

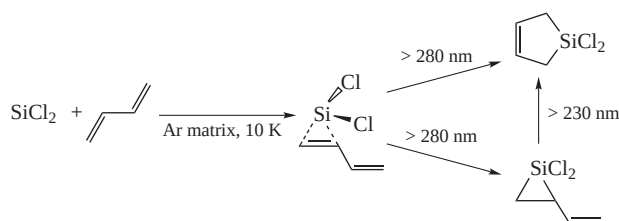
Formation of 1,1-dichloro-2-vinyl-1-silacyclopropane by a photoinduced reaction between dichlorosilylene and 1,3-butadiene

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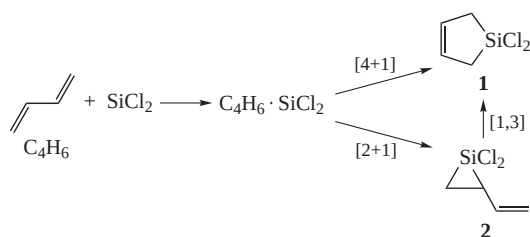
A matrix FTIR study of interaction between SiCl_2 and 1,3-butadiene revealed that at low temperatures, it stops at the step of complexation between the reactants. This allowed us to investigate a photochemical version of this interaction resulting in the formation of both 1,1-dichloro-1-silacyclopent-3-ene and 1,1-dichloro-2-vinylsilirane in contrast to the thermal reaction giving only the first of these products.



Silylenes are an important class of silicon compounds including both labile¹ and stable² species. Due to the inherent high reactivity of any silylene, their chemistry has been basically developed as the chemistry of thermal reactions. Reactions of stable 2,2,5,5-tetrakis(trimethylsilyl)-1-silacyclopent-1-ylidene with a series of aromatic compounds^{3–5} and alkenes⁴ initiated by an irradiation are the only known example of photoinduced intermolecular reactions observed for such compounds under conventional conditions.

Generally, thermal reactions of labile silylenes with different substrates proceed in two steps via an initial formation of usually weak complexes and their subsequent rearrangement into the final products.^{6,7} Carrying out the reaction in a low-temperature inert matrix allows one to stop it at the first step. The second step can then be activated by irradiation, which makes it possible to study the photochemical version of the same reaction. Photoinduced transformations resulting in the products of corresponding thermal reactions were observed earlier for a number of complexes stabilized in matrices, e.g., $\text{H}_2\text{O} \cdot \text{SiH}(\text{OH})$,⁸ $\text{R}_2\text{C}=\text{X} \cdot \text{SiMe}_2$ ($\text{R}_2\text{C}=\text{X}$ is 1,1,3,3-tetramethyl-2-indanone or analogous tetramethylindanethione),⁹ $\text{Pr}_2\text{C}=\text{O} \cdot \text{SiR}_2$ ($\text{R} = \text{Me}, \text{Mes}$),⁹ $\text{O}_2 \cdot \text{SiF}_2$,¹⁰ $\text{H}_3\text{P} \cdot \text{SiMePh}$,¹¹ $\text{MeHal} \cdot \text{SiMeHal}$ ($\text{Hal} = \text{F}, \text{Cl}, \text{Br}, \text{I}$),¹² $\text{Me}_2\text{O} \cdot \text{SiMe}(\text{OMe})$,¹³ and $\text{AlHal} \cdot \text{SiCl}_2$ ($\text{Hal} = \text{Cl}, \text{Br}$).¹⁴

One of the most important thermal reactions of silylenes is the reaction with conjugated dienes, which leads to silacyclopent-3-enes either by direct [4+1] cycloaddition or by [2+1] cycloaddition with the following [1,3]-sigmatropic rearrangement of the formed vinylsiliranes.^{1,15–19}



Scheme 1

In particular, labile SiCl_2 readily reacts with 1,3-butadiene (hereinafter, C_4H_6) at 200–500 °C, producing 1,1-dichloro-1-silacyclopent-3-ene (1,1-dichloro-2,5-dihydro-1H-silole, **1**) in high yields of up to 90% (Scheme 1).^{20,21} The G3(MP2)//B3LYP calculations suggested¹⁸ that this reaction starts with formation of a complex, wherein SiCl_2 acting as a Lewis acid is coordinated to the double bond of C_4H_6 (see Scheme 1). This complex is represented by a number of conformers stabilized relative to the starting compounds by 5 kcal mol^{–1} at most. The subsequent [4+1] cycloaddition leading to product **1** is kinetically and, especially, thermodynamically more favorable than the [2+1] cycloaddition resulting in 1,1-dichloro-2-vinylsilirane **2** ($\Delta G^\ddagger = 12$ and 16 kcal mol^{–1} and $\Delta G_{298}^\circ = -45$ and -5 kcal mol^{–1}, respectively). Thus, formation of product **2** upon thermal interaction between SiCl_2 and C_4H_6 could be expected only in the minor amounts at best. This instance illustrates why the examples of direct spectroscopic (UV^{22,23} or NMR^{15,22,24–28}) detection of vinylsiliranes and, especially, their isolation^{29,30} are rare. Here, we report on the formation of compound **2** in Ar matrices by photoinduced transformation of a primarily formed complex between SiCl_2 and C_4H_6 and its detection using FTIR spectroscopy.

The experimental setup used in the present study has been previously described¹⁴ in details.† Deposition of matrices led to the formation of mixture of the conformers of complex between SiCl_2 and C_4H_6 , which manifested themselves by groups of IR bands lying in the vicinity of SiCl_2 and some C_4H_6 bands [Figure 1(a);

† Matrices were produced via the co-deposition of $\text{C}_4\text{H}_6/\text{Ar}$ mixtures (1:100–800) and Si_2Cl_6 pyrolysis products (SiCl_2 and SiCl_4 ,³¹ $T_{\text{pyr}} \approx 900$ °C, the resulting $\text{SiCl}_2:\text{Ar}$ ratio was 1:400–1000) on a mirror copper plate cooled to ~10 K. In some experiments, compound **1** was used as a thermal precursor of SiCl_2 . Its decomposition (~70%) occurred at ~1000 °C with the formation of SiCl_2 , C_4H_6 , and little amounts of SiHCl_3 and C_4H_6 decomposition products such as acetylene, ethylene, etc. A DRSh-500 high pressure Hg arc lamp (500 W) equipped with a water and suitable cut-off filters was used to irradiate the matrices. IR spectra were recorded using a Bruker IFS 113v FTIR spectrometer in the range of 4000–400 cm^{–1} with a resolution of 0.5 cm^{–1}.

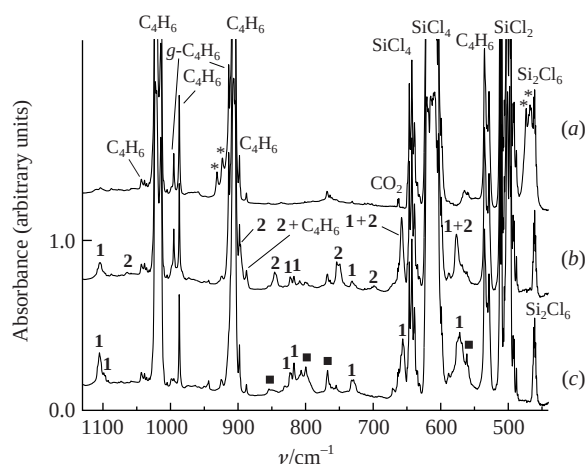


Figure 1 Fragments of IR spectra of a matrix with $\text{SiCl}_2:\text{C}_4\text{H}_6:\text{Ar} = 2:7:1000$ (a) after deposition, (b) after photolysis with $\lambda > 280$ nm for 15 min, and (c) after subsequent photolysis with unfiltered light for 30 min. Bands of the complex, **1** and **2** are marked with asterisks and numbers, respectively, while the intense unassigned bands are labeled with black squares.

Figure S1 and Table S4 in Online Supplementary Materials]. Intensities of these bands increased with the increase in either SiCl_2 or C_4H_6 concentrations. None of these bands was observed upon the co-deposition of $\text{C}_4\text{H}_6/\text{Ar}$ mixtures with SiCl_4 , which is the only species present in large concentrations in matrices in addition to SiCl_2 and C_4H_6 when Si_2Cl_6 was used as a SiCl_2 precursor. Observation of these new bands at dilutions of reactants by Ar as high as 1:500 implies that their carriers have the simplest 1:1 composition. The annealing of matrices at 35–42 K for several minutes resulted in a considerable enhancement of some of these new bands, indicating that they belong to the products formed without any significant activation barrier. Other new bands almost disappeared upon annealing, but reappeared upon irradiation with light of $\lambda > 450$ or 510 nm for 15 min, which led to the strong decrease of bands growing upon annealing. This cycle of interconversions of conformers by successive annealing and photolysis can be repeated several times until the partial loss of complex due to its transformations into the photoproducts upon photolysis and deterioration of matrices by annealing made further cycling inappropriate. Photolysis with light of shorter wavelengths also resulted in the transformation of conformers formed upon annealing into those generated upon photolysis at $\lambda > 450$ nm, but it was accompanied by the rearrangement of complex into the photoproducts. The shorter the wavelengths were applied, the stronger the rearrangement occurred. According to the integral intensities of bands, the mixture of conformers formed upon deposition of matrices contained conformers whose concentration was increased by annealing and conformers whose content was increased by photolysis in a ratio of $\sim 2:1$.

A number of conformers of the complex of SiCl_2 with C_4H_6 were revealed at the M06-2X/6-311++G(d,p)^{32–34} and G3(MP2)//B3LYP³⁵ levels of theory (implemented in the Gaussian 09 software package³⁶). They differ by the orientation of SiCl_2 moiety over a double bond and by the conformation of C_4H_6 moiety, with conformers containing *gauche*- C_4H_6 being less stable by several kcal mol^{-1} than those containing *trans*- C_2H_6 (Figure S2 and Table S1, Online Supplementary Materials). The calculated sets of most intensive bands of these conformers, which are significantly shifted relative to the corresponding bands of the starting reactants, as well as the shifts themselves reasonably agree with those experimentally observed (see Table S4). Interconversions of conformers with the same conformation of C_4H_6 chains, naturally, have low activation barriers ($\leq 2 \text{ kcal mol}^{-1}$), whereas interconversions of conformers with the different conformations

of the C_4H_6 chains have barriers slightly larger than the corresponding barriers in free C_4H_6 (Table S5, Online Supplementary Materials). Therefore, the transformation of conformers with *gauche*- C_4H_6 into the more stable conformers with *trans*- C_4H_6 upon annealing should be slow similarly to the isomerization of *gauche*- C_4H_6 into *trans*- C_4H_6 . Consequently, the observation of fairly fast interconversions of the conformers upon annealing and also the fact that concentration of *gauche*- C_4H_6 in matrices was always very low (even when C_4H_6 was mainly generated by the pyrolysis of **1**) imply that all the observed conformers are those with *trans*- C_4H_6 moieties, such as the three conformers suggested by the calculations and, apparently, additional conformers formed due to the matrix environment effects, while the observed photo- and thermally-induced conformational transformations do not affect the C_4H_6 chain.

Two major photoproducts were produced in the same ratio independently of the conformational composition of isolated complex upon its irradiation with any used wavelengths [Figure 1(b); Figure S8 in Online Supplementary Materials] except unfiltered light (~ 230 –1000 nm). Their formation was very slow upon irradiation at $\lambda > 510$ nm (corresponding bands could hardly be seen in spectra after the irradiation for 60 min) and very fast upon irradiation at $\lambda > 300$ or 280 nm (complete transformation of the complex occurred in 10–15 min). One of these photoproducts can readily be identified as compound **1** by the comparison of its spectrum with a matrix IR spectrum of an authentic sample (see Figure S4). However, to achieve a better agreement, the annealing of matrices partly removing matrix splitting of the bands of **1** was required. The theoretical IR spectra of compound **1** obtained by both M06-2X/6-311++G(d,p) and B3LYP/6-31G(d) [a part of the G3(MP2)//B3LYP method] calculations are also in a good agreement with the matrix IR spectrum of this compound obtained experimentally (Figure S3 and Table S6, Online Supplementary Materials).

The other photoproduct was found to be unstable against the unfiltered light and decayed upon its influence for ~ 30 min with predominant formation of **1** [Figure 1(c)]. This fact implies that both the second photoproduct and compound **1** possess the same composition. Since the thermal reactions of silylenes with 1,3-dienes can proceed as either [4+1] or [2+1] cycloaddition,^{1,17–19} vinylsilirane **2** also seems to be the best candidate for the role of the second product of the photoinduced addition of SiCl_2 to C_4H_6 , especially, due to the known sensitivity^{23–25,29} of vinylsilranes to the light of $\lambda \approx 250$ nm and their capability to rearrange into the corresponding silacyclopent-3-enes upon the irradiation.^{23–25} Performed quantum chemical calculations predicted existence of three conformers for compound **2** (Figure S5, Online Supplementary Materials), two of which are practically isoergic, while one is less stable by $\sim 1 \text{ kcal mol}^{-1}$.¹⁸ The theoretical IR spectra of all conformers obtained using both the methods are rather similar and differ mainly by variations in intensities of bands (Figure S6, Online Supplementary Materials). On the whole, the theoretically predicted sets of bands of different conformers of **2** having noticeable intensities well correspond to the experimentally observed set of bands of the second photoproduct, especially, in the case of the most stable conformers (Figure 2; Figure S7 and Table S7, Online Supplementary Materials). Thus, on the basis of photochemical behavior and well reproduction of the set of observed bands in the calculations, the second photoproduct has been identified as vinylsilirane **2**. Some of the detected bands of product **2** had complex structures, which were partially changed upon annealing (Table S7, Online Supplementary Materials). However, neither the initial structures of the bands, nor those acquired upon annealing agree with the structures expected according to the theoretical data for any mixture of conformers. Therefore, this splitting of bands should

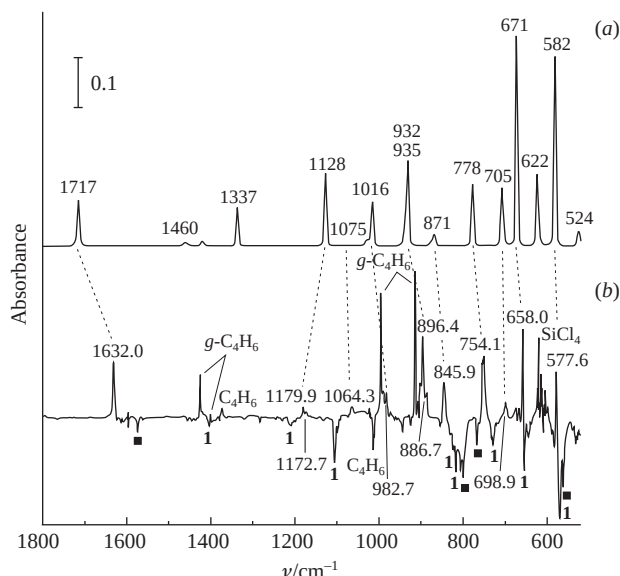


Figure 2 (a) The M06-2X/6-311++G(d,p) calculated spectrum of *cis*-2 and (b) experimental difference IR spectrum of a matrix with $\text{SiCl}_2:\text{C}_4\text{H}_6:\text{Ar} = 2:7:1000$ after photolysis at $\lambda > 280$ nm for 15 min and after subsequent photolysis by the unfiltered light for 30 min. Calculated and experimentally measured fundamental frequencies of **2** are shown. The bands of **1**, unidentified products, *gauche*- C_4H_6 , and not well subtracted bands of *trans*- C_4H_6 and SiCl_4 are marked with symbols **1**, ■, *g*- C_4H_6 , C_4H_6 and SiCl_4 , respectively.

be attributed to the matrix splitting analogous to that observed for the bands of **1**.

In addition to compounds **1** and **2**, the formation of some minor yet unidentified products stable to any used light occurred upon phototransformations of the complex. Their appearance indicates the overall complexity of photochemical behavior of the studied system. The formation of only the same additional products, but in larger amounts, also accompanied rearrangement of **2** into **1** caused by unfiltered light. Thus, the reactions occurring during the phototransformations of the complex and compound **2** are the same. This allows one to suppose that the rearrangement of **2** into **1** proceeds mostly *via* an initial decomposition of **2** into starting reactants (into the complex), rather than directly.

In conclusion, the photoinduced transformation of the complex between butadiene and SiCl_2 caused by the light of $\lambda > 280$ nm was estimated as providing 1,1-dichloro-2-vinylsilirane **2** and 1,1-dichloro-1-silacyclopent-3-ene **1** in a ratio of $\sim 3:2$ on the basis of integral intensities of bands of **1** and **2**, and their changes in the course of the isomerization of **2** into **1** (Figure S8, Online Supplementary Materials). Thus, in contrast to the thermal reaction between SiCl_2 and C_4H_6 , wherein **2** can be formed only as a minor product (*vide supra*), the photoinduced reaction provides **2** as the major product.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.11.002.

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