass spectrometry, used recently.[75]

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