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Communications

Selective Formation of Rearranged Silenes from Polysilylenones via 1,3- and 1,5-Silyl Migration

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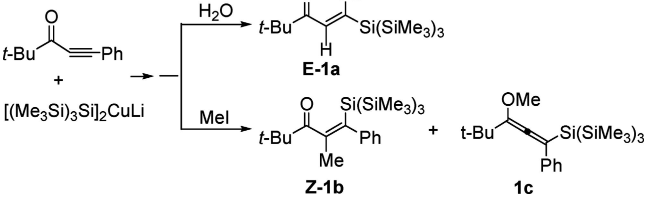
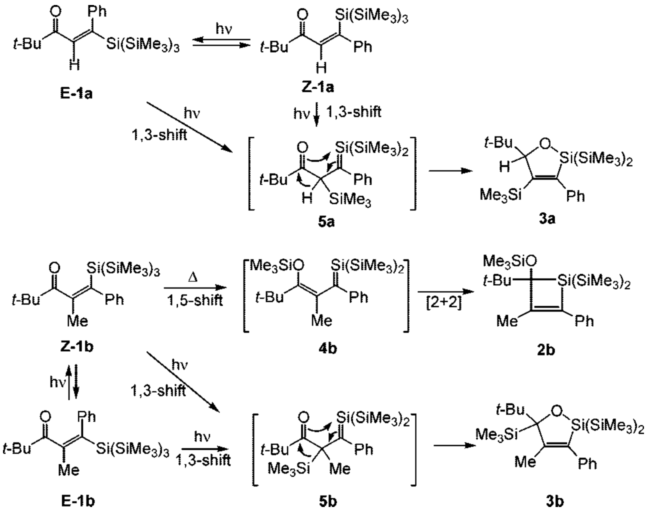
*Summary: The polysilylenones (E)-1-phenyl-2-pivaloyl-1-(tris(trimethylsilyl)silyl)ethene (***E-1a***) and (Z)-2-methyl-1-phenyl-2-pivaloyl-1-tris((trimethylsilyl)silyl)ethene (***Z-1b***) were prepared, and their isomerization under thermal and photochemical conditions was studied. These polysilylenones underwent 1,3- and 1,5-silyl rearrangement selectively, producing the respective silenes, depending on the reaction conditions.*

Silenes are important organosilicon species as the analogues of alkenes.[1] Acylpolysilanes have been studied extensively as useful silene precursors,[2−4] after the first isolable silene was prepared by photochemical isomerization of adamantoyltris(trimethylsilyl)silane by Brook and co-workers.[3a] 1,3-Silyl migration from the polysilane unit to the carbonyl oxygen atom in acylpolysilanes under photochemical[2,3] and thermal conditions[2,4] produces the corresponding silenes in high yield. It was also demonstrated that treatment of acylpolysilanes with organolithium reagents gives the corresponding silenes by addition of the organolithiums to the carbonyl group, followed by Peterson type reactions of the resulting lithium alkoxides.[5] However, the acylpolysilanes that have been studied so far are limited to simple ones, with a few exceptions. Synthesis and some

Scheme 1



Scheme 2



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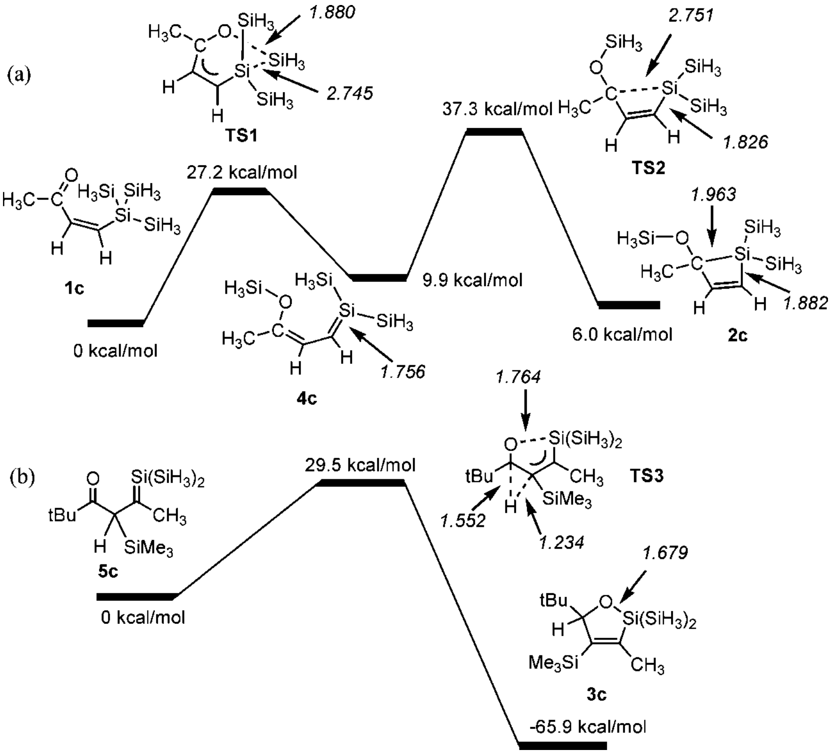

Figure 1. Energy diagrams for the isomerization of (a) polysilylenone to silacyclobutene via a 1,3-silenone intermediate and (b) 1-silen-4-one to oxasilacyclopentene, derived from DFT calculations (B3LYP/6-31G(d)). Numbers in italics are bond lengths, given in Å.

reactions of acylpolysilanes bearing an ethenyl group on the carbonyl carbon was reported by Brook et al.[6] Recently, we synthesized 1-adamantoyl-1-ethenyldisilane[7] and bis(acyl)polysilane[8] and found that their thermal reactions afforded products that would be formed via interesting intermediates, including 2-siladiene and 2,3-disiladiene, respectively. To explore further the scope of the chemistry of acylpolysilane derivatives, we prepared polysilylenones (**E-1a** and **Z-1b**) and examined their isomerization. The present polysilylenones underwent 1,3- and 1,5-silyl rearrangement selectively, producing the respective silenes, depending on the reaction conditions.

Polysilylenones **E-1a** and **Z-1b** were synthesized as shown in Scheme 1. A reaction of tris(trimethylsilyl)silyl cuprate with pivaloylphenylacetylene gave the 1,4-adduct. Hydrolysis of the latter gave **E-1a** in 21% isolated yield, while treatment with methyl iodide gave **Z-1b** in 11% yield, together with allene **1c** (41%). The structures of **E-1a** and **Z-1b** were verified by spectroscopic analysis as well as by the X-ray crystallographic analyses.

When a toluene solution of **E-1a** was heated at 170 °C for 22 h in a degassed sealed glass tube, no reaction occurred and the starting **E-1a** was recovered unchanged. In marked contrast to this, heating **Z-1b** at 100 °C for 1 h gave silacyclobutene **2b** in 71% yield as the sole volatile product (Scheme 2). On the other hand, irradiation of **E-1a** with a low-pressure mercury lamp bearing a Vycor filter (254 nm) in hexane for 100 min afforded an oxasilacyclopentene derivative (**3a**) in 24% yield. Photolysis of **Z-1b** proceeded in a manner similar to that of **E-1a**, to give oxasilacyclopentene **3b** in 34% yield, after 100 min of irradiation. In both of the photoreactions, trace amounts of the olefinic isomerization products **Z-1a** and **E-1b** were formed. No formation of products analogous to **2b** was detected by either spectroscopic analysis or chromatography of the reaction mixtures.

Scheme 2 represents a plausible mechanistic interpretation for the formation of the rearranged cyclic products in these reactions. The formation of **2b** can be best explained by assuming a 1-siladiene intermediate (**4b**) via 1,5-silyl migration from the polysilane unit to the carbonyl oxygen atom. Intramolecular [2 + 2] addition of intermediate **4b** directly produces **2b**. Similar intramolecular cycloaddition of siladienes has been reported previously for 2,3-disiladienes.[7-9] Barton et al. have reported similar thermal isomerization of (*Z*)-1-(pentamethyldisilanyl)hex-1-en-3-one at 430 °C,[10] in which a rearranged cyclic product arising from 1,2-silyl migration was obtained, in contrast to the present thermal isomerization of **Z-1b**. Under the photochemical conditions, 1,3-silyl migration from the polysilane unit to the olefinic carbon atom is involved, leading to the 1-silen-4-one intermediates **5a**,**b**. The silenone intermediates undergoes cyclization, accompanied by 1,2-hydride or silyl migration, to give **3a**,**b**, respectively. We examined thermal reactions and photoreactions of **E-1a** and **Z-1b** in the presence of methanol and bis(trimethylsilyl)acetylene, as the silene trapping reagents. However, these attempts were unsuccessful and the trapping reagents had no effect on the reactions.

To learn more about the reaction mechanism, hybrid type density functional theory (DFT) calculations have been carried out at the B3LYP functional level.[12] The 6-31G(d) basis sets

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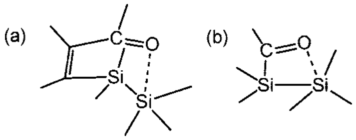
Chart 1. Schematic Representation for the Transition States of (a) 1,5-Silyl and (b) 1,3-Silyl Migration, for the Formation of Silenes from Polysilylenone and Acylpolysilane, Respectively



were employed, which are implemented in the Gaussian03 Win program package.[13] To make the calculation tractable, the real reacting systems were simplified to model the systems. The model systems and their energies are shown in Figure 1. As can be seen in Figure 1a, the thermal isomerization of polysilylenone **1c** to silacyclobutene **2c** involves two steps: i.e., the concerted suprafacial 1,5-migration of the silyl group to the carbonyl oxygen atom in **1c** leading to a silene intermediate (**4c**) and the subsequent intramolecular ring closure in **4c**. At the transition state of the first step (**TS1**), the Si−Si−O−C dihedral angle is about 92°, indicating that the migrating silicon interacts with the carbonyl π orbital (Chart 1a). This is in contrast to the thermal 1,3-silyl migration in acylpolysilanes leading to the corresponding silenes, reported previously. The Si−Si−O−C dihedral angle at the transition state of this 1,3-silyl migration was calculated to be approximately 0°, indicating that intramolecular nucleophilic attack by the carbonyl oxygen atom is involved (Chart 1b).[11] The activation energy of the present isomerization from **1c** to **4c** (27.2 kcal/mol) is lower than that of the 1,3-silyl migration in acylpolysilanes on the basis of B3LYP/6-311G* calculations (36−39 kcal/mol).

Conrotatory intramolecular [2 + 2] addition would take place in siladiene **4c** to give the final silacyclobutene product (**2c**) through transition state **TS2**. No transition state for disrotatory cyclization was found. Similar conrotatory [2 + 2] addition was suggested for the intramolecular ring closure of 2,3-disiladienes by DFT calculations.[8] In the present calculations, the end product **2c** was predicted to be less stable than the starting polysilylenone and the silene intermediate. Presumably, introduction of sterically bulky substituents in the real product relatively stabilizes the silacyclobutene system.

The isomerization from **5c** to **3c** was also examined by DFT calculations. In these calculations, no reaction path was obtained, unless less simplified models bearing *t*-Bu, $SiMe_3$, and CH_3 groups were employed, as shown in Figure 1b. At the transition state of this reaction (**TS3**), the Si−O distance of 1.764 Å is close to that of the product (1.679 Å), indicating that the Si−O single-bond formation occurs at the early stage of the reaction, which is followed by H migration. The formation of the thermodynamically stable Si−O bond seems to provide the driving force of this reaction.

In conclusion, we demonstrated that photochemically and thermally induced silyl migration proceeded in 1,3- and 1,5-fashions, respectively. This is the first example of selective silene formation from a single molecule, controlled by the Woodward−Hoffmann rule.

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Supporting Information Available: Text and tables giving details of the experimental procedures, DFT calculations, and ORTEP drawings for compounds **E-1a** and **Z-1b** and CIF files giving X-ray crystallographic data for **E-1a** and **Z-1b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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