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Reactions of an Isolable Dialkylsilylene with Ketones[†]

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Received May 14, 2010

The reactions of isolable dialkylsilylene 2,2,5,5-tetrakis(trimethylsilyl)-1-silacyclopentane-1,1-diyl with different types of ketones such as adamantanone, acetone, benzophenone, and cyclopropanones proceed smoothly at room temperature to afford the corresponding siloxirane, silyl enol ether, 2-oxasilacyclopentene, and unusual cyclopropenylsilanes, respectively, without formation of any secondary or side-reaction products. The electronic structure of various types of model carbonyl silaylides was investigated using DFT calculations. The diversity of the reaction modes is explained by invoking the substituent effects on the electronic nature of the initially formed carbonyl silaylides.

Introduction

A number of organosilylenes (divalent organosilicon compounds) have been generated as transient species since the discovery of dimethylsilylene extrusion via high-temperature thermolysis of dibenzo-7-silanorbornadienes by Gilman et al. more than 40 years ago.^{1,2} Among useful methods for the generation of dimethylsilylene are the thermolysis of 1,2-dimethoxytetramethyldisilane at 225 °C³ and hexamethylsilirane at > 60 °C⁴ and photolysis of linear and cyclic permethylpolysilanes at lower temperatures.⁵ A

number of substituted silylenes such as di-*tert*-butylsilylene,⁶ phenylmethylsilylene,⁷ diphenylsilylene,⁸ and other diarylsilylenes⁹ are also available as transient silylenes using related methods as above. It is therefore natural that the reactions of the transient silylenes with aldehydes and ketones have been investigated extensively by many authors¹⁰ since the late 1970s as one of the fundamental reactions of silylenes. The reactions were found however not to be straightforward, giving diverse types of final products depending on the structures of silylenes and carbonyl compounds. Typically, Ando et al. have found that the reactions of thermally or photochemically generated dimethylsilylene with benzophenone^{10a} and adamantanone^{10b} afford mainly 1-sila-2-oxa-4,5-benzocyclopentene **1** and a mixture of 1:2- and 2:2-cycloadducts (**2** and **3**), respectively. Siloxirane **4** was isolated through the reaction of photochemically generated dimesitylsilylene with 1,1,3,3-tetramethyl-2-indanone, and its structure was determined by X-ray crystallography.^{10d,11} Belzner

[†] Part of the Dietmar Seyferth Festschrift. Dedicated to Professor Dietmar Seyferth in honor of his outstanding contributions as Editor-in-Chief of *Organometallics*.

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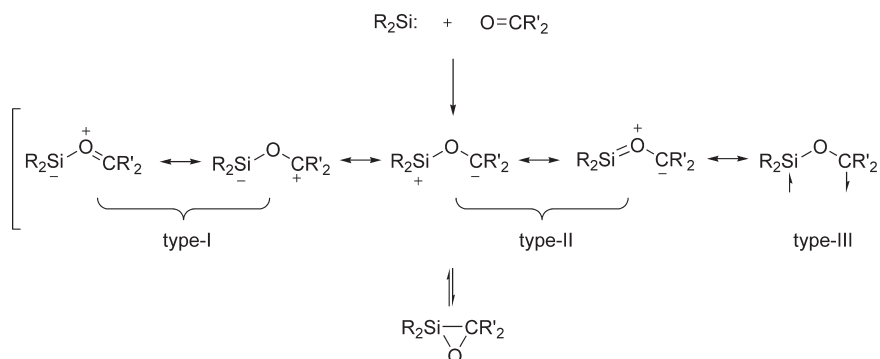
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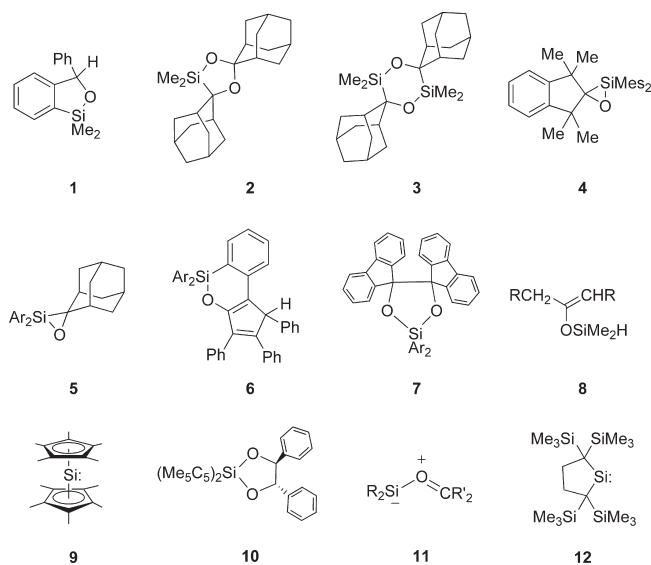
Scheme 1



et al. have reported that the reaction of a diarylsilylene, bis[2-((dimethylamino)methyl)phenyl]silylene ($\text{Ar}_2\text{Si:}$), with adamantanone gives the corresponding siloxirane **5** as an isolable compound.^{10j} They found that the reactions of $\text{Ar}_2\text{Si:}$ with tetraphenylcyclopentadienone and fluorenone gave **6** and **7**, respectively, as major products. Enolizable ketones have been reported to react with various silylenes, giving the corresponding silyl enol ethers such as **8**.^{10a,h,12a} Jutzi et al. have found that decamethylsilicocene **9**, the first stable divalent silicon(II), gives 1,3-dioxasilolane **10** during the reaction with benzaldehyde.^{10k} Although **2**, **7**, and **10** are all 1:2 cycloadducts, the ring structure of **7** and **10** is isomeric to that of **2**. Recently, a number of interesting and useful synthetic reactions via the addition of dimesitylsilylene¹² and di-*tert*-butylsilylene¹³ to various carbonyl compounds have been explored.

Among reaction mechanisms proposed, those involving intermediary formation of the corresponding carbonyl silaylides **11** are dominant, and actually, the existence of a carbonyl silaylide has been evidenced spectroscopically during the reaction of dimesitylsilylene with 1,1,3,3-tetramethyl-2-indanone in low-temperature matrices.^{10g} However, the origin of the diversity of the reactions has not yet been well discussed until now. To draw an entire picture of the reactions of silylenes with carbonyl compounds, the electronic structure of carbonyl silaylides, especially its dependence on the substituents on silicon and carbon atoms in the skeleton, should be elucidated. As shown in Scheme 1, we can expect that five resonance forms contribute to the electronic struc-

Chart 1



ture of a carbonyl silaylide as a silicon congener of carbonyl ylide,^{15,16} a well-known 1,3-dipole. The five forms are classified into three types: type I, with nucleophilic silicon; type II, with electrophilic silicon; and type III with a 1,3-biradical nature. The relative importance among types I–III may depend on the electronic nature of silylenes and ketones, although only type I is usually used for descriptive purposes. The carbonyl silaylide may be equilibrated with the corresponding siloxirane. These factors should influence the diversity of the reaction modes.

Because isolable dialkylsilylene **12** (Chart 1), which is sterically well protected but electronically similar to dimethylsilylene, is now available,¹⁷ we have had an opportunity to investigate the reactions of **12** with different types of ketones such as adamantanone, acetone, benzophenone, and two cyclopropanones. All the reactions proceed smoothly at room temperature to afford single products in high yields without formation of any secondary or

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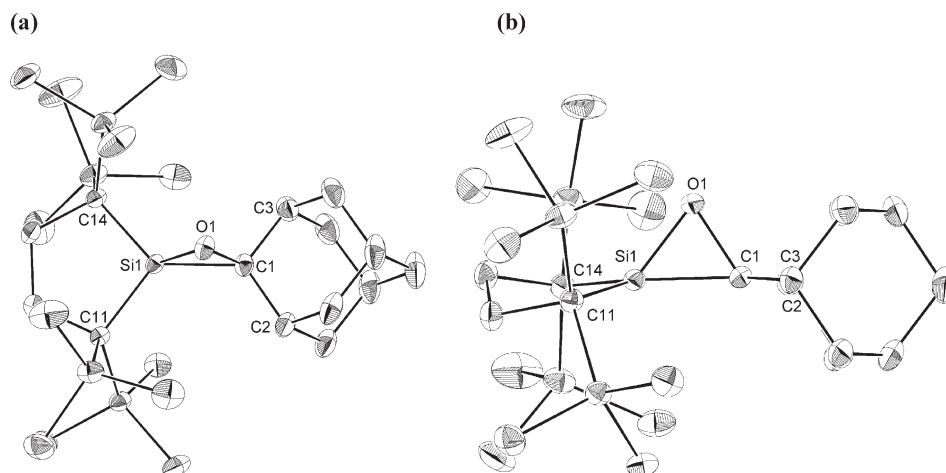


Figure 1. ORTEP drawing of siloxirane **13**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1–C1 = 1.849(2), Si1–O1 = 1.666(1), C1–O1 = 1.523(2), Si1–C11 = 1.881(2), Si1–C14 = 1.894(2), C1–C2 = 1.528(2), C1–C3 = 1.529(2); Si1–O1–C1 = 70.71(8), C1–Si1–O1 = 51.03(6), O1–C1–Si1 = 58.26(7).

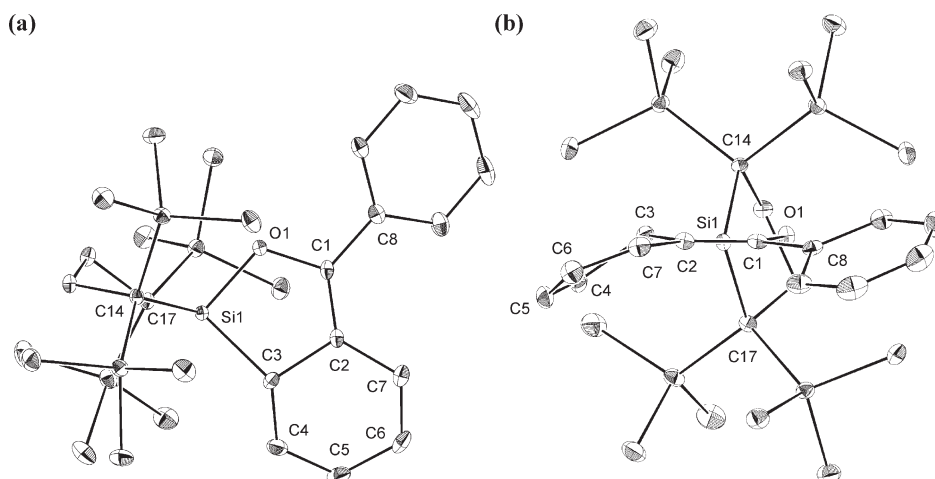


Figure 2. ORTEP drawing of **15**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1–C3 = 1.908(3), Si1–O1 = 1.701(2), C1–O1 = 1.380(3), Si1–C14 = 1.891(3), Si1–C17 = 1.892(3), C1–C2 = 1.352(4), C1–C8 = 1.469(4), C2–C3 = 1.527(4), C2–C7 = 1.451(4), C3–C4 = 1.500(4), C4–C5 = 1.335(4), C5–C6 = 1.451(5), C6–C7 = 1.337(4); O1–Si1–C3 = 92.4(1), Si1–O1–C1 = 113.4(2), O1–C1–C2 = 116.1(2), C1–C2–C3 = 115.0(3), C2–C1–C8 = 130.6(3), Si1–C3–C2 = 102.0(2), C2–C3–C4 = 110.5(2), Si1–C3–C4 = 125.5(2).

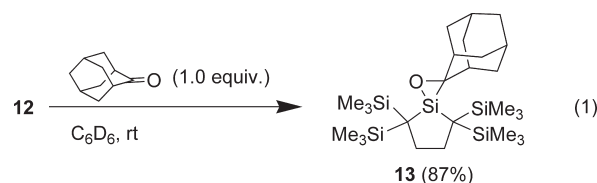
side-reaction products. With the hope of understanding the origin of the diversity, the electronic structure of various model carbonyl silaylides has been investigated using DFT calculations.

The preparation of carbonyl silaylides through the addition of silylenes to carbonyl compounds would be less limited than that of carbonyl ylides, which are usually generated by the ring-opening of the corresponding oxiranes with electron-withdrawing substituents^{15a} and by the transition-metal-catalyzed reactions of diazomethane derivatives with carbonyl compounds.^{15b,c}

Results

Reaction of 12 with Adamantanone. Dialkylsilylene **12** reacted with an equimolar amount of adamantanone at room temperature in benzene to give siloxirane **13** as the sole product (eq 1). Compound **13** was very stable toward water and oxygen and remained intact more than 3 years in

the air probably due to effective steric protection around the siloxirane ring.



The structure of **13** was determined by ¹H, ¹³C, and ²⁹Si NMR spectroscopies, elemental analysis, and X-ray crystallography. The molecular structure of **13** determined by X-ray analysis is shown in Figure 1. The structural parameters for the central siloxirane ring are almost the same as those found for **4**;^{10d} the Si–C, Si–O, and C–O bond lengths in the siloxirane ring are 1.849(2), 1.666(1), and 1.523(2) Å, respectively, and the C–Si–O, Si–C–O, and C–O–Si bond angles are 51.03(6)°, 58.26(7)°, and 70.71(8)°. Interestingly,

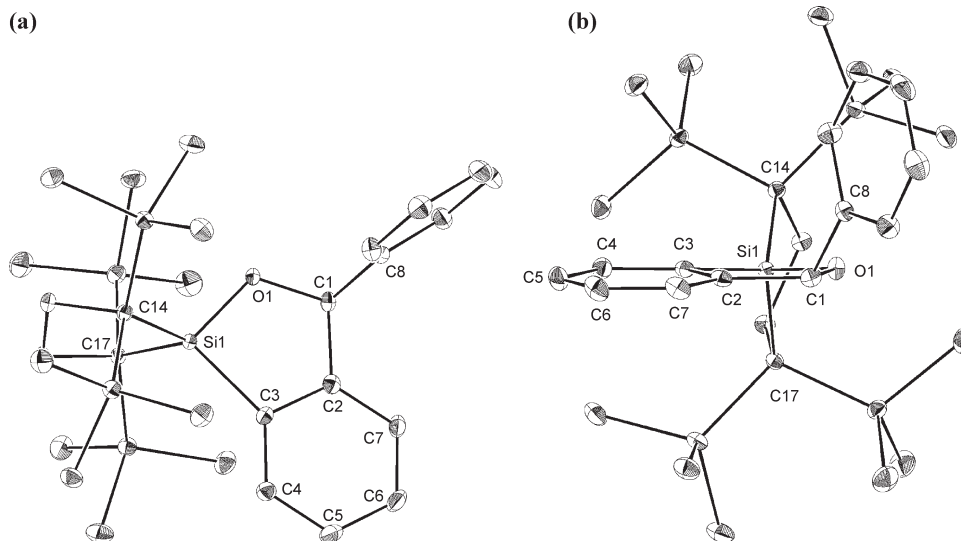
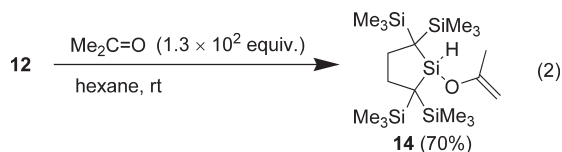


Figure 3. ORTEP drawing of **16**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1–C3 = 1.893(2), Si1–O1 = 1.670(1), C1–O1 = 1.432(2), Si1–C14 = 1.903(2), Si1–C17 = 1.892(2), C1–C2 = 1.514(3), C1–C8 = 1.515(3), C2–C3 = 1.400(3), C2–C7 = 1.394(3), C3–C4 = 1.398(3), C4–C5 = 1.387(3), C5–C6 = 1.392(3), C6–C7 = 1.376(3); O1–Si1–C3 = 91.90(7), Si1–O1–C1 = 117.0(1), O1–C1–C2 = 107.9(2), C1–C2–C3 = 115.8(2), C2–C1–C8 = 112.1(2), Si1–C3–C2 = 106.7(1), C2–C3–C4 = 117.4(2), Si1–C3–C4 = 135.6(2).

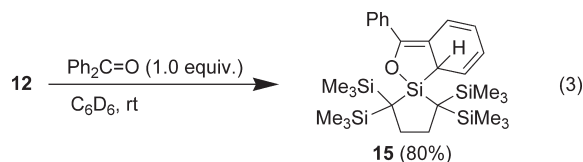
not only are the C11–Si1–C14 plane and the C2–C1–C3 plane in the trispiro compound perpendicular to the central siloxirane ring, but these two planes are almost coplanar together with the Si1–C1 bond in the central ring; the sum of bond angles except for oxygen bonds around Si1 and C1 is 358.71(6)° and 359.64(12)°, respectively. The angle between the planes C11–Si1–C14 and C2–C1–C3 is 15.80°. In addition to the severe steric repulsion between bulky substituents on Si1 and C1, an increased π -complex character between the Si=C double bond and negative O may contribute to its origin, although the ring Si–C and Si–O bond lengths are normal.¹⁸

Reaction of 12 with Acetone. The reaction of silylene **12** with a large excess acetone at room temperature in hexane gave the corresponding silyl enol ether **14** in a high yield (eq 2), similarly to the reactions of dimethylsilylene and dimethylsilylene with acetone and other enolizable ketones.^{10a,12a} The structure was determined using ¹H, ¹³C, and ²⁹Si NMR, MS, and elemental analysis.

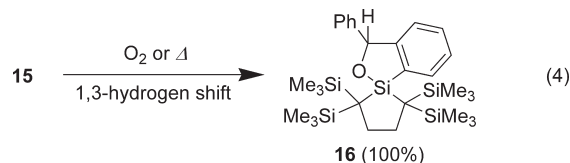


Reaction of 12 with Benzophenone. The reaction of silylene **12** with an equimolar amount of benzophenone at room temperature in benzene gave 2-oxasilacyclopentene **15** as yellow crystals (eq 3). The structure of **15** was unequivocally determined by X-ray structural analysis. As shown in Figure 2, the molecular structure of **15** was characterized especially by the shorter C1–C2, C4–C5, and C6–C7 bond lengths [1.352(4), 1.335(4), and 1.337(4) Å], longer C2–C3, C2–C7, and C3–C4 bond lengths [1.527(4), 1.451(4), and 1.500(4) Å], and planarity around the C1 atom [sum of bond angles

around C1 = 359.9(7)°]. Obviously, an aromatic ring in benzophenone is destroyed in the product **15**.



The reaction mode is similar to that for the addition of transient silylenes to benzophenone,^{10a,j} while usually the corresponding aromatized products are obtained in the latter. Compound **15** was able to be stored in a refrigerator in a glovebox but was not very stable toward oxygen and moisture, isomerizing gradually to aromatized product **16** at room temperature (eq 4). The molecular structure of compound **16** was determined by X-ray crystallography as shown in Figure 3. A similar type of cyclic adduct to **15** was obtained by Jutzi et al.^{10k} during the reactions of decamethylsilicocene with benzophenone and benzaldehyde, but the adducts are reported not to aromatize through 1,3-hydrogen migration even if they were heated at 100 °C for 6 days.



Reaction 12 with Di(*tert*-butyl)- and Diphenylcyclopropanones. The reaction of silylene **12** with an equimolar amount of di(*tert*-butyl)cyclopropanone at room temperature in benzene gave the quite unusual product **17** as a single product. Although there are two chiral centers in **17**, only the *R**,*R**-isomer was obtained (eq 5). Similarly, the reaction of **12** with diphenylcyclopropanone produced adduct **18** with the same stereochemistry as that of **17** (eq 6). The structure of **17** and **18** is rather unexpected but was confirmed by ¹H, ¹³C, and ²⁹Si NMR spectroscopies, MS, and

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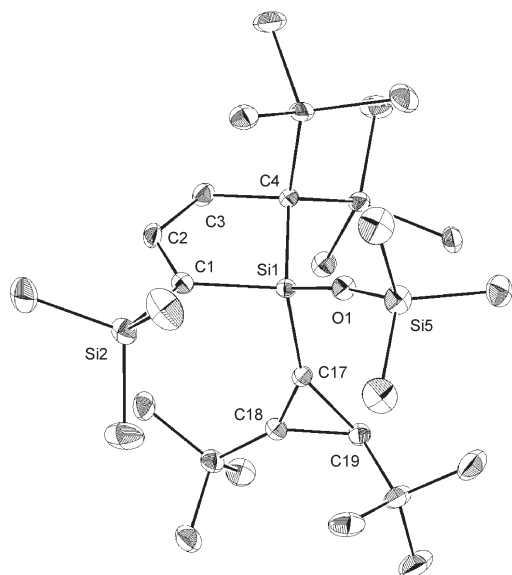
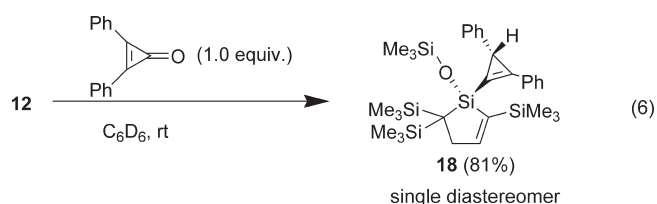
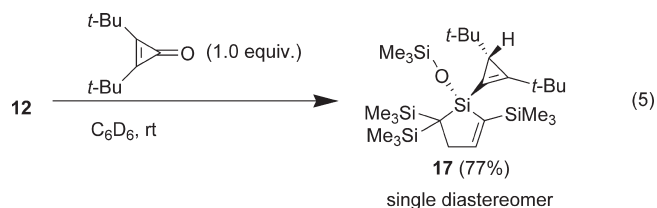


Figure 4. ORTEP drawing of **17**. One of the three crystallographically independent molecules (**17A**) is shown. The other molecular structures of **17** are described in the Supporting Information. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1–O1 = 1.618(2), Si1–C17 = 1.856(3), Si1–C1 = 1.861(3), Si1–C4 = 1.889(3), C1–C2 = 1.337(5), C2–C3 = 1.521(5), C3–C4 = 1.578(4), Si5–O1 = 1.640(2), C17–C18 = 1.309(4), C18–C19 = 1.480(4), C17–C19 = 1.550(4); C1–Si1–C4 = 114.0(1), Si1–O1–Si5 = 172.0(2).

finally X-ray crystallography. The reaction mechanism for formation of **17** and **18** is not straightforward and should involve the migration of a trimethylsilyl group on dialkylsilylene **12**. The mechanism is discussed in detail in the following section.



Single crystals of **17** and **18** suitable for X-ray crystallography were obtained by the recrystallization from THF. There were three crystallographically independent molecules (**17A**, **17B**, and **17C**) in an asymmetric unit of a single crystal of **17**, and disorder was observed in a molecule of **17C** (**17C**:**17C'** = 81:19). The molecular structures of **17A** and **18** are shown in Figures 4 and 5. The detailed discussion of the X-ray structures of **17** is given in the Supporting Information.

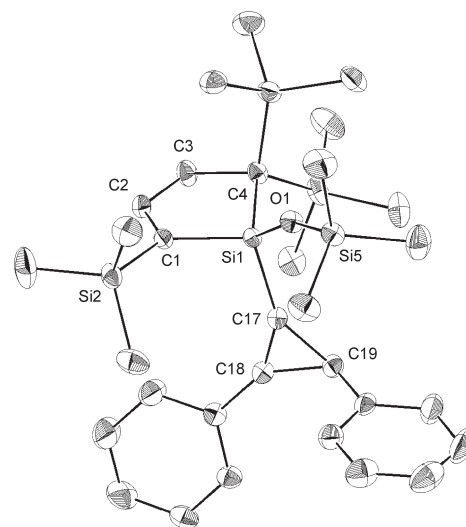


Figure 5. ORTEP drawing of **18**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1–O1 = 1.620(1), Si1–C17 = 1.850(2), Si1–C1 = 1.856(2), Si1–C4 = 1.887(2), C1–C2 = 1.336(2), C2–C3 = 1.507(3), C3–C4 = 1.582(3), Si5–O1 = 1.639(2), C17–C18 = 1.303(3), C18–C19 = 1.491(3), C17–C19 = 1.552(3); C1–Si1–C4 = 96.49(9), Si1–O1–Si5 = 159.1(1).

Discussion

Several interesting issues emerge about the structural discussion of the carbonyl silylides that will play key roles in the reactions of silylenes with ketones: (1) Is there a facile equilibrium between a carbonyl silylide, the corresponding siloxirane, and a set of its fragments, silylene + ketone? (2) Is there any significant substituent dependence of the geometric and electronic structure of the carbonyl silylide? (3) Do the substituents on the carbonyl silylide affect the reaction modes? To obtain a basic idea about the electronic structures of carbonyl silylides, we have performed DFT calculations for model carbonyl silylides, dimethylcyclopropanone (**19a**), acetone (**19b**), acetophenone (**19c**), benzophenone (**19d**), and cyclopentadienone silylide (**19e**), and the related singlet carbonyl ylide **20** at the theoretical level of B3LYP/6-31+G-(d) (Chart 2),¹⁹ where the electron-withdrawing ability of the substituents on the skeletal carbon atom increases in the order **19a** < **19b** < **19c** < **19d** < **19e**; a phenyl group is more electron-accepting than a methyl group, and the important contribution of the following resonance forms exists for cyclopropanone and cyclopentadienone (Chart 3). The structural parameters of **19a**–**19e** and **20** and their energies relative to the corresponding siloxiranes **19a'**–**19e'** and **20'** are compared in Table 1.

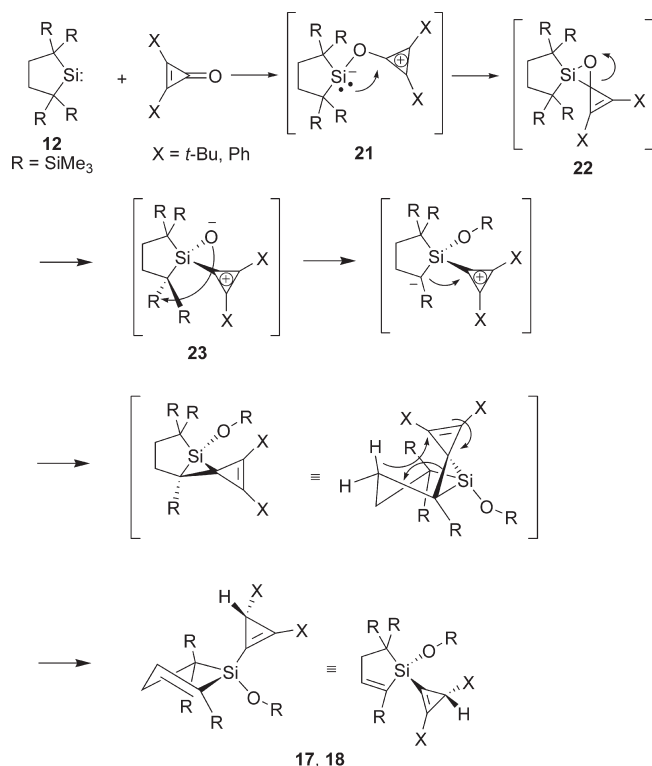
Our theoretical calculations indicate that the ring closure of carbonyl silylides **19b**–**19e** to the corresponding siloxiranes **19b'**–**19e'** is more than 20 kcal/mol exothermic. Siloxirane **19a'** expected for the cyclization of cyclopropenyl-substituted carbonyl silylide **19a** was not located as a local minimum in our calculations. Instead, the corresponding ring-opened silyloxide **19a''** was found as a minimum (eq 7). Silyloxide **19a''** would be more stable than siloxirane

(19) All calculations were carried out with Gaussian 03 package programs; full reference of Gaussian 03 is shown in the Supporting Information.

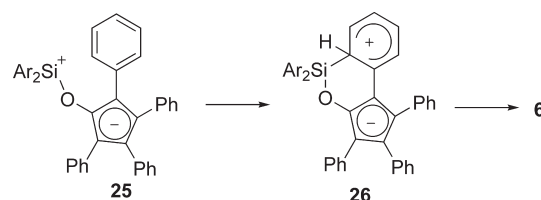
Table 1. Selected Structural Parameters of **19a**–**19e** and **20** and Their Relative Energies Calculated at the B3LYP/6-31G+(d) Level

ylide	$d(\text{Si}-\text{O})/\text{\AA}$	$d(\text{C}-\text{O})/\text{\AA}$	$\sum @\text{Si}^d/\text{deg}$	Mulliken group charge			$\Delta E/(\text{kcal/mol})^e$
				Si ^b	O ^c	C ^d	
19a	2.049	1.245	283.4	−0.14	−0.69	+0.57	−25.58 ^f
19b	1.897	1.259	293.5	−0.05	−0.36	+0.39	−25.67
19c	1.810	1.283	302.7	+0.05	−0.23	+0.19	−22.40
19d	1.767	1.285	306.7	+0.07	−0.19	+0.12	−23.62
19e	1.691	1.312	325.4	+0.35	−0.24	−0.11	−22.12
20	1.328 ^g	1.328	352.0 ^h	+0.11 ⁱ	−0.22	+0.11	−44.18 ^j

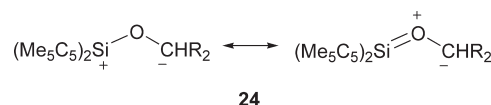
^a Sum of bond angles around the silicon atom unless otherwise noted. ^b Group charge of the Me₂Si moiety. ^c Atomic charge on oxygen. ^d Group charge of the R₂C moiety. ^e $E_{\text{total}}(\mathbf{19}) - E_{\text{total}}(\mathbf{19}')$ in kcal/mol unless otherwise noted. ^f The siloxirane was not found as a local minimum. Instead, an intramolecular ion pair **19a''** formed via the C–O bond cleavage of the siloxirane was located as an energy minimum. The ΔE is given as that based on the energy of **19a''**. ^g $d(\text{C}-\text{O})/\text{\AA}$. ^h Sum of bond angles around the carbonyl ylide carbon. ⁱ Group charge of the Me₂C moiety. ^j Energy (kcal/mol) of **20** based on the corresponding oxiranes.

Scheme 2

Notably, the regioselectivity of the 1:2 adducts **7** and **10** (Scheme 1) has been reported to be different from that of **2**. These three adducts are regarded to form via the [2+3] cycloaddition between carbonyl and carbonyl silyl ylide. The reversed regioselectivity of **7** and **10** compared with that of **2** is compatible with the inversed polarity of the cyclopentadienylidene-substituted carbonyl silyl ylide **19e**. In a carbonyl silyl ylide formed from the reaction of (Me₅C₅)₂Si,^{10k}

Scheme 3

the resonance forms **24** similar to type II in Scheme 1 may be predominant due to the cation-stabilizing effects of the Cp rings, although steric effects also favor the observed regioselectivity.²¹



Formation of six-membered silacycle **6** (Scheme 3) by the reaction of Ar₂Si⁺ with tetraphenylcyclopentadienone^{10j} is not unexpected if the corresponding carbonyl silyl ylide has a strong contribution of type II resonance forms in Scheme 1, i.e., if it is represented by the structure **25**. Intramolecular electrophilic aromatic addition of silyl cations in **25** to a neighboring phenyl substituent will lead to **6** via an intermediate **26**.²²

The reaction of silylene **12** with acetone gave the corresponding silyl enol ether **14** as the sole product, suggesting that the reaction is more rapid than the competitive cyclization into the corresponding siloxirane. Although the preferred formation of the silyl enol ethers is common for the reaction of enolizable ketones with dimethylsilylene, dimethylsilylene, etc., no such reaction has been found for (Me₅C₅)₂Si,^{10k} which is reported to give typically a cyclic compound with a similar ring structure to **7** by the reaction with acetone. The results may suggest that a silyl enol ether is formed via the [2+3] reaction between the corresponding carbonyl silyl ylide and an intramolecular C–H bond, and the reaction requires the strong contribution of type I resonance forms (Scheme 1) in the carbonyl silyl ylide because of the C(−)–H(+) polarity (Scheme 4).

Conclusion

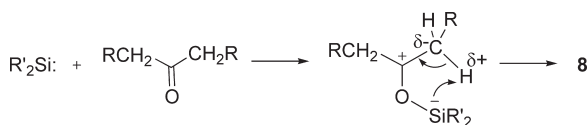
The reactions of isolable dialkylsilylene **12** with adamantane, acetone, and benzophenone proceed smoothly at

(20) (a) Eaborn, C.; Safa, K. D. *J. Organomet. Chem.* **1982**, 234, 7. (b) Damrauer, R.; Eaborn, C.; Happer, D. A. R.; Mansour, A. I. *J. Chem. Soc., Chem. Commun.* **1983**, 348. (c) Al-Mansour, A. I.; Al-Gurashi, M. A. M. R.; Eaborn, C.; Fattah, F. A.; Lickiss, P. D. *J. Organomet. Chem.* **1990**, 393, 27. A review: Kira, M.; Iwamoto, T. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John-Wiley: Chichester, 2001; Vol. 3, p 853.

(21) The origin of the regioselectivity and stereoselectivity for the 1:2 adducts may be more complicated than that proposed here. Woerpel et al. have reported that the regioselectivity for the 1:2 adducts obtained by the reactions of metal-coordinated di-*tert*-butylsilylene with benzaldehyde and *n*-butanal is different from each other.^{13h} In addition, the stereochemistry between two phenyl groups in the former adduct is *syn*, while it is *anti* in **10**^{10k} (Chart 1).

(22) Aromatic electrophilic substitution of silyl cations has been reported recently by Kawashima et al.: Furukawa, S.; Kobayashi, J.; Kawashima, T. *J. Am. Chem. Soc.* **2009**, 131, 14192.

Scheme 4



room temperatures to afford the corresponding siloxirane, silyl enol ether, and 2-oxa-silacyclopentene without formation of any secondary or side-reaction products. The diverse reaction modes are similar to those found previously in the reactions of dimethylsilylene and related organosilylenes. Rather unexpectedly, the reactions of **12** with di-*tert*-butyl- and diphenylcyclopropanones in similar reaction conditions to those above afford cyclopropenylsilanes **17** and **18** involving the migration of a trimethylsilyl group in **12** to the cyclopropanone oxygen. DFT calculations for various types of carbonyl silylides, possible intermediates of the reactions, revealed the remarkable substituent effects on the electronic structure; the silicon atom in the carbonyl silylides is either nucleophilic or electrophilic depending on the substituents on the skeletal carbon atom. The diversity of the reactions of organosilylenes including **12** with different carbonyl compounds is in accord with the diverse nature of the carbonyl silylides. Further works including the search for the transition states will be required for elucidating the detailed reaction mechanisms of these reactions.

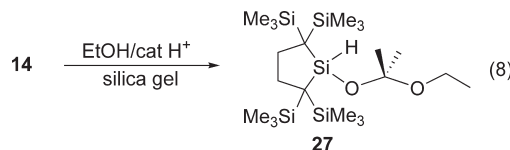
Experimental Section

All synthetic experiments were performed under argon or nitrogen in a standard vacuum system unless otherwise noted. ^1H (300 MHz), ^{13}C (75 MHz), and ^{29}Si (59 MHz) NMR spectra were recorded on a Bruker AC-300P spectrometer. Mass spectra were obtained on a JEOL JMS-600W mass spectrometer. Sampling of silylene **12** and other air-sensitive materials was carried out in a VAC MO-40-M glovebox. Di(*tert*-butyl)-cyclopropanone²³ was prepared according to a literature procedure. Adamantanone and benzophenone were sublimed under reduced pressure prior to use.

Reaction of Silylene 12 with Adamantanone. In an NMR tube, silylene **1** (59 mg, 0.16 mmol) and adamantanone (27 mg, 0.16 mmol) were placed and then deoxygenated. Dry benzene- d_6 (0.5 mL) was transferred to the tube by using a vacuum line. After the color of the solution disappeared, NMR spectra were recorded. Quantitative formation of siloxirane **13** was evidenced by NMR spectroscopies. Analytically pure **13** was obtained in 87% yield (73 mg, 0.14 mmol) by HPLC (ethanol). Single crystals suitable for X-ray crystallography were obtained by recrystallization from ethanol. **13**: colorless crystals; mp 200 °C; ^1H NMR (C_6D_6 , δ) 0.23 (s, 18H), 0.30 (s, 18H), 1.51–1.62 (brs, 2H), 1.74 (brs, 2H), 1.80–1.95 (m, 8H), 2.05–2.10 (m, 4H), 2.70–2.75 (brs, 2H); ^{13}C NMR (C_6D_6 , δ) 2.5 (SiMe₃), 3.2 (SiMe₃), 5.9 (C), 27.4 (CH), 28.4 (CH), 32.1 (CH₂), 33.8 (CH₂), 36.5 (CH₂), 37.2 (CH), 38.1 (CH₂), 74.2 (C); ^{29}Si NMR (C_6D_6 , δ) 2.4 (SiMe₃), 4.4 (SiMe₃), 4.7 (Si); MS (70 eV, EI) m/z (%) 507 ($\text{M}^+ - 15$, 2), 373 (46), 299 (35), 225 (21), 135 (100), 73 (69). Anal. Calcd for $\text{C}_{26}\text{H}_{54}\text{OSi}_5$: C, 59.69; H, 10.40. Found: C, 59.43; H, 10.28.

Reaction of Silylene 12 with Acetone. To silylene **12** (83 mg, 0.22 mmol) in a Schlenk tube (10 mL) was transferred dried and deoxygenated acetone (10 mL). After the yellow color of the silylene in the solution disappeared, volatiles were removed in

vacuo. Silyl-enol ether **14** was isolated in 70% yield (66 mg, 0.15 mmol). An attempted isolation of **14** by HPLC using ethanol as eluent failed, because during the HPLC procedure compound **14** was converted to **27** quantitatively probably due to the addition of ethanol to **14** catalyzed by a small amount of acid in the silica gel column (eq 8). Analytically pure **12** was obtained by GPC (toluene). **14**: colorless crystals; mp 76 °C; ^1H NMR (C_6D_6 , δ) 0.21 (s, 18H), 0.30 (s, 18H), 1.75 (s, 3H), 1.70–2.05 (m, 4H), 4.12 (brs, 1H), 4.36 (brs, 1H), 5.60 (brs, 1H); ^{13}C NMR (C_6D_6 , δ) 2.6 (SiMe₃), 3.3 (SiMe₃), 9.5 (C), 32.2 (CH₂), 43.6 (CH₃), 90.4 (CH₂), 156.7 (C); ^{29}Si NMR (C_6D_6 , δ) 2.9 (SiMe₃), 3.5 (SiMe₃), 18.5 (Si); MS (70 eV, EI) m/z 430 (M^+ , 11), 415 ($\text{M}^+ - 15$, 18), 387 (40), 373 (90), 73 (100). Anal. Calcd for $\text{C}_{19}\text{H}_{46}\text{OSi}_5$: C, 52.95; H, 10.76. Found: C, 53.02; H, 10.70.



27: colorless crystals; mp 85 °C; ^1H NMR (C_6D_6 , δ) 0.26 (s, 18H), 0.33 (s, 18H), 1.13 (t, $J = 7.1$ Hz, 3H), 1.38 (s, 6H), 1.90–2.00 (m, 4H), 3.30 (q, $J = 7.1$ Hz, 2H), 5.51 (s, 1H); ^{13}C NMR (C_6D_6 , δ) 2.6 (SiMe₃), 3.6 (SiMe₃), 8.5 (C), 15.9 (CH₂CH₃), 27.5 (CH₃), 32.1 (CH₂), 58.5 (OCH₂CH₃), 101.3 (C); ^{29}Si NMR (C_6D_6 , δ) 2.5 (SiMe₃), 3.7 (SiMe₃), 7.4 (Si); MS (70 eV, EI) m/z (%) 476 (M^+ , 1), 461 (2), 403 (5), 373 (9), 232 (13), 73 (100). Anal. Calcd for $\text{C}_{21}\text{H}_{52}\text{O}_2\text{Si}_5$: C, 52.87; H, 10.99. Found: C, 52.58; H, 11.23.

Reaction of Silylene 12 with Benzophenone. The reaction of **12** (166 mg, 0.45 mmol) with benzophenone (79 mg, 0.45 mmol) was performed in a similar manner to the reaction of **12** with adamantanone. Compound **15** was obtained as yellow crystals in 80% yield (199 mg, 0.36 mmol). **15**: pale yellow crystals; ^1H NMR (C_6D_6 , δ) 0.170 (s, 9H), 0.171 (s, 9H), 0.27 (s, 9H), 0.29 (s, 9H), 1.72–2.15 (m, 4H), 3.77 (brs, 1H), 5.75 (m, 1H), 6.02 (m, 1H), 6.24 (m, 1H), 6.76 (m, 1H), 7.04–7.25 (m, 5H); ^{13}C NMR (C_6D_6 , δ) 3.6 (SiMe₃), 3.7 (SiMe₃), 4.0 (SiMe₃), 4.8 (SiMe₃), 10.0 (C), 16.6 (C), 32.4 (CH₂), 33.6 (CH₂), 34.0 (CH), 115.2 (C), 122.6 (CH), 124.8 (CH), 125.7 (CH), 125.8 (CH), 128.6 (CH), 128.5 (CH), 128.3 (CH), 135.3 (C), 150.2 (C); ^{29}Si NMR (C_6D_6 , δ) 1.0 (SiMe₃), 2.0 (SiMe₃), 4.17 (SiMe₃), 4.21 (SiMe₃), 57.2 (Si). Compound **15** was stored intact for a long time in a refrigerator in a glovebox but reacted with oxygen and moisture to gradually isomerize into **16** at room temperature. **16**: colorless crystals; mp 174–176 °C; ^1H NMR (C_6D_6 , δ) 0.10 (s, 9H), 0.11 (s, 9H), 0.18 (s, 9H), 0.31 (s, 9H), 2.02–2.13 (m, 4H), 6.17 (s, 1H), 6.92 (d, $J = 7.2$ Hz, 1H), 7.00–7.15 (m, 5H), 7.25 (m, 2H), 7.99 (d, $J = 7.2$ Hz, 1H); ^{13}C NMR (C_6D_6 , δ) 4.1 (SiMe₃), 4.2 (SiMe₃), 4.23 (SiMe₃), 4.24 (SiMe₃), 13.1 (C), 14.1 (C), 32.6 (CH₂), 33.2 (CH₂), 83.0 (CH), 124.9 (CH), 126.9 (CH), 127.7 (CH), 128.5 (C), 129.3 (CH), 129.8 (CH), 134.2 (CH), 136.9 (CH), 142.8 (C), 152.4 (C); ^{29}Si NMR (C_6D_6 , δ) 1.9 (SiMe₃), 2.6 (SiMe₃), 3.5 (SiMe₃), 3.9 (SiMe₃), 41.1 (Si); MS (70 eV, EI) m/z (%) 554 (M^+ , 18), 539 (17), 341 (42), 105 (42), 73 (100). Anal. Calcd for $\text{C}_{29}\text{H}_{50}\text{OSi}_5$: C, 62.74; H, 9.08. Found: C, 62.97; H, 9.15.

Reaction of Silylene 12 with Di(*tert*-butyl)cyclopropanone. Reaction of silylene **12** (85 mg, 0.23 mmol) with di(*tert*-butyl)cyclopropanone (41 mg, 0.23 mmol) was performed in a similar manner to the reaction of **12** with adamantanone. Compound **17** was obtained in 77% yield (99 mg, 0.18 mmol). When monitored by NMR, the reaction was very clean and no other products than **17** appeared during the reaction. **17**: colorless crystals; mp 65–68 °C; ^1H NMR (C_6D_6 , δ) 0.14 (s, 9H), 0.17 (s, 9H), 0.28 (s, 9H), 0.35 (s, 9H), 1.06 (s, 9H), 1.12 (s, 9H), 1.53 (s, 1H), 2.51 (m, 2H), 6.96 (m, 1H); ^{13}C NMR (C_6D_6 , δ) 0.4 (SiMe₃), 2.0 (SiMe₃), 2.8 (SiMe₃), 3.8 (SiMe₃), 12.4 (C), 29.1

(23) Ciabattini, J.; Nathan, E. C.; Feiring, A. E.; Kocienski, P. J. *Organic Synthesis*; Wiley: New York, 1988; Collect. Vol. VI, p 991. We thank Prof. Kenkichi Sakamoto and Dr. Yoshihiro Kon, Tohoku University, for the preparation of these compounds.

(CH₃), 30.1 (CH₃), 32.9 (C), 33.8 (C), 37.2 (CH₂), 37.7 (CH), 112.3 (C), 144.6 (C), 151.5 (CH), 159.2 (C); ²⁹Si NMR (C₆D₆, δ) −7.4 (SiMe₃), 1.6 (SiMe₃), 2.9 (Si), 3.1 (SiMe₃), 7.0 (SiMe₃); MS (70 eV, EI) *m/z* (%) 523 (M⁺ − 15, 9), 481 (100), 387 (100), 73 (79). Anal. Calcd for C₂₇H₅₈OSi₅: C, 60.15; H, 10.84. Found: C, 60.14; H, 10.62. Single crystals suitable for X-ray crystallography were obtained by the recrystallization from THF.

Reaction of Silylene 12 with Diphenylcyclopropenone. Reaction of silylene **12** (97 mg, 0.26 mmol) with diphenylcyclopropenone (48 mg, 0.23 mmol) was performed in a similar manner to the reaction of **12** with adamantanone. Compound **18** was obtained in 81% yield (108 mg, 0.19 mmol). When monitored by NMR, the reaction was very clean, and no other products than **18** appeared during the reaction. **18**: colorless crystals; mp 113–115 °C; ¹H NMR (C₆D₆, δ) −0.02 (s, 9H), 0.16 (s, 9H), 0.20 (s, 9H), 0.29 (s, 9H), 2.67 (m, 2H), 3.12 (s, 1H, cyclopropene ring), 6.98 (m, 1H), 7.08 (t, *J* = 7.2 Hz, 3H), 7.18 (t, *J* = 6.8 Hz, 3H), 7.35 (d, *J* = 7.2 Hz, 2H), 7.56 (d, *J* = 6.8 Hz, 2H); ¹³C NMR (C₆D₆, δ) −0.2 (SiMe₃), 1.7 (SiMe₃), 2.0 (SiMe₃), 2.2

(SiMe₃), 11.6 (C), 27.2 (CH), 38.5 (CH₂), 117.4 (C), 125.8 (CH), 126.9 (CH), 128.5 (CH), 128.8 (CH), 129.5 (CH), 129.7 (CH), 130.7 (C), 131.2 (C), 144.8 (C), 146.5 (CH), 161.2 (C); ²⁹Si NMR (C₆D₆, δ) −6.5 (SiMe₃), −1.2 (SiMe₃), 2.7 (Si), 3.6 (SiMe₃), 9.5 (SiMe₃); MS (70 eV, EI) *m/z* (%) 578 (M⁺, 0.7), 563 (2), 387 (100), 73 (33). Anal. Calcd for C₃₁H₅₀OSi₅: C, 64.29; H, 8.70. Found: C, 64.53; H, 8.50.

Acknowledgment. This work was supported by the Ministry of Education, Culture, Sports, Science, and Technology of Japan (Grants-in-Aid for Specially Promoted Research No. 17002005 (M.K. and T.I.)).

Supporting Information Available: X-ray analysis of **17**, details for the calculations of **19a–19e**, **19b'–19e'**, **19a''**, **20**, and **20'**, and X-ray crystallographic data of **13**, **15**, **16**, **17**, and **18** in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.