

Intramolecular cycloadditions of silacarbonyl ylides tethered to unactivated dipolarophiles: a new route to bicyclosilaoxolanes

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Abstract

The intramolecular 1,3-dipolar cycloaddition of silacarbonyl ylides derived from a silylene and unsaturated aldehydes tethered to unactivated olefinic or acetylenic dipolarophiles successfully proceeded to directly afford bicyclosilaoxolane derivatives in good yields.

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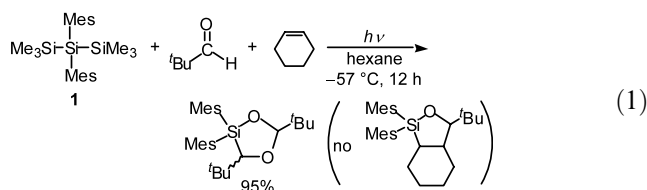
Keywords: Bicyclosilaoxolanes; Silacarbonyl ylides; Intramolecular cycloaddition; 1,3-Dipoles

1. Introduction

1,3-Dipolar cycloadditions are powerful tools for the efficient synthesis of monocyclic and polycyclic molecules containing various heteroatoms [1]. Among these, cycloaddition of carbonyl ylides derived from carbenes and carbonyl compounds [2] are one of the most important methods for the formation of oxygen-containing heterocyclic compounds. On the other hand, silylenes, such as silicon analogues of carbenes represent important intermediates which have attracted considerable attention for use in the construction of new silaheterocycles, silicon atom-embedded heterocyclic compounds [3], since several of these compounds show a higher biological activity or functionality than their carbon counterparts [4]. In this context, we previously reported on the facile synthesis of silaheterocycles via the intermolecular cycloaddition of silacarbonyl ylides

derived from a photochemically induced silylene and carbonyl compounds with activated dipolarophiles (Scheme 1) [5].

While the generated silacarbonyl ylide intermolecularly cycloadded to carbonyl compounds or an enone, a preliminary experiment indicated that the cycloaddition of a silacarbonyl ylide derived from trisilane **1** and pivaldehyde with an unactivated dipolarophile such as cyclohexene did not proceed as shown in Eq. (1). Such low reactivity of simple olefins can often be overcome by intramolecular reaction [6] or high pressure conditions [7].

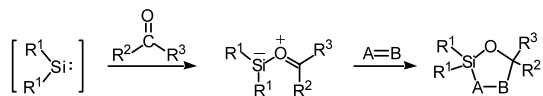


Thus, our interests have been focused on the application of the method to intramolecular cycloaddition in an attempt to expand the utility of ylides that contain a silicon atom. In this paper, we report on the intramolecular 1,3-dipolar cycloaddition of silacarbonyl ylides

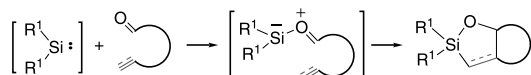
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Scheme 1.



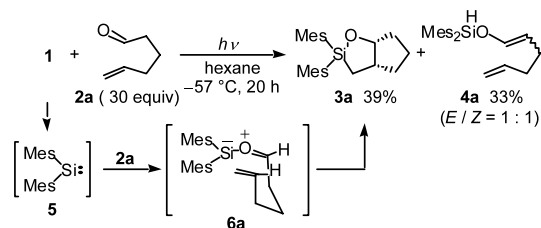
Scheme 2.

tethered to unactivated olefinic or acetylenic dipolarophiles to afford fused silaheterocycles (Scheme 2).

2. Results and discussion

When a solution of 2,2-dimesityl-1,1,1,3,3,3-hexamethyltrisilane (**1**) and 5-hexenal (**2a**, 30 equivalents) in hexane was irradiated at $-57\text{ }^{\circ}\text{C}$ for 20 h with a low pressure mercury lamp under an atmosphere of nitrogen, bicyclo[3.3.0]oxasilacyclooctane **3a** was produced in 39% yield along with enol silyl ether **4a** (33% yield). The structure and stereochemistry of cycloadduct **3a** was determined by spectral analysis and NOE measurements. As shown in Scheme 3, the silacarboxyl ylide intermediate **6a** was initially formed from silylene **5** that has been generated by the irradiation of **1** and aldehyde **2a**, followed by intramolecular 1,3-dipolar cycloaddition affording cycloadduct **3a**. The formation of the silyl enol ether **4a** can also be accounted for by the 1,4-shift [8] of a hydrogen α to the carbonyl group to the silicon in ylide **6a**.

The results of intramolecular cycloaddition of bismesitylsilylene **1** with other non-conjugated unsaturated carbonyl compounds are summarized in Table 1. Since a large amount of enol silyl ether was produced in the reaction of **2a**, carbonyl compounds **2b–i** having methyl group(s) at the α -position were employed in the present reaction. The irradiation of a hexane solution of trisilane **1** and 30 equivalents of aldehyde **2b** was carried out at $-57\text{ }^{\circ}\text{C}$ for 15 h to give cycloadduct **3b** in 68% yield with no detectable formation of the corresponding enol silyl ether (entry 1). The replacement of a methylene unit with an oxygen atom also afforded bicyclooxasilacyclopentane derivatives condensed with a furan ring in



Scheme 3.

Table 1
Intramolecular cycloaddition of bismesitylsilylene with non-conjugated unsaturated aldehydes **2b–i**^a

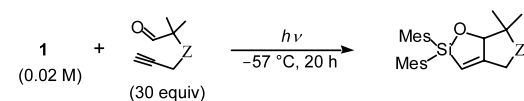
entry	aldehydes (equiv)	temp. ($^{\circ}\text{C}$)	time (h)	products (%)
1	2b (30)	-57	15	3b 68%
2	2c (35)	-52	20	3c 74% (1 : 1)
3	2d (30)	-50	12	3d 76%
4	2e (30)	-57	20	3e 73%
5	2f (30)	-57	20	3f 50%
6	2g (35)	-50	15	3g 40%
7	2f (30)	-57	20	3h 50%
8	2i (30)	-57	20	3i 70%

^a Conditions: Solution of 1,1,1,3,3,3-hexamethyltrisilane in hexane (0.01 M), irradiation by a low pressure Hg lamp.

good yields (entries 2 and 3). The results of entries 4 and 5 indicate that internal alkene and ketone can also be used as substrates in the intramolecular cycloadditions. Moreover, unique bicyclic compounds, oxasilacyclopentanes fused to a six- or four-membered carbocyclic ring were produced in one step using the present methods (entries 6–8). The products are regarded as potential building blocks from the synthetic points of view [9].

The method was then applied to unsaturated aldehydes tethered to an inactivated acetylenic dipolarophile **2j** and **2k** (Table 2). Treatment of aldehyde **2j** with trisilane **1** under irradiation gave the bicyclic oxasilacyclopentene derivative **3j** in 65% yield. The requirement of a cosolvent (CH_2Cl_2) for the reaction is due to the low solubility of **2j** in hexane at the low temperature used.

Table 2
Intramolecular cycloaddition of bismesitylsilylene with non-enolizable acetylenic aldehydes



Z	Solv.	Yield (%)
CH ₂ (2j)	CH ₂ Cl ₂ /hexane	65 (3j)
O (2k)	Hexane	73 (3k)

The oxygen-containing aldehyde **2k** was also converted to the corresponding bicyclic compound **3k** in good yield.

In summary, we have succeeded in the photochemical generation of novel 1,3-dipoles, silacarbonyl ylides, from a silylene and non-conjugated unsaturated aldehydes and their intramolecular cycloaddition leading to silicon-atom embedded bicyclic heterocycles in a one-step reaction. Such intramolecular cycloadditions with unactivated olefinic or unactivated acetylenic dipolarophiles, in particular, are unprecedented. Further studies of the intramolecular cycloaddition of silacarbonyl ylides with various types of dipolarophiles is currently underway.

3. Experimental

Infrared spectra were obtained on a Jasco FT/IR-410 infrared spectrophotometer. ¹H- and ¹³C-NMR spectra were recorded on a JEOL FT-NMR JNM EX 270 spectrometer (¹H-NMR, 270 MHz; ¹³C-NMR, 68 MHz) using tetramethylsilane as an internal standard. Mass spectra were measured using a Shimadzu model GCMS-QP5000 spectrometer. High-resolution mass spectral data were obtained on a JEOL DX-303 mass spectrometer. Flash column chromatography (FCC) was performed using silica gel BW-300 (Fuji Silysia Chemical Co.). Preparative gel permeation liquid chromatography (GPLC) was performed on a JAI (Japan Analytical Industry) LC-908 instrument with JAIGEL 1H-2H columns and chloroform as an eluent. Analytical thin layer chromatography was performed using EM reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light and ethanolic phosphomolybdic acid followed by heating.

3.1. Cycloaddition reactions of silacarbonyl ylides: general procedure

A solution of 2,2-dimesityl-1,1,1,3,3,3-hexamethyltrisilane (0.15 mmol) and aldehydes (4.5–5.3 mmol) in dry hexane (15 ml) was introduced into a quartz tube

equipped with a J. Young high-vacuum valve and stopcock. The solution was repeatedly degassed by the freeze–thaw method. The reaction mixture was irradiated for 12–20 h in a cold bath (an immersion cooler using *i*-PrOH as coolant) with a low-pressure mercury lamp under nitrogen atmosphere. When the reaction bath filled with *i*-PrOH was precooled for 4 h at –57 °C and the temperature was maintained during the period of the reaction, by means of CryoCool CC-60II, the temperature could be kept even under irradiation conditions. After irradiation, the solvent and volatile materials were evaporated in vacuo at room temperature (r.t.), and the residue was purified by flash column chromatography.

3.2. 2,2-bis(2,4,6-Trimethylphenyl)-1-oxa-2-silabicyclo[3.3.0]octane (**3a**)

Colorless oil. IR (neat): 1063 cm⁻¹. ¹H-NMR (270 MHz, CDCl₃): δ = 1.40–2.00 (m, 8H), 2.23 (s, 6H, Mes), 2.39 (s, 6H, Mes), 2.45 (s, 6H, Mes), 2.48–2.55 (m, 1H, CH₂CHCH₂), 4.59 (ddd, 1H, *J* = 3.5, 6.2, 7.8 Hz, SiOCH), 6.74 (s, 2H, Mes), 6.76 (s, 2H, Mes). ¹³C-NMR (68 MHz, CDCl₃): δ = 21.1, 21.2, 22.9, 23.2, 23.9, 24.1, 33.5, 34.9, 41.8, 82.8, 128.8, 128.9, 132.7, 133.1, 138.7, 138.8, 143.6. MS (EI): *m/z* = 364 [M⁺]. HRMS: *m/z* Calc. for C₂₄H₃₂OSi: 364.2222. Found: 364.2211.

3.3. 7,7-Dimethyl-2,2-bis(2,4,6-trimethylphenyl)-1-oxa-2-silabicyclo[3.3.0]octane (**3b**)

Colorless oil. IR (neat): 1031 cm⁻¹. ¹H-NMR (270 MHz, CDCl₃): δ = 0.92 (s, 3H, Me), 0.98 (s, 3H, Me), 1.21–1.28 (m, 1H), 1.38–1.60 (m, 4H), 1.80–2.00 (m, 1H), 2.20 (s, 6H, Mes), 2.39 (s, 6H, Mes), 2.49 (s, 6H, Mes), 2.76 (m, 1H, CH₂CHCH₂), 3.91 (d, 1H, *J* = 5.7 Hz, SiOCH), 6.74 (s, 2H, Mes), 6.76 (s, 2H, Mes). ¹³C-NMR (68 MHz, CDCl₃): δ = 20.9, 21.0, 22.7, 23.8, 24.0, 27.0, 31.6, 38.0, 40.5, 43.3, 90.3, 128.8, 128.9, 132.5, 133.4, 138.8, 143.8. MS (EI): *m/z* = 392 [M⁺]. HRMS: *m/z* Calc. for C₂₆H₃₆OSi: 392.2535. Found: 392.2549.

3.4. 7-Methyl-2,2-bis(2,4,6-trimethylphenyl)-1,6-dioxa-2-silabicyclo[3.3.0]octane (**3c**)

cis-Adduct: colorless oil. IR (neat): 1011 cm⁻¹. ¹H-NMR (270 MHz, CDCl₃): δ = 1.26 (d, 3H, *J* = 6.6 Hz, Me), 1.38 (dd, 1H, *J* = 5.3, 15 Hz, SiCHH), 1.65 (dd, 1H, *J* = 8.6, 15 Hz, SiCHH), 2.23 (s, 6H, Mes), 2.39 (s, 6H, Mes), 2.49 (s, 6H, Mes), 2.88 (m, 1H, CH₂CHCH₂), 3.45 (t, 1H, *J* = 8.6 Hz, CHHO), 3.91 (dt, 1H, *J* = 3.6, 6.6 Hz, CHMe), 4.14 (t, 1H, *J* = 8.6 Hz, CHHO), 4.24 (dd, 1H, *J* = 3.6, 6.6 Hz, SiOCH), 6.76 (s, 4H, Mes). ¹³C-NMR (68 MHz, CDCl₃): δ = 19.1, 19.5, 21.0, 23.0, 23.7, 41.3, 73.9, 77.5, 87.1, 129.0, 129.1, 132.0, 132.2,

139.3, 143.6, 143.7. MS (EI): $m/z = 380 [M^+]$. HRMS: m/z Calc. for $C_{24}H_{32}O_2Si$: 380.2172. Found: 380.2168.

trans-Adduct: colorless oil. IR (neat): 1031 cm^{-1} . $^1\text{H-NMR}$ (270 MHz, CDCl_3): $\delta = 1.19$ (d, 3H, $J = 6.6$ Hz, Me), 1.53 (dd, 1H, $J = 5.3, 15$ Hz, SiCHH), 1.65 (dd, 1H, $J = 8.6, 15$ Hz, SiCHH), 2.29 (s, 6H, Mes), 2.41 (s, 6H, Mes), 2.45 (s, 6H, Mes), 2.90 (m, 1H, CH_2CHCH_2), 3.60 (t, 1H, $J = 8.6$ Hz, CHHO), 3.83 (t, 1H, $J = 8.6$ Hz, CHHO), 3.92 (dt, 1H, $J = 3.6, 6.6$ Hz, CHMe), 4.51 (dd, 1H, $J = 3.6, 6.6$ Hz, SiOCH), 6.76 (s, 4H, Mes). $^{13}\text{C-NMR}$ (68 MHz, CDCl_3): $\delta = 15.2, 21.0, 22.9, 23.8, 42.5, 73.2, 79.4, 82.5, 128.9, 129.1, 132.6, 139.2, 143.7, 143.8$. MS (EI): $m/z = 380 [M^+]$. HRMS: m/z Calc. for $C_{24}H_{32}O_2Si$: 380.2172. Found: 380.2180.

3.5. 7,7-Dimethyl-2,2-bis(2,4,6-trimethylphenyl)-1,6-dioxo-2-silabicyclo[3.3.0]octane (3d)

Colorless oil. IR (neat): 1069 cm^{-1} . $^1\text{H-NMR}$ (270 MHz, CDCl_3): $\delta = 1.17$ (s, 3H, Me), 1.20 (s, 1H, Me), 1.40 (d, 1H, $J = 4.3$ Hz, SiCHH), 1.65 (d, 1H, $J = 4.3$ Hz, SiCHH), 2.23 (s, 6H, Mes), 2.40 (s, 6H, Mes), 2.46 (s, 6H, Mes), 2.98 (m, 1H, CH_2CHCH_2), 3.52 (t, 1H, $J = 7.6$ Hz, CHHO), 3.98 (t, 1H, $J = 7.6$ Hz, CHHO), 4.22 (d, 1H, $J = 5.9$ Hz, SiOCH), 6.76 (s, 4H, Mes). $^{13}\text{C-NMR}$ (68 MHz, CDCl_3): $\delta = 19.8, 19.9, 20.9, 21.0, 22.7, 22.8, 23.0, 23.2, 23.4, 23.9, 27.1, 42.2, 71.6, 83.7, 87.1, 128.8, 128.9, 129.1, 129.2, 131.7, 132.6, 139.2, 139.3, 143.7$. MS (EI): $m/z = 394 [M^+]$. HRMS: m/z Calc. for $C_{25}H_{34}O_2Si$: 394.2328. Found: 394.2330.

3.6. 3,3,7,7-Tetramethyl-2,2-bis(2,4,6-trimethylphenyl)-1,6-dioxo-2-silabicyclo[3.3.0]octane (3e)

Colorless oil. IR (neat): 1078 cm^{-1} . $^1\text{H-NMR}$ (270 MHz, CDCl_3): $\delta = 0.95$ (s, 3H, Me), 1.13 (s, 3H, Me), 1.20 (s, 3H, Me), 1.45 (s, 3H, Me), 2.20 (s, 3H, Mes), 2.21 (s, 3H, Mes), 2.40 (m, 1H, $(\text{Me})_2\text{CCHCH}_2$), 2.40 (s, 6H, Mes), 2.48 (s, 6H, Mes), 3.66 (dd, 1H, $J = 2.2, 8.3$ Hz, $(\text{Me})_2\text{COCHH}$), 3.99 (dd, 1H, $J = 8.3, 8.3$ Hz, $(\text{Me})_2\text{COCHH}$), 4.22 (d, 1H, $J = 4.6$ Hz, SiOCH), 6.71 (s, 2H, Mes), 6.74 (s, 2H, Mes). $^{13}\text{C-NMR}$ (68 MHz, CDCl_3): $\delta = 20.9, 21.0, 23.0, 25.1, 26.9, 27.7, 30.0, 31.3, 58.8, 69.5, 84.2, 84.8, 128.7, 128.9, 133.2, 134.4, 138.2, 138.4, 143.1$. MS (EI): $m/z = 422 [M^+]$. HRMS: m/z Calc. for $C_{27}H_{38}O_2Si$: 422.2641. Found: 422.2636.

3.7. 7,7-Dimethyl-8-isopropyl-2,2-bis(2,4,6-trimethylphenyl)-1-oxa-2-silabicyclo[3.3.0]octane (3f)

Colorless oil. IR (neat): 1080 cm^{-1} . $^1\text{H-NMR}$ (270 MHz, CDCl_3): $\delta = 0.83$ (d, 3H, $J = 7.0$ Hz, Me), 0.96 (s, 3H, Me), 1.01 (s, 3H, Me), 1.08 (d, 3H, $J = 7.0$ Hz, Me), 1.38–1.45 (m, 3H), 1.63–1.72 (m, 2H), 1.86–2.02 (m, 2H), 2.21 (s, 6H, Mes), 2.57 (s, 6H, Mes), 2.62 (s, 6H, Mes), 2.71 (m, 1H, CH_2CHCH_2), 6.75 (s, 4H, Mes).

$^{13}\text{C-NMR}$ (68 MHz, CDCl_3): $\delta = 18.6, 20.1, 21.0, 23.6, 23.8, 24.3, 24.6, 25.3, 26.6, 31.5, 35.4, 41.3, 45.8, 47.0, 98.9, 128.8, 129.0, 132.6, 133.3, 138.1, 138.4, 143.4, 144.1$. MS (EI): $m/z = 434 [M^+]$. HRMS: m/z Calc. for $C_{29}H_{42}OSi$: 434.3004. Found: 434.3010.

3.8. 8,8-Dimethyl-2,2-bis(2,4,6-trimethylphenyl)-1-oxa-2-silabicyclo[3.4.0]nonane (3g)

Colorless oil. IR (neat): 1051 cm^{-1} . $^1\text{H-NMR}$ (270 MHz, CDCl_3): $\delta = 0.92$ (s, 3H, Me), 1.03 (s, 3H, Me), 1.20–1.60 (m, 6H), 1.80–2.00 (m, 1H), 2.20 (s, 6H, Mes), 2.30–2.40 (m, 1H), 2.43 (s, 6H, Mes), 2.53 (s, 6H, Mes), 2.76 (m, 1H, CH_2CHCH_2), 3.49 (d, 1H, $J = 5.2$ Hz, SiOCH), 6.74 (s, 2H, Mes), 6.76 (s, 2H, Mes). $^{13}\text{C-NMR}$ (68 MHz, CDCl_3): $\delta = 21.0, 21.1, 21.4, 22.7, 23.9, 25.3, 25.9, 28.7, 32.9, 34.1, 35.4, 83.5, 128.8, 128.9, 133.6, 138.5, 138.8, 143.6, 143.8$. MS (EI): $m/z = 406 [M^+]$. HRMS: m/z Calc. for $C_{27}H_{38}OSi$: 406.2692. Found: 406.2649.

3.9. 6,6-Dimethyl-2,2-bis(2,4,6-trimethylphenyl)-1-oxa-2-silabicyclo[3.2.0]heptane (3h)

Colorless oil. IR (neat): 1072 cm^{-1} . $^1\text{H-NMR}$ (270 MHz, CDCl_3): $\delta = 0.74$ (s, 3H, Me), 1.11 (s, 3H, Me), 1.35 (dd, 1H, $J = 5.1, 7.6$ Hz, $\text{C}(\text{Me})_2\text{CHH}$), 1.40 (dd, 1H, $J = 6.2, 10.2$ Hz, SiCHH), 1.60 (dd, 1H, $J = 2.0, 10.2$ Hz, SiCHH), 1.74 (ddd, 1H, $J = 1.9, 7.6, 10.7$ Hz, $\text{C}(\text{Me})_2\text{CHH}$), 2.22 (s, 3H, Mes), 2.23 (s, 3H, Mes), 2.33 (s, 6H, Mes), 2.52 (s, 6H, Mes), 2.81 (dddd, 1H, $J = 2.0, 3.8, 5.1, 6.2, 10.7$ Hz, SiCH₂CH), 4.27 (dd, 1H, $J = 1.9, 3.8$ Hz, SiOCH), 6.74 (s, 2H, Mes), 6.79 (s, 2H, Mes). $^{13}\text{C-NMR}$ (68 MHz, CDCl_3): $\delta = 21.0, 21.2, 22.5, 23.0, 23.3, 24.5, 27.7, 32.0, 37.3, 39.3, 84.8, 128.8, 128.9, 133.0, 133.0, 138.7, 138.8, 143.5, 143.6$. MS (EI): $m/z = 379 [M^+]$. HRMS: m/z Calc. for $C_{25}H_{34}OSi$: 378.2379. Found: 379.2450.

3.10. 6-Cyclohexyl-2,2-bis(2,4,6-trimethylphenyl)-1-oxa-2-silabicyclo[3.2.0]heptane (3i)

Colorless oil. IR (neat): 1080 cm^{-1} . $^1\text{H-NMR}$ (270 MHz, CDCl_3): $\delta = 1.27$ –1.48 (m, 12H), 1.63 (dd, 1H, $J = 2.7, 15.4$ Hz, SiCHH), 1.85 (ddd, 1H, $J = 2.7, 8.6, 11.3$ Hz, $\text{C}(\text{C}_5\text{H}_{10})\text{CHH}$), 2.22 (s, 3H, Mes), 2.25 (s, 3H, Mes), 2.33 (s, 6H, Mes), 2.51 (s, 6H, Mes), 2.91 (dddd, 1H, $J = 2.7, 4.3, 5.1, 6.8, 11.3$ Hz, SiCH₂CH), 4.33 (dd, 1H, $J = 2.7, 4.3$ Hz, SiOCH), 6.75 (s, 2H, Mes), 6.79 (s, 2H, Mes). $^{13}\text{C-NMR}$ (68 MHz, CDCl_3): $\delta = 21.0, 21.6, 22.7, 22.8, 22.9, 23.0, 24.4, 26.2, 32.0, 32.9, 36.6, 37.9, 41.2, 83.6, 128.7, 128.9, 132.8, 133.2, 138.7, 143.6, 143.7$. MS (EI): $m/z = 418 [M^+]$. HRMS: m/z Calc. for $C_{28}H_{38}OSi$: 418.2692. Found: 418.2688.

3.11. 7,7-Dimethyl-2,2-bis(2,4,6-trimethylphenyl)-1-oxa-2-silabicyclo[3.3.0]-3-octene (**3j**)

Colorless oil. $^1\text{H-NMR}$ (270 MHz, CDCl_3): δ = 0.60 (s, 3H, Me), 1.11 (s, 3H, Me), 1.31–1.98 (m, 4H), 2.22 (s, 3H, Mes), 2.23 (s, 3H, Mes), 2.40 (s, 6H, Mes), 2.43 (s, 6H, Mes), 4.53 (s, 1H, SiOCH), 5.95 (s, 1H, SiCH), 6.75 (s, 4H, Mes).

3.12. 7,7-Dimethyl-2,2-bis(2,4,6-trimethylphenyl)-1,6-dioxo-2-silabicyclo[3.3.0]-3-octene (**3k**)

Colorless oil. IR (neat): 1051 cm^{-1} . $^1\text{H-NMR}$ (270 MHz, CDCl_3): δ = 0.90 (s, 3H, Me), 1.38 (s, 3H, Me), 2.23 (s, 6H, Mes), 2.41 (s, 6H, Mes), 2.43 (s, 6H, Mes), 4.26 (d, 1H, J = 14 Hz, $(\text{Me})_2\text{COCH}$), 4.66 (d, 1H, J = 14 Hz, $(\text{Me})_2\text{COCH}$), 4.75 (s, 1H, SiOCH), 6.19 (s, 1H, SiCHC), 6.77 (s, 4H, Mes). $^{13}\text{C-NMR}$ (68 MHz, CDCl_3): δ = 19.4, 21.0, 21.1, 22.8, 23.4, 26.3, 65.6, 69.3, 79.1, 90.0, 121.0, 128.8, 129.0, 131.8, 132.3, 139.3, 139.5, 143.3, 143.4, 163.9. MS (EI): m/z = 392 $[\text{M}^+]$. HRMS: m/z Calc. for $\text{C}_{25}\text{H}_{32}\text{O}_2\text{Si}$: 392.2172. Found: 392.2164.

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References

- [1] For selected reviews on 1,3-dipolar cycloaddition, see: (a) A. Padwa (Ed.) 1,3-Dipolar Cycloaddition Chemistry, vols. I and II, Wiley, New York, 1984 and references therein; (b) B.M. Trost, I. Fleming, (Eds.) Comprehensive Organic Synthesis, vol. 4, Pergamon Press, New York, 1991, pp. 1069–1168.
- [2] (a) For selected reviews and papers on carbonyl ylides, see: A. Padwa, J. Organomet. Chem. 617 (2001) 3; (b) A. Padwa, M.D. Weingarten, Chem. Rev. 96 (1996) 223 (and references therein); (c) A.F. Khlebnikov, M.S. Novikov, R.R. Kostikov, Adv. Heterocycl. Chem. 65 (1996) 93; (d) A. Padwa, Acc. Chem. Res. 24 (1991) 22; (e) N.J. Turro, Y. Cha, Tetrahedron Lett. 28 (1987) 1723; (f) T. Ibata, M.T.H. Liu, J. Toyoda, Tetrahedron Lett. 27 (1986) 4383; (g) T. Ibata, J. Toyoda, M. Sawada, T. Tanaka, J. Chem. Soc. Chem. Commun. (1986) 1266.; (h) M.E. Alonso, M.C. Garcia, A.W. Chitty, J. Org. Chem. 50 (1985) 3445; (i) P. de March, R. Huisgen, J. Am. Chem. Soc. 104 (1982) 4952; (j) M. Takebayashi, T. Ibata, K. Ueda, Bull. Chem. Soc. Jpn. 43 (1970) 1500.
- [3] (a) For selected examples of trapping of silylenes with carbonyl compounds, see: A.K. Franz, K.A. Woerpel, J. Am. Chem. Soc. 121 (1999) 949; (b) J. Belzner, H. Ihmels, Adv. Organomet. Chem. 43 (1998) 1; (c) B. Gehrhus, P.T. Hitchcock, M.F. Lappert, Organometallics 16 (1997) 4861; (d) J. Belzner, H. Ihmels, L. Pauletto, M. Noltemeyer, J. Org. Chem. 61 (1996) 3315; (e) P. Jutzi, D. Eikenberg, A. Mohrke, B. Neumann, H.-G. Stammler, Organometallics 15 (1996) 753; (f) P. Jutzi, D. Eikenberg, E.-A. Bunte, A. Mohrke, B. Neumann, H.-G. Stammler, Organometallics 15 (1996) 1930; (g) J.W. Heinicke, B. Gehrhus, Heteroatom Chem. 6 (1995) 461; (h) W. Ando, K. Hagiwara, A. Sekiguchi, Organometallics 6 (1987) 2270; (i) W. Ando, Y. Hamada, A. Sekiguchi, J. Chem. Soc. Chem. Commun. 952 (1983).; (j) W. Ando, M. Ikeno, A. Sekiguchi, J. Am. Chem. Soc. 100 (1978) 3613.
- [4] For example, see: E. Lukevics, L. Ignatovich, Appl. Organomet. Chem. 6 (1992) 113.
- [5] N. Sakai, T. Fukushima, S. Minakata, I. Ryu, M. Komatsu, J. Chem. Soc. Chem. Commun. 1857 (1999).
- [6] For selected review on intramolecular 1,3-dipolar cycloaddition, see: M. Trost, I. Fleming (Eds.), Comprehensive Organic Synthesis, vol. 4, Pergamon Press, New York, 1991, pp. 1111–1168.
- [7] A. Dijca, C.D. Hubbard, R. van Eldik, T. Asano, M.V. Basilevsky, W.J. li Noble, Chem. Rev. 98 (1998) 2167.
- [8] M. Ishikawa, M. Kumada, Adv. Organomet. Chem. 19 (1981) 51 (and references therein).
- [9] M.R. Hale, A.H. Hoveyda, J. Org. Chem. 57 (1992) 1643.