Thermal and photochemical isomerization of exocyclic 1,3-dienes: 1,1-diphenyl-3,4-bis(trimethylsilylmethylene)-1-silacyclopentane s-*cis*(E,E)

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Abstract

This paper describes the photochemical and the thermal isomerization of s-*cis*(E,E) 1,1-diphenly-3,4-bis(trimethylsilylmethylene)-1-silacyclopentane (**1a**). Under thermal conditions a 1,3-sigmatropic of the methylene hydrogen occurs, yielding the s-*trans* isomer (**1b**). The photochemical irradiation of (**1a**) at 300 nm for 1 h in deoxygenated benzene gives the corresponding s-*cis*(E,Z) isomer (**1c**) and then the s-*cis*(Z,Z) isomer (**1d**) after prolonged irradiation (3 h). There was no evidence for the formation of the corresponding cyclobutene resulting from the ring closure of the exocyclic diene.
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1. Introduction

The photochemistry of exocyclic 1,3-dienes has been extensively investigated [1–3]. It has been found that direct irradiation of these 1,3-dienes in dilute solution at room temperature results mostly in cyclobutene formation [4,5] and double bond isomerization [6,7]. There are examples that illustrate the preferred disrotatory stereochemistry of the photochemical ring closure of 1,3-butadiene derivatives to the corresponding cyclobutene [8–10]. For example, (E,E)-2,4-hexadiene has been re-

ported to yield *cis*-3,4-dimethyl-cyclobutene stereospecifically, albeit in low quantum yield, owing to competing *cis* ↔ *trans* isomerization, upon direct photolysis in solution [10]. Several reports have demonstrated that direct photolysis of alkyl-substituted cyclobutenes in solution results predominantly in nonstereospecific ring opening to the corresponding conjugated dienes, in competition with fragmentation to the corresponding alkene and alkyne.

It is recognized that most acyclic 1,3-dienes exist as a mixture of two conformers [11]. In most cases the more stable conformation is planar and s-*trans* about the central bond [12], while the minor form has an s-*cis* configuration. Although much of the thermal chemistry and photochemistry of 1,3-dienes proceeds through this minor conformer, direct examination of s-*cis* chemistry has been limited because of its high energy relative to the

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s-*trans* isomer and the small barrier separating the s-*cis* from the s-*trans* isomer.

In the last few years, we have been interested in the synthesis of heterocyclic compounds containing silicon, because of their potential as building blocks for the preparation of functional macromolecules and polymers. These compounds are easily obtained by the reaction of (di) allyl and (di) propargylsilanes with reactive zirconocene "Cp$_2$Zr" generated in situ by addition of butyllithium to Cp$_2$ZrCl$_2$. This versatile method is easy to carry out and allows the synthesis of various functionalized main group heterocylopentanes and cyclopentadienes (Si, Ge, P) starting from bis allylic and propargylic derivatives [13–17]. Direct reaction of the reactive zirconocene "Cp$_2$Zr" with dipropargylic derivatives of Si, Ge, Sn and P yields bicyclocomplexe intermediates, which can be easily converted to the corresponding *exo* dienic metallacyclopentanes by reaction with different electrophiles. While, the cyclozirconation of the diallylic derivatives leads to the corresponding saturated metallacyclopentanes, after exposure to different electrophiles. This way, it was possible to prepare racemic phosphines and diphosphines.

In this paper, we investigate the thermal and the photochemical behavior of the *exo* diene: s-*cis*(E,E) 1,1-diphenly-3,4-bis(trimethylsilylmethylene)-1-silacyclopentane (**1a**). It is the first example of a diene bearing two bulky trimethylsilyl groups reported in the literature, so far. The different steps and the resulting products were characterized using ^{1}H and ^{13}C NMR.

2. Results

Compound (**1a**) was prepared by reaction of α,ω-(trimethylsilyl) dipropargyldiphenyl silane with "Cp$_2$Zr" followed by protonation of the zirconium complex intermediate, in 72% yield (Scheme 1).

The cyclozirconation reaction of bis-trimethylsilyl-propargyl-1,1-diphenylsilane followed by the electrophilic addition of H$^+$ leads to the stereoselective formation of (**1a**) in the s-*cis*(E,E) exocyclic configuration. ^{1}H NMR spectrum (Table 1) exhibits a triplet (δ

6.25) for the vinylic protons and a doublet at δ 2.25 for the two hydrogens in the α position to Si with a coupling constant of 1.7 Hz. The Me$_3$Si groups are seen as a singulet at 0.19 ppm. There is a full symmetry in the molecule. This structure was confirmed by ^{13}C NMR spectrum of the s-*cis*(E,E). In fact, the intracyclic (C$_2$/C$_5$, C$_3$/C$_4$) [18] and the exocyclic carbons (including the TMS group) are magnetically equivalent, which is in agreement with the existence of a symmetry in the molecule (Fig. 1). A previous example based on titanium-mediated stereoselective cyclization of diynes to E,E-exocyclic dienes have been reported by Nugent et al. [19].

In a similar way, electrophilic addition of bromine (Br$_2$) at low temperature to the zirconium intermediates obtained by reaction of "Cp$_2$Zr" with the above dipropargylsilanes (and germanes) afforded the corresponding 3,4-bis(bromo-trimethysilyl-methylene)1-sila (and germa)cyclopentane in 35% and 52% yield, respectively [14]. Comparison of ^{1}H and ^{13}C NMR spectra of **1a** with the brominated product **2**, obtained by electrophilic displacement of the same zirconium intermediate with Br$_2$ (Scheme 1), is interesting from a stereochemical point of view. The two hydrogen atoms of the methylene groups in α position to the silicon atom in the brominated molecule display an AB system ($J_{AB} = 14$ Hz). The two bulky bromine atoms in the *endo* position induce a noticeable and stable twisting of the silacyclopentane ring. So, the two hydrogen atoms of the methylene groups in α to silicon are always magnetically equivalent in **1a**, whereas they remain an AB system in the brominated compound **2**.

The product s-*cis*(E,E) **1a** is stable at room temperature in solution in hexane, benzene and diethyl ether. However, heating the s-*cis*(E,E) compound **1a** in benzene solution at 50 °C led to the formation of s-*trans*(E) isomer **1b** after one week in 70% yield. The thermal isomerization of **1a** compound is a consequence of a 1,3-sigmatropic rearrangement of a methylene hydrogen (Scheme 2).

^{1}H NMR displays a doublet at δ 2.26 with a coupling constant of 1.6 Hz and a singulet (δ 2.09) for the methylene protons on the C$_2$ and C$_7$, respectively. The vinylic
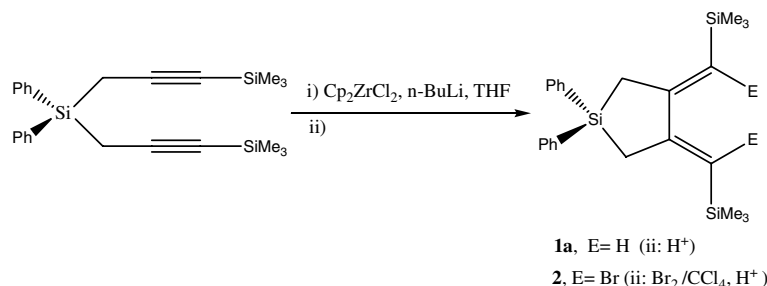
Scheme 1. Synthesis of s-*cis*(E,E) isomers **1a** and **2**.

Table 1
^{13}C and ^1H NMR characteristics of the 1a–d isomers

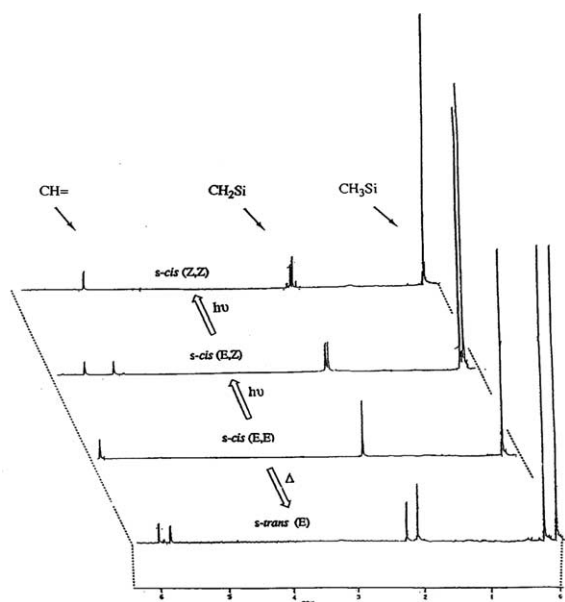|		1a:s-cis(E,E)	1b:s-trans(E)	1c:s-cis(E,Z)	1d:s-cis(Z,Z)
^{13}C NMR	$\delta\ ^{13}C$				
	C_2, C_5	21.25	127.11 19.98	26.44 22.70	29.57
	C_3, C_4	160.56	166.11 159.25	163.93 160.12	159.80
	C_6, C_7	122.89	124.11 24.78	124.99 124.52	124.53
	$SiMe_3$	−0.07	−0.09 −0.94	0.96 −0.08	0.45
^1H NMR	$\delta\ ^1H$				
	CH_2Si ($^4J_{HH}$ Hz)	2.25 (d) (1.7)	2.26 (d) (1.6) 2.09 (s)	2.25 (d) (1.6) 2.21 (d) (1.6)	$\delta_B = 2.20$ $\delta_A = 2.25$ $^4J_{AB} = 14$ (2.1)
	CH = ($^4J_{HH}$ Hz)	6.25 (t) (1.7)	6.06 (s) 5.88 (t) (1.6)	5.92 (t) (1.6) 5.49 (t) (1.6)	5.35 (d) (1.6)
	CH_3Si	0.19	0.21 (s) 0.03 (s)	0.24 (s) 0.19 (s)	0.21 (s)

Fig. 1. ^1H NMR spectra of the 1a–d isomers.

protons on C_5 and C_6 appear as a triplet ($^4J = 1.6$ Hz) and a singulet, respectively. All the carbons are magnetically non equivalent (Table 1 and Fig. 1), which is in agreement with a symmetry loss induced by the thermal rearrangement.
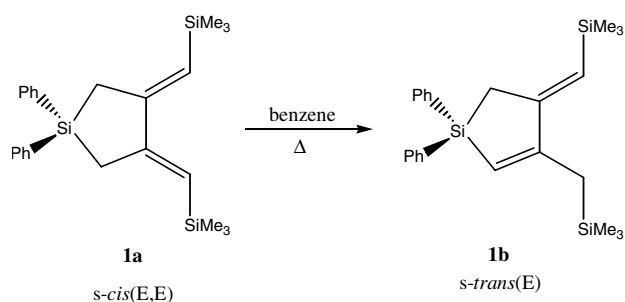
Scheme 2. Thermal isomerization of s-cis(E,E) isomer 1a.

Photochemical irradiation of the s-cis(E,E) isomer 1a at 254 nm in deoxygenated benzene solution after 13 h led to the formation of a mixture of isomers: 20% s-cis(E,E), 30% s-trans(E) 1b and 50% of unknown products. The s-trans(E) resulted more likely from the thermal isomerization of 1a as shown in the above section. Indeed, the prolonged irradiation (13 h) can cause an heating effect responsible of the observed reaction pathway. However, irradiation for 1 h of the s-cis(E,E) isomer at a higher wavelength (300 nm) instead of 254 nm led to the quantitative formation of s-cis(E,Z) isomer. This isomer was formed by single double bond photochemical isomerization of the diene1,3-dienes [20] (Scheme 3).
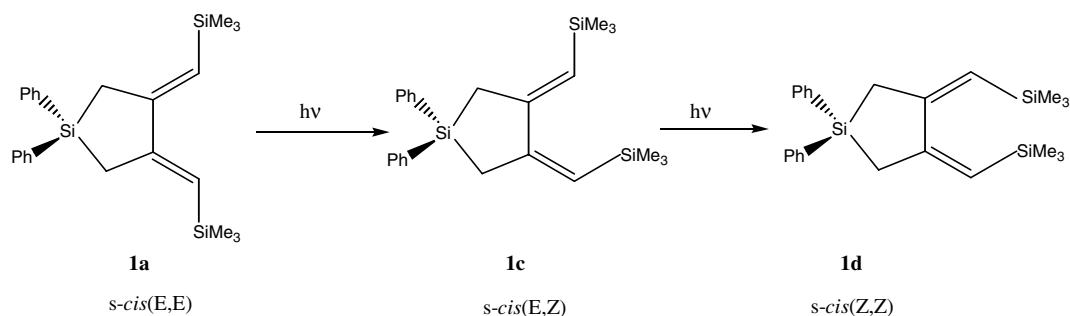
Scheme 3. Photochemical isomerization of s-*cis*(E,E) isomer **1a**.

From ^{1}H NMR spectrum of **1c** one can see two doublets (δ 2.21 and 2.25) for the methylene protons and two triplets (δ 5.49 and 5.92) for the vinylic protons with a coupling constant of 1.6 Hz. The TMS groups display two singulets at δ 0.19 and 0.24 ppm. ^{13}C NMR confirms the ^{1}H NMR results and shows features that are compatible with a disrupted symmetry of the s-*cis*(E,Z) molecule (Table 1 and Fig. 1). Indeed, all the carbons are magnetically non equivalent.

When the irradiation at 300 nm in deoxygenated benzene solution was prolonged the s-*cis*(E,Z) isomer **1c** slowly disappears to give the s-*cis*(Z,Z) isomer **1d**. The reaction conversion is quantitative after 3 h irradiation. NMR spectra analysis indicates the recovery of the symmetry of the molecule, but the two bulky trimethylsilyl groups in the *endo* position induce a noticeable and stable twisting of the silacyclopentane ring. The two hydrogen atoms of the methylene groups in the α position to the silicon are clearly seen as an AB system ($^2J_{AB} = 14$ Hz) and the vinylic protons as a doublet ($^4J_{AX} = {}^4J_{BX} = 2.1$ Hz) [14] (Table 1). This transformation is easily characterized by ^{13}C NMR. The high symmetry of the s-*cis*(Z,Z) isomer **1d** involves an equivalence of C_2/C_5, C_3/C_4 and C_6/C_7 carbons and the TMS groups, while these carbons are diastereotopic in the s-*cis*(E,Z) form.

Continuation of the photochemical irradiation of the s-*cis*(Z,Z) isomer **1d** under the same conditions did not show any changes in the reaction mixture composition as revealed by ^{1}H and ^{13}C NMR. This result indicates that this isomer corresponds to the final stage of the isomerization. It should also be noted that the s-*cis*(E,Z) isomer and s-*cis*(Z,Z) isomer had been observed previously by irradiation of the s-*cis*(E,E) isomer at 254 nm with the yield 32% and 28% yields, respectively.

3. Discussion

Direct photochemical irradiation of conjugated dienes is known to give rise to both double bond isomerization and cyclobutene formation. The application of the rules proposed by Woodward and Hoffmann would predict that the ring closure to a cyclobutene in the electronically excited state is disrotatory. This will lead to the formation of a *cis* bicyclobutene (where the TMS groups are in a *cis* position). In accordance to the orbital symmetry, the conrotatory thermal ring opening of the cyclobutene will give the s-*cis*(Z,E) isomer.

Srinivasan [21] have studied the thermal decomposition of *cis*-3,4-dimethylcyclobutene. At high temperatures (420–450 K), the (Z,E) 2,4-hexadiene was obtained quantitatively in a conrotatory process. However, more recent reports have shown that the photochemistry (193 or 214 nm) of constrained cyclobutenes results in the formation of (E,E) and (E,Z) isomers. The photochemical ring opening reaction is not stereospecific even though that partial orbital symmetry controls the process.

The photolysis of 1,1-diphenyl-3,4-bis(trimethylsilylmethylene)-1-silacyclopentane s-*cis*(E,E) **1a** can lead directly to the formation of the (E,Z) isomer **1c** (photoisomerization reaction: E/Z) [20,22]. The same product can be obtained in a stepwise process: disrotatory photochemical cyclization of (**1a**) to the corresponding *cis*-bicyclobutene, followed by a thermal ring opening reaction. However, the latter step, according to the orbital symmetry control requires heating of the mixture. The heat generated in the photochemical reactor at 300 nm is not high enough to cause the ring opening reaction (the rise of the temperature in the "Rayonet" would not exceed 40 °C). We believe that the most probable reaction mechanism is the direct Z/E isomerization. Similarly, a further photochemical isomerization of s-*cis*(E,Z) isomer **1c** leads to the s-*cis*(Z,Z) isomer **1d**. As previously, one can assume a stepwise mechanism: disrotatory photoprocess leading to the formation of a *trans*-bicyclobutene intermediate, accompanied with a thermal ring opening. However without an extra heating source, the photoisomerization is believed to be the dominant pathway. Moreover, the AB system observed for the methylene protons ($^4J_{AB} = 14$ Hz) in the **1d** s-*cis*(Z,Z) is comparable to
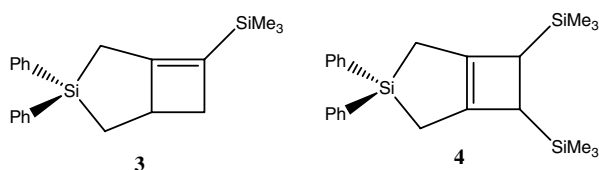
Scheme 4.

the one obtained with the brominated compound (**2**) implying a twisted form induced by the two bulky TMS in the *endo* position.

The accuracy of the percentages of the different isomers, estimated from NMR, do not allow us to conclude that the described photoisomerization at 300 nm are univocal reactions. Consequently, we can not assert that a "one way" mechanism, as described by Tokumaru and Arai [22], is involved.

In conclusion, we have shown that the thermal treatment of the *exo* diene *s-cis*(E,E) (**1a**) leads stereospecifically to *s-cis/s-trans* isomerization, whereas the photochemical irradation at 300 nm of (**1a**) results in the selective isomerization of one double bond to yield the isomer *s-cis*(E,Z) **1c**. The prolonged irradiation causes the isomerization of the second double bond to produce the constrained *s-cis*(Z,Z) isomer **1d**. Whereas the bicyclo[3.2.0]hept-1(7)ene **3** was recently described [17], we had no evidence for cyclobutene formation of **4** (Scheme 4).

4. Experimental

All manipulations were carried out under an argon atmosphere. The product s-*cis*(E,E) **1a** was synthesized by cyclozirconation of diyne correspondent [14]. The photochemical irradiation was effected with a Rayonet RPR 100 at 254 or 300 nm. All NMR spectra were recorded at 25 °C on Bruker AC 80 and 250 MHz in CDCl$_3$. The ^{1}H and ^{13}C chemical shifts were referenced relative to Me$_4$Si. Coupling constants are given in Hertz.

4.1. Thermal isomer

The s-*trans*(E) **1b** isomer was obtained by heating 100 mg of the **1a** isomer at 50 °C for 1 week in deoxygenated C$_6$D$_6$ solution in 70% yield or for 10 days in deoxygenated CDCl$_3$ solution in 100% yield.

4.2. Photochemical isomers

In a quartz tube, a 100 mg of the **1a** isomer in deoxygenated C$_6$D$_6$ solution was irradiated at 300 nm for the time indicated. As shown by ^{1}H and ^{13}C NMR spectra, the **1c** isomer was only obtained after 1 h photochemical irradiation of **1a** isomer. Similarly, the **1d** isomer was obtained after 3 h irradiation of the **1c** isomer, was only characterized by ^{1}H and ^{13}C NMR (see Fig. 1).

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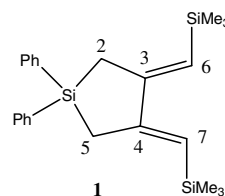
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