Novel generation of silacarbonyl ylides by trapping of silylene with carbonyl compounds and their cycloaddition leading to silaheterocycles

Norio Sakai, Tsuyoshi Fukushima, Satoshi Minakata, Ilhyong Ryu and Mitsuo Komatsu*

Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Yamadaoka 2-1, Suita, Osaka 565-0871, Japan. E-mail: komatsu@ap.chem.eng.osaka-u.ac.jp

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The photochemical generation of silacarbonyl ylides from a silylene and carbonyl compounds and their inter- or intramolecular 1,3-dipolar cycloaddition with olefins leading to silicon heterocycles in one step was successful.

Over the past few decades the capture of a carbene with a carbonyl compound to form the corresponding carbonyl ylide has been the subject of extensive study.[1] Recently silylenes, the silicon analogues of carbenes, have attracted considerable attention in the construction of new silaheterocycles as possible new biologically active compounds and functional materials.[2] While several methods for the *in situ* generation of silylenes by photolysis have been developed,[3,4] the trapping of silylenes with aldehydes, ketones and an α-diketone leading to silaheterocycles has emerged as the result of studies on the chemical properties of silylenes.[4,5] However, specific research into the trapping of silylenes with carbonyl compounds has not been reported, nor has their application as silacarbonyl ylides in the one-step synthesis of silaheterocycles. We report herein some unprecedented examples of the 1,3-dipolar cycloaddition of photochemically generated silacarbonyl ylides, as silicon analogues of carbonyl ylides, with dipolarophiles to give silaheterocycles (Scheme 1).

The reaction of a silylene with a simple aliphatic aldehyde was investigated as an initial example. A solution of trisilane[6] **1** and acetaldehyde **2a** (100 equiv.) in hexane was irradiated at −57 °C for 40 h in a cold bath with a low pressure mercury lamp.[4] The resulting mixture was separated on a silica gel column (hexane–EtOAc = 95:5) to afford 1,4-dioxa-2-silacyclopentane **3a** in 50% yield (Scheme 2). The structure of the cycloadduct **3a** was characterized as a 1 : 2 cycloadduct of bismesitylsilylene **4** (*vide infra*) and aldehyde **2a** by spectral analysis. ^{1}H NMR observation showed that silaheterocycle **3a** was a mixture of diastereomers (*cis* : *trans* = 1 : 1), but no regioisomers such as a 1,3-dioxa-2-silacyclopentane were formed. The cycloadditions of trisilane **1** with other carbonyl compounds **2b–e** leading to 1 : 2 cycloadducts **3b–e** are summarized in Table 1.

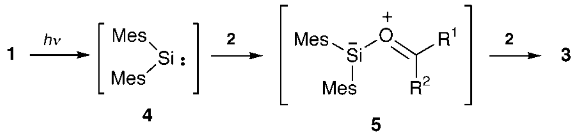
With less bulky aldehydes such as acetaldehyde and propionaldehyde, the yields of **3** were moderate. However, when a more bulky aldehyde **2c** was employed, the yield of cycloadduct **3c** was dramatically improved to 81%. It is noteworthy that a nearly quantitative yield was observed with a non-enolizable bulky aldehyde **2d**. When acetone **2e** was employed, cycloadduct **3e** was produced in 15% isolated yield (26% by ^{1}H NMR before silica gel column separation).

Table 1 The results of the cycloaddition reactions of silylene **4** with carbonyl compounds **2a–e** leading to 1 : 2 cycloadducts **3a–e**[a]

Entry	Carbonyl compounds	R^1	R^2	equiv.	*t*/h	Yield (%)[b]
1	**2a**	Me	H	100	40	50[c]
2	**2b**	Et	H	70	24	34[c]
3	**2c**	Pr^i	H	70	20	81[c]
4	**2d**	Bu^t	H	100	17	98[c]
5	**2e**	Me	Me	100	17	15[d]

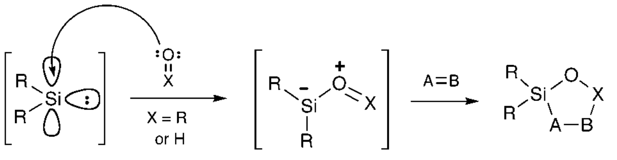
[a] Hexane solutions were irradiated at −57 °C. [b] Yield of the isolated products. [c] *cis, trans*-mixtures. [d] A large amount of enol silyl ether was detected.

The findings suggest that the silacarbonyl ylide intermediate **5** was initially generated from the silylene **4** and the carbonyl compounds **2** followed by 1,3-dipolar cycloaddition with **2** affording the cycloadduct **3**, where the aldehyde **2** plays two roles, first as a constituent of the ylide **5** and, subsequently, as a dipolarophile (Scheme 3).

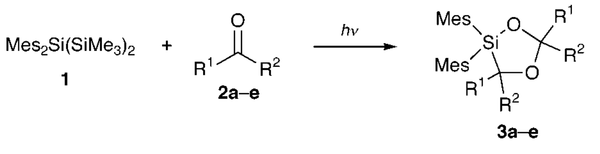


Scheme 3

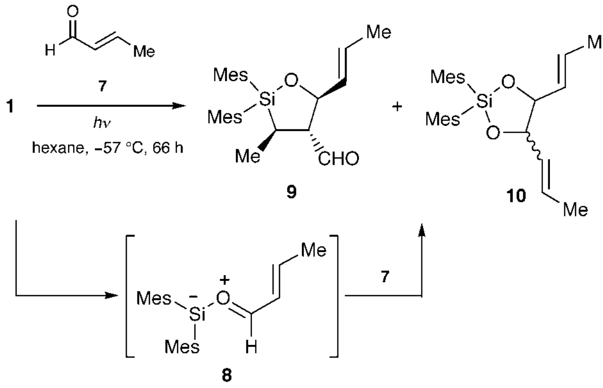
Trisilane **1** was then reacted with α,β-unsaturated aldehydes in the hope of observing intramolecular cycloaddition. Contrary to our expectation, the reaction of **1** with crotonaldehyde **7** (70 equiv.) gave the intermolecular 1:2 cycloadducts 1-oxa-2-silacyclopentane **9** and 1,3-dioxa-2-silacyclopentane **10** in 27 and 25% yields, respectively (Scheme 4). The oxasilacyclo-



Scheme 1



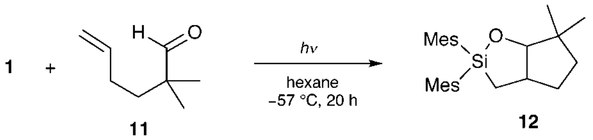
Scheme 2



Scheme 4

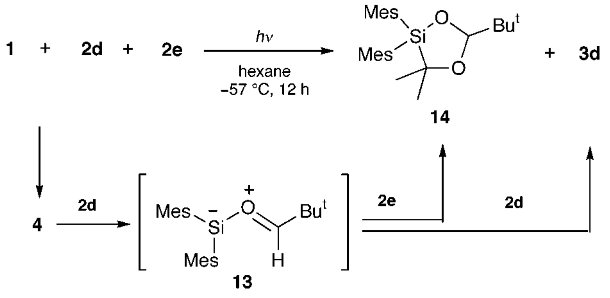
pentane structure of cycloadduct **9** was determined by spectral analysis and NOE measurement of its hydrazone derivative,[7] while product **10** had the same ring system as the 1:2 cycloadduct reported for the reaction with benzaldehyde.[8] As shown in Scheme 4, the generated silacarbonyl ylide **8** was trapped by the C=C bond of aldehyde **7** to afford **9** and by the carbonyl group of **7** to give **10**. The formation of **9** represents the first example of the cycloaddition of a silacarbonyl ylide with an olefinic dipolarophile, which strongly supports our view that this type of reaction proceeds *via* the 1,3-dipolar intermediate and not *via* a siloxirane intermediate.

Intramolecular cycloaddition was successful with a non-conjugated olefinic aldehyde leading to a silicon-atom embedded bicyclic compound. Thus, a solution of trisilane **1** and 2,2-dimethylhex-5-enal **11** (45 equiv.) in hexane was irradiated at −57 °C for 20 h to afford bicyclo[3.3.0]oxasilacyclooctane **12** in 51% yield (87% by ^{1}H NMR before SiO$_2$ column purification) (Scheme 5).



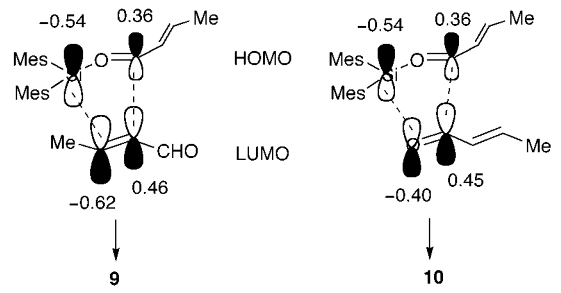
Scheme 5

Moreover, these results suggest the possibility of a three-component coupling reaction involving a silylene and two different carbonyl compounds. When a solution of trisilane **1**, pivalaldehyde **2d** (25 equiv.) and acetone **2e** (50 equiv.) in hexane was photolyzed at −57 °C for 12 h, a three-component cycloadduct **14** was successfully obtained as the major product in 37% yield along with cycloadduct **3d** in 21% yield (Scheme 6). In this three-component reaction, the 1:2 cycloadduct of silylene **4** and **2e** was not obtained at all (see entry 5, Table 1). This result implies that the generation of silacarbonyl ylide **13** from the silylene **4** and aldehyde **2d** occurred predominantly, which was followed by cycloaddition with acetone leading to **14**.



Scheme 6

Finally, the regioselectivities of the cycloadditions of silylene **4** and the aldehydes were examined by semiempirical MO calculations (PM3 method).[9] For the case of an aliphatic aldehyde such as pivalaldehyde, the orbital coefficient (−0.54) on the silicon atom is larger than that (+0.30) on the carbonyl carbon (HOMO), and the orbital coefficient (−0.64) on the carbonyl carbon of the aldehyde is larger than that (+0.47) on oxygen (LUMO).[10] The prediction of the regiochemistry of the cycloaddition by this orbital correlation was in good agreement with the structure of the isolated 1:2 cycloadduct **3d**. In the case of aldehyde **7**, the orbital coefficient on the β-carbon in the LUMO is the largest, so that cycloaddition occurs preferentially across the C=C bond of **7** leading to cycloadduct **9** as the major product (Scheme 7). However, when the difference between the orbital coefficients is small, the regioselectivity of cycloadduct **10** appears to be controlled, not by the correlation of the coefficients, but by the strong affinity between silicon and oxygen.



Scheme 7

Thus far, we have succeeded in the photochemical generation of novel 1,3-dipoles, silacarbonyl ylides, from a silylene and various carbonyl compounds, and their inter- or intra-molecular cycloaddition leading to silicon-embedded heterocycles in one step. The inter- and intra-molecular cycloadditions with olefins, in particular, are unprecedented.

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Notes and references

1 A. Padwa and M. D. Weingarten, *Chem. Rev.*, 1996, **96**, 223; A. F. Khlebnikov, M. S. Novikov and R. R. Kostikov, *Adv. Heterocycl. Chem.*, 1996, **65**, 93; N. J. Turro and Y. Cha, *Tetrahedron Lett.*, 1987, **28**, 1723; T. Ibata, M. T. H. Liu and J. Toyoda, *Tetrahedron Lett.* 1986, **27**, 4383; K. T. Potts, in *1,3-Dipolar Cycloaddition Chemistry*, ed. A. Padwa, Wiley-Interscience, New York, 1984 and references therein.

2 E. Lukevics and L. Ignatovich, *Appl. Organomet. Chem.*, 1992, **6**, 113.

3 S. Masamune, Y. Hanzawa, S. Murakami, T. Bally and J. F. Blount, *J. Am. Chem. Soc.*, 1982, **104**, 1150.

4 M. Ishikawa and M. Kumada, *Adv. Organomet. Chem.*, 1981, **19**, 51 and references therein.

5 A. K. Franz and K. A. Woerpel, *J. Am. Chem. Soc.*, 1999, **121**, 949; J. Belzner and H. Ihmels, *Adv. Organomet. Chem.*, 1998, **43**, 1; J. Belzner, H. Ihmels, L. Pauletto and M. Noltemeyer, *J. Org. Chem.*, 1996, **61**, 3315; W. Ando, K. Hagiwara and A. Sekiguchi, *Organometallics*, 1987, **6**, 2270; W. Ando, Y. Hamada and A. Sekiguchi, *J. Chem. Soc., Chem. Commun.*, 1983, 952.

6 M. J. Fink, M. J. Michalczyk, K. J. Haller, R. West and J. Michl, *Organometallics*, 1984, **3**, 793.

7 M. Behforouz, J. L. Bolan and M. S. Flyynt, *J. Org. Chem.* 1985, **50**, 1186.

8 P. Jutzi, D. Eikenberg, E.-A. Bunte, A. Mohrke, B. Neumann and H.-G. Stammler, *Organometallics*, 1996, **15**, 1930.

9 Calculations were carried out with Cache MOPAC Ver. 94.1.

10 R. Sustmann, *Tetrahedron Lett.*, 1971, **12**, 2717, 2721.

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