Tetrahedron 67 (2011) 9500–9508

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

An efficient synthesis of cyclopropyl silyl ketones

Mitsunori Honda *, Kenta Nakae, Toshiaki Nishizawa, Mitsuhiro Suda, Ko-Ki Kunimoto, Masahito Segi

Division of Material Sciences, Graduate School of Natural Science and Technology, Kanazawa University, Kakuma-machi, Kanazawa, Ishikawa 920-1192, Japan

ARTICLE INFO

Article history:
Received 31 August 2011
Received in revised form 3 October 2011
Accepted 5 October 2011
Available online 12 October 2011

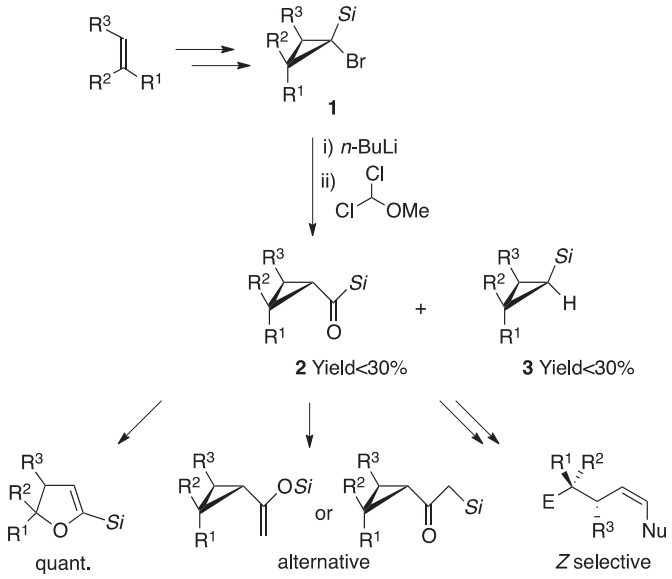
ABSTRACT

The reaction of silylcyclopropyl bromides with dichloromethyl methyl ether in the presence of *n*-butyllithium is investigated. Under basic reaction conditions, the corresponding cyclopropylidene derivatives are exclusively obtained. The resulting cyclopropylidene compounds are subjected to protonolysis or trapping with electrophiles in a one-pot to give the cyclopropyl silyl ketone derivatives in good yields. Acidic treatment of derived cyclopropyl silyl ketone allows isomerization to give the thermodynamically favorable trans form exclusively.

1. Introduction

Acylsilanes have received considerable attention due to their unusual spectroscopic properties, novel chemical reactivity, and their utility as useful synthons in organic synthesis.[1,2] In particular cyclopropyl silyl ketones have attracted attention as useful synthetic intermediates, because three specific reaction sites, cyclopropyl group, silyl group, and carbonyl group are present in one molecule.[3] Therefore we have become interested in exploring the chemistry of cyclopropyl silyl ketones. For example, we have previously described a route to cyclopropyl silyl ketones **2** via three steps beginning with simple alkenes,[4] and then reported that the efficient synthesis of silyl-substituted dihydrofurans,[5] silyl enol ethers or β-ketosilanes[6] and the stereoselective synthesis of *Z*-homoallyl derivatives[7] using specific reaction sites of cyclopropyl silyl ketones (Scheme 1). Our synthetic method is convenient and gives many kinds of cyclopropyl silyl ketones having various substituents on 2- or 3-position of cyclopropane ring, therefore that procedure has been extensively used.[2a,3b] However, the low yield was a huge drawback for our procedure. The isolated yield of cyclopropyl silyl ketones **2** was less than 30%[8] and more than an equivalent amount of the protonated compounds **3** was obtained as a by-product (Scheme 1). To make things worse, our route is not applicable to the synthesis of cyclopropyl silyl ketones possessing a substituent on the 1-position of cyclopropane ring. There have already been just a few reports on the preparation of cyclopropyl silyl ketones,[3] the synthesis of 1-substituted cyclopropyl silyl ketones in particular is less well-known. For these reason, we decided to investigate the reaction conditions to enhance the yield of cyclopropyl silyl ketones and to clarify the mechanism, even though an ambiguous pathway has been previously proposed.[4] Furthermore, we aimed to apply our procedure to synthesis of 1-substituted cyclopropyl silyl ketones. In a preceding letter we described the preliminary results that are improvement of reaction conditions to allow the significant increase of yield of desired cyclopropyl silyl ketones and the formation of cyclopropylidene derivatives, which are precursors of cyclopropyl silyl ketones.[9]

Herein, we wish to describe the preparation of silylcyclopropyl bromide having various substituents as starting materials, further attempt to improve the yield of cyclopropyl silyl ketones, the stereochemistry of cyclopropylidene derivatives and cyclopropyl silyl ketones that has not been assigned, and new detailed evidence that



Scheme 1. Synthesis and reactions of cyclopropyl silyl ketones.

* Corresponding author. E-mail address: honda@se.kanazawa-u.ac.jp (M. Honda).

0040-4020/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2011.10.013

supports our mechanistic consideration. Additionally, the isomerization of cyclopropyl silyl ketone **2**, that makes possible the stereoselective synthesis of **2**, was clarified. As a result reasonable yields of cyclopropyl silyl ketones **2** possessing various substituents on cyclopropane ring that contains 1-substituted derivatives were achieved.

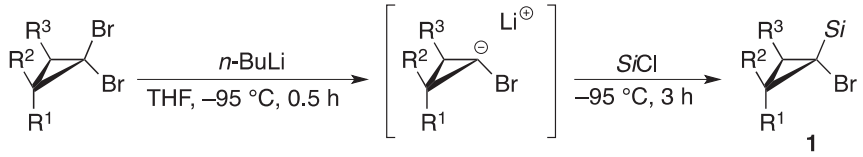
2. Results and discussion

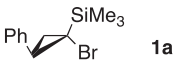
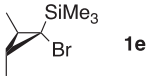
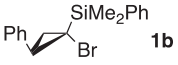
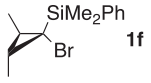
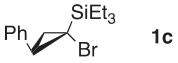
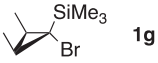
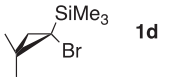
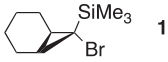
2.1. Preparation of silylcyclopropyl bromides

The preparation of silylcyclopropyl bromides was accomplished as follows. The treatment of simple alkenes with dibromocarbene generated from the reaction of bromoform with *t*-BuOK gave the corresponding dibromocyclopropanes.[10] The resulting dibromocyclopropane derivatives were treated with *n*-butyllithium and the subsequent reaction with chlorosilanes gave the desired silylcyclopropyl bromides **1** (Table 1).[11] Although the products **1a**–**c**, **1g**, and **1h** were yielded as a diastereomeric mixture in each case, these mixtures were used as starting materials without separation of the diastereomers.

reactions under the various conditions were carried out. Then the reaction using 3 equiv of *n*-butyllithium was examined. Nevertheless the reaction mixture became quite complex and the trace amount of **4a** was obtained (entry 2). The reaction quenched with methanol at ambient temperature also gives the complex mixture (entry 3). It is noteworthy that the quenching of the reaction with water afforded **4a** in moderate yield. This result suggests that the methoxy group of **4a** was derived from DCME and not from methanol. On the other hand, the reaction using *tert*-butyllithium as a base instead of *n*-butyllithium gave the desired cyclopropylidene derivatives **4a** in low yield (entry 4). The reactions with different order of addition of reagents, for instance the addition of *n*-butyllithium to the THF solution of silylcyclopropyl bromide **1a** and DCME, did not afford **4a** at all. In these cases the corresponding silylcyclopropane **3a** was often yielded exclusively. Stereochemical assignment of the cyclopropylidene product **4a** was confirmed by the NOE measurements. When **4a** was formed, complete *E*-selectivity was observed. The structures of *E* and *Z* isomers of **4a** were optimized at the DFT-B3LYP level with a 6-31G+ basis set from the Gaussian 09 suite,[12] as a result, it became clear that *E* isomer was 23.3 kcal/mol stable than *Z* isomer.

Table 1
Preparation of silylcyclopropyl bromides



Entry	*Si*Cl	Products	Yield[a] (%)	Entry	*Si*Cl	Products	Yield[a] (%)
1	Me_3SiCl	 **1a**	73	5	Me_3SiCl	 **1e**	80
2	$Me_2PhSiCl$	 **1b**	52	6	$Me_2PhSiCl$	 **1f**	74
3	Et_3SiCl	 **1c**	87	7	Me_3SiCl	 **1g**	60
4	Me_3SiCl	 **1d**	85	8	Me_3SiCl	 **1h**	80

[a] Isolated yield.

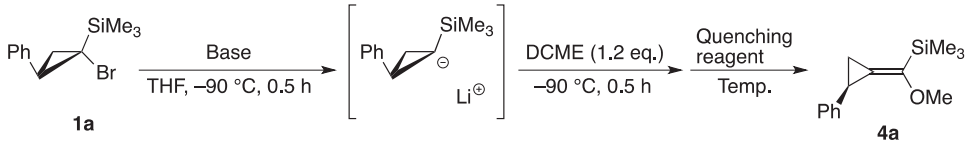
2.2. Optimization of reaction conditions for synthesis of cyclopropyl silyl ketones

The treatment of 2-phenyl-1-trimethylsilylcyclopropyl bromide **1a** with base gave the corresponding carbanion. The following reaction with dichloromethyl methyl ether (DCME) was carried out and quenched with methanol or hydrous THF. The reaction proceeded to afford the corresponding cyclopropylidene derivative **4a** and in all cases cyclopropyl silyl ketone **2a** and silylcyclopropane **3a** as mentioned above were not yielded at all. The results are summarized in Table 2. In accordance with the previous study,[9] 2.5 equiv of *n*-butyllithium was used to lithiate the cyclopropyl bromide at −90 °C and then 1.2 equiv of DCME was added to the reaction mixture and quenched with methanol at that temperature (entry 1). In this case, the cyclopropylidene derivative **4a** was afforded in good yield. **4a** is synthetic equivalent to desired cyclopropyl silyl ketone **2a**.[9] Therefore, to improve the yield of **4a**, the

The reaction of other 1-silylcyclopropyl bromides **1** having different groups on the cyclopropane ring or silicon atom was carried out. These results are shown in Table 3. These reactions also proceeded smoothly to furnish the corresponding cyclopropylidene derivatives **4** in good yields, regardless of the kind of the substituents. As previously indicated, of the two possible diastereomeric products, *E*-isomers were selectively obtained (entries 1–3 and 8). The reaction of **1a** with butyl dichloromethyl ether instead of DCME afforded the corresponding cyclopropylidene derivative **4i** in moderate yield (entry 8). This result also provided the evidence that the methoxy groups in **4a**–**h** were derived from DCME and not from methanol as a quenching reagent.

When an equimolar mixture of **1f** and **1h** were treated with *n*-buthyllithium and DCME, the corresponding cyclopropylidene derivatives **4f** and **4h** were obtained with no crossover products (Scheme 2). Thus the reaction involves the intramolecular 1,2-silyl migration from carbon to carbon.

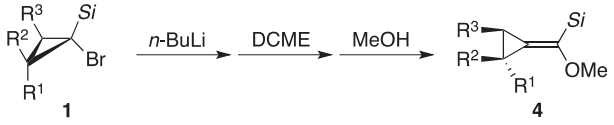
Table 2
Optimization of reaction conditions

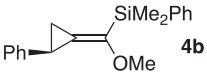
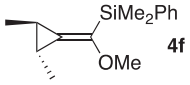
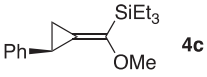
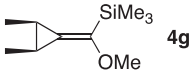
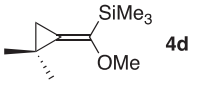
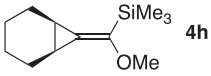
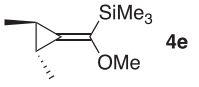
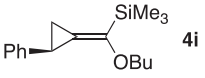


Entry	*n*-BuLi[b]	Quenching reagent	Temp (°C)	Yield[a] (%)
1	*n*-BuLi (2.5)	MeOH	−90	81
2	*n*-BuLi (3.0)	MeOH	−90	Trace
3	*n*-BuLi (2.5)	MeOH	rt	32
4	*n*-BuLi (2.5)	H_2O/THF	−90	62
5	*t*-BuLi (2.5)	MeOH	−90	18[c]

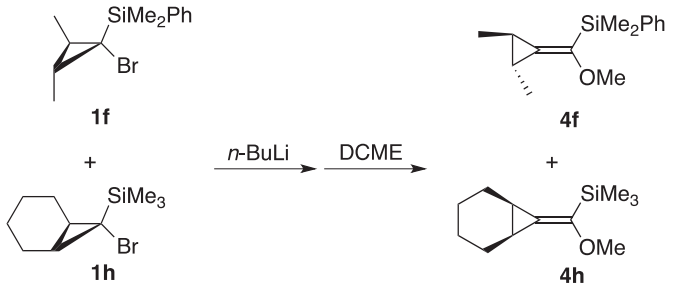
[a] Isolated yield.
[b] The equiv values are given in parentheses.
[c] Determined by ^{1}H NMR analysis.

Table 3
Effect of substituents on cyclopropane ring and silicon atom



Entry	Substrate	Products	Yield[a] (%)	Entry	Substrate	Products	Yield[a] (%)
1	**1b**	 **4b**	74 (>99/1)[b]	5	**1f**	 **4f**	69
2	**1c**	 **4c**	64 (>99/1)[b]	6	**1g**	 **4g**	72
3	**1d**	 **4d**	74 (>99/1)[b]	7	**1h**	 **4h**	76
4	**1e**	 **4e**	70	8[c]	**1a**	 **4i**	43 (>99/1)[b]

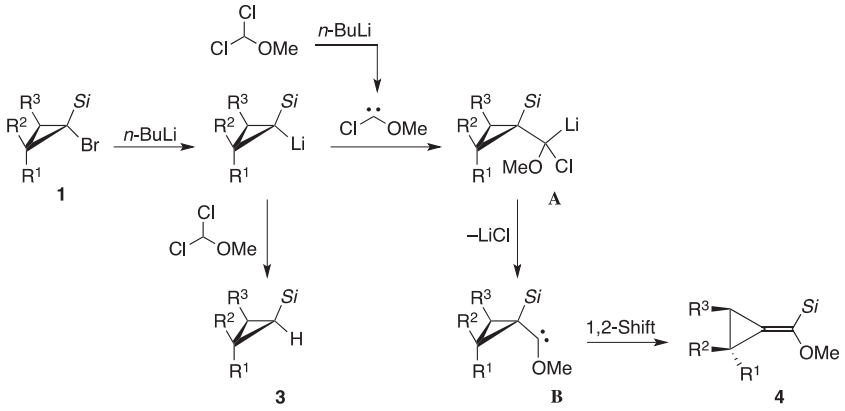
Molar ratio, **1**/*n*-BuLi/DCME=1:2.5:1.2.
[a] Isolated yield.
[b] The *E*/*Z* ratios of the compounds are given in parentheses.
[c] Butyl dichloromethyl ether was used instead of DCME.



Scheme 2. Crossover experiment of 1,2-silyl migration.

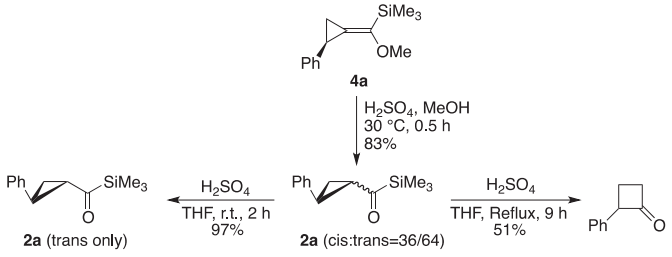
The results mentioned above suggest the following mechanism for the reaction (Scheme 3). The bromine–lithium exchange between *n*-butyllithium and cyclopropyl bromides **1** affords the corresponding cyclopropyllithium. In the reaction using 1 equiv of *n*-buthyllithium, resulting cyclopropyllithium behaves as a base and abstracts a proton from DCME to afford appreciable amounts of silylcyclopropane **3**.[4] On the other hand, however, in the case that excess amounts of *n*-butyllithium is present, *n*-butyllithium also acts as a base and formally eliminates HCl from DCME to give the chloromethoxycarbene.[13] The following reaction of the resulting chloromethoxycarbene with the cyclopropyllithium provides lithium carbenoid intermediate **A**.[14] The loss of lithium chloride from **A** gives cyclopropylmethoxycarbene **B**. The intramolecular 1,2-migration of the silyl group on the adjacent carbon to this carbene center affords the cyclopropylidene derivative **4**.[15] In this migration process, the thermodynamically favored *E*-isomer is exclusively produced. The quenching reagents only deactivate the excessive base and disassociate from the formation of **4**.

These cyclopropylidene derivatives **4** were not very stable and hydrolyzed slowly during attempted chromatography on silica gel to give the cyclopropyl silyl ketones in the purification of crude products. Thus triethylamine (2.5%) was added to an eluent. On the contrary, the protonolysis of the resulting cyclopropylidene derivative **4a** with sulfuric acid in methanol gave the corresponding cyclopropyl silyl ketone **2a** in good yield. In this reaction, trans isomer of the two possible diastereomeric isomers was preferentially formed (Scheme 4). The stereoisomers were characterized by NOESY experiment, and confirmed by the ^{1}H NMR spectra. It was



Scheme 3. Plausible reaction mechanism.

also found that cis isomer was easily transformed to the thermodynamically favorable trans form by treatment with sulfuric acid in THF as an aprotic solvent for 2 h at rt in excellent yield. On the other hand, the reaction under THF reflux for 9 h proceeded to give cyclobutanone derivative (Scheme 4).



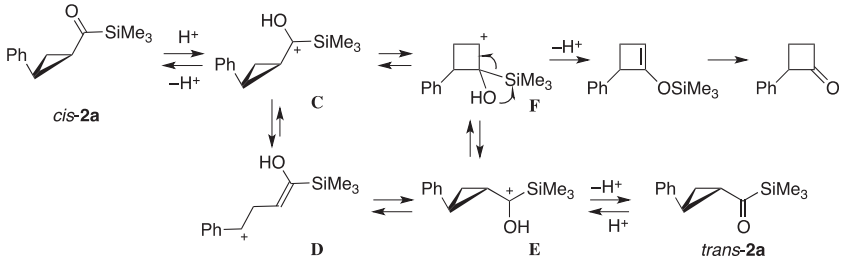
Scheme 4. Isomerization and ring-expanding of **2a** with sulfuric acid.

It appears that these reactions proceeded as follows (Scheme 5). The oxygen atom of starting acylsilane *cis*-**2a** was protonated by sulfuric acid and carbocation species **C** is formed. The cation **C** transforms thermodynamically favored cation **E** via homoallyl cation **D** derived by opening of cyclopropane ring.[7,16,17] On the other hand, under reflux condition, cyclobutonium cation **F** is formed by the ring enlargement of **C** and **E**,[17] because of the dissolution of ring strain of three-membered ring and the stabilization of the resulting carbocation with β-effect of silyl group.[18] The following Brook rearrangement[19] and hydrolysis gives the cyclobutanone derivative.

shown in Table 4. The moderate yields were observed in the reaction of **1** possessing 2,2-dimethylcyclopropyl and *trans*-2,3-dimethylcyclopropyl group, however, the desired cyclopropyl silyl ketones **2** were generally provided with much higher isolated yields than that reported in Ref. 4 in all reactions.

2.3. Synthesis of 1-substituted cyclopropyl silyl ketones

Only few synthetic routes to cyclopropyl silyl ketones have been recorded until now, particularly the preparation of 1-substituted cyclopropyl silyl ketones has not been well-known.[3b,d] So then, trapping of cyclopropylidene derivatives **4** with some electrophiles instead of protic acid in a one-pot procedure was carried out to obtain the cyclopropyl silyl ketones possessing different substituents at 1-position of cyclopropane ring. The results are summarized in Table 5. The reaction with NCS, NBS, PhSCl and PhSeCl as an electrophile proceeded to afford the corresponding cyclopropyl silyl ketones **5** having different substituents on the 1-position of cyclopropane ring in moderate yields. However, it was impossible to introduce an alkyl group into the 1-position of cyclopropane ring by use of alkyl halide as electrophile (entry 5). In these reactions, trans isomer of the two possible diastereomeric isomers was preferentially formed (trans refers to the relationship between the substituents R^2 or R^3 and the introduced functional group E on the cyclopropane ring). The stereoisomers were characterized by NOESY experiment. These results suggest that the approach of electrophile to cyclopropylidene moiety proceeds from the opposite direction of sub-

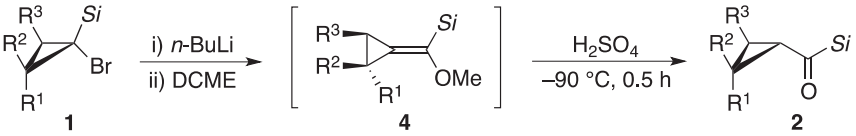


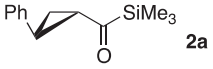
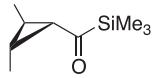
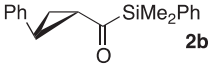
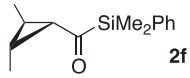
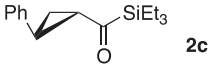
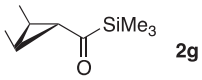
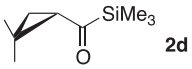
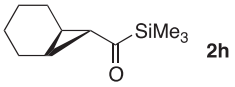
Scheme 5. Plausible reaction pathway.

Then the one-pot synthesis of cyclopropyl silyl ketones **2** having different groups on the cyclopropane ring or silicon atom from silylcyclopropyl bromides **1** was investigated. The reaction of cyclopropyllithium derived from **1** with DCME and the following treatment of sulfuric acid at low temperature after the addition of methanol to reaction mixture gave the intended **2**. These results are

stituent on cyclopropane ring to avoid the steric repulsion between them (Scheme 6). Thus, higher diastereoselectivity was observed in the reaction of silylcyclopropyl bromides having *cis*-2,3-disubsutituted cyclopropyl group (Table 5, entries 8 and 9) than that of monosubstituted cyclopropyl group (Table 5, entries 1–4). Similarly, when protic acid was used as an electrophile

Table 4
One-pot synthesis of cyclopropyl silyl ketones



Entry	Substrate	Products	Yield[a] (%)	Entry	Substrate	Products	Yield[a] (%)
1	**1a**	 **2a**	73 (64/36)[b]	5	**1e**	 **2e**	66
2	**1b**	 **2b**	67 (74/26)[b]	6	**1f**	 **2f**	62
3	**1c**	 **2c**	60 (66/34)[b]	7	**1g**	 **2g**	47 (77/23)[b]
4	**1d**	 **2d**	48	8	**1h**	 **2h**	68 (85/15)[b]

Molar ratio, **1**/*n*-BuLi/DCME=1:2.5:1.2.
[a] Isolated yield.
[b] The trans/cis ratios of the compounds are given in parentheses.

(Table 4), cis isomer might be preferentially formed by the approach of the proton to cyclopropylidene moiety from the opposite direction of substituent on cyclopropane ring (in this case, cis refers to the relationship between the substituents R^2 or R^3 and the carbonyl group on the cyclopropane ring). However, the following isomerization under acidic conditions mentioned above would occur. As a consequence, trans isomer was preferentially furnished.

3. Conclusion

In conclusion, the reaction of DCME with 1-silylcyclopropyl anions in the presence of *n*-butyllithium was investigated. Under basic conditions the reaction proceeded smoothly to afford the corresponding cyclopropylidene derivatives. The resulting cyclopropylidene compounds were subjected to protonolysis, which gave the cyclopropyl silyl ketones in good yields. The cis isomer of cyclopropyl silyl ketone was easily transformed to the trans form by treatment with sulfuric acid. On the other hand, cyclopropyl silyl ketones possessing various substituents at 1-position of cyclopropane ring are conveniently prepared in a one-pot reaction of 1-silylcyclopropyl anions with DCME followed by the electrophilic reaction in good yields.

4. Experimental section

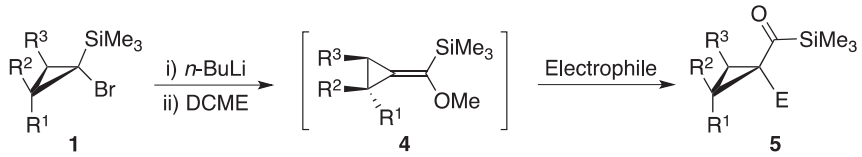
4.1. General

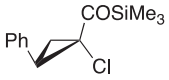
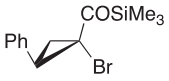
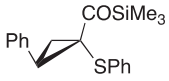
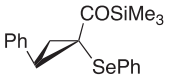
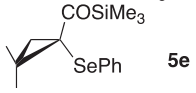
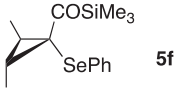
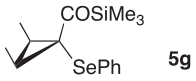
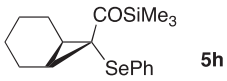
IR spectra were recorded on Horiba FTIR-720 or Shimadzu FTIR-8300 infrared spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on JEOL JNM EX-270, LA-400 or ECA-500 spectrometer. Chemical shifts of ^{1}H NMR were expressed in parts per million downfield from tetramethylsilane (TMS) with reference to internal residual $CHCl_3$ (δ=7.26) in $CDCl_3$. Chemical shifts of ^{13}C NMR were expressed in parts per million downfield from $CDCl_3$ (δ=77.0) as an internal standard. Coupling constants (*J*) were reported in hertz (Hz). Following abbreviations were used to designate the multiplicities: s=singlet; d=doublet; t=triplet; q=quartet; quin=quintet; sext=sextet; br=broad; m=multiplet. Mass spectra were recorded on JEOL JMS-700 or JMS-SX102A mass spectrometer. Melting points were measured on a Yanaco MP-J3 and were uncorrected. Analytical thin layer chromatography (TLC) was performed on precoated glass plates (Merck Kieselgel 60 F_{254}, layer thickness 0.25 mm). Visualization was accomplished with UV light (254 nm) and molybdophosphoric acid. Flash column chromatography was carried out using Kanto Chemical silica gel 60 N (40–50 mm). Preparative HPLC was performed on JAI LC-908 and LC-918 chromatograph equipped with JAIGEL-1H and -2H and JAIGEL-SIL. GC analysis was performed on a Shimadzu GC-14B equipped with a CBP1-M25-O20 column (Shimadzu, 25 m×0.22 mm, detector=FID) with a helium gas as a carrier. Unless otherwise noted, commercially available reagents were used without purification. All the solvents were distilled and stored over a drying agent. *n*-Butyllithium (1.6 M solution in hexane) was purchased from Kanto Chemical Co., Inc. All reactions were carried out under an argon atmosphere in dried glassware.

4.2. General procedure for the reaction of silylcyclopropyl bromides and dichloromethyl methyl ether with *n*-BuLi

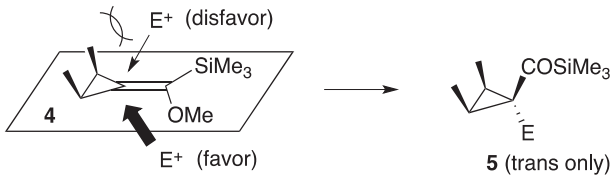
To a stirred solution of silylcyclopropyl bromide (1 mmol) in THF (20 mL) at −90 °C was added slowly a 1.6 M solution of *n*-BuLi (1.5 mL, 2.5 mmol) in hexane. The resulting reaction mixture was stirred at −90 °C for 0.3 h, and then dichloromethyl methyl ether (138 mg, 1.2 mmol) in THF (2 mL) was added. After stirring for 0.5 h, methanol (1 mL) was added and the reaction mixture was allowed to warm to ambient temperature and then poured into saturated $NaHCO_3$ aq. The aqueous layer was extracted with diethyl ether for three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on a silica gel using 40:1 hexane/triethylamine as eluent to give methoxycyclopropylidenemethylsilane derivatives.

Table 5
One-pot synthesis of 1-substituted cyclopropyl silyl ketones



Entry	Substrate	Electrophile	Products	Yield[a] (%)
1	**1a**	NCS	 **5a**	64 (76/24)[b]
2	**1a**	NBS	 **5b**	56 (75/25)[b]
3	**1a**	PhSCI	 **5c**	48 (86/14)[b]
4	**1a**	PhSeCI	 **5d**	59 (71/29)[b]
5	**1a**	MeI	 **2a**	53 (66/34)[b]
6	**1d**	PhSeCI	 **5e**	17
7	**1e**	PhSeCI	 **5f**	63
8	**1g**	PhSeCI	 **5g**	28 (>99/1)[b]
9	**1h**	PhSeCI	 **5h**	50 (>99/1)[b]

Molar ratio, **1**/*n*-BuLi/DCME=1:2.5:1.2.
[a] Isolated yield.
[b] The trans/cis ratios of the compounds are given in parentheses.



Scheme 6. Stereoselective electrophilic attack to **4**.

*4.2.1. (Methoxy-2-phenylcyclopropylidenemethyl)trimethylsilane (**4a**).* IR (neat) 3028, 2958, 1720, 1604, 1496, 1452, 1248, 1203, 1147, 839 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.25–7.08 (m, 5H), 3.82 (s, 3H), 2.52 (dd, J=4.2, 7.8 Hz, 1H), 2.01 (t, J=7.6 Hz, 1H), 1.43 (dd, J=4.2, 7.6 Hz, 1H), −0.01 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.5, 143.9, 128.2, 125.8, 125.5, 107.8, 56.0, 18.4, 18.3, −2.1. HRMS calcd for $C_{14}H_{20}OSi$ (M^+) 232.1283, found 232.1280.

*4.2.2. (Methoxy-2-phenylcyclopropylidenemethyl)dimethyllphenylsilane (**4b**).* IR (neat) 3052, 2957, 1715, 1614, 1486, 1251, 1132, 843 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.86–7.01 (m, 10H), 3.83 (s, 3H), 2.55 (dd, J=4.6, 7.8 Hz, 1H), 2.05 (t, J=7.8 Hz, 1H), 1.42 (dd, J=4.4, 7.6 Hz, 1H), 0.53 (s, 3H), 0.50 (s, 3H). HRMS calcd for $C_{19}H_{22}OSi$ (M^+) 294.1440, found 294.1439.

*4.2.3. (Methoxy-2-phenylcyclopropylidenemethyl)triethylsilane (**4c**).* IR (neat) 3033, 2942, 1711, 1604, 1456, 1250, 845 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.56–7.02 (m, 5H), 3.83 (s, 3H), 2.60–2.55 (m, 1H), 2.03 (t, J=7.4 Hz, 1H), 1.420–1.39 (m, 1H), 1.07–1.99 (m, 9H), 0.88–0.78 (m, 6H). HRMS calcd for $C_{17}H_{26}OSi$ (M^+) 274.1753, found 274.1749.

*4.2.4. (2,2-Dimethylcyclopropylidenemethoxymethyl)trimethylsilane (**4d**).* IR (neat) 2957, 1724, 1458, 1442, 1248, 1200, 1144, 843 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 3.29 (s, 3H), 1.47–1.22 (m, 2H), 1.20 (s, 3H), 1.19 (s, 3H), 0.09 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8, 117.89, 57.6, 35.7, 30.2, 24.9, 24.0, 2.1. HRMS calcd for $C_{10}H_{20}OSi$ (M^+) 184.1283, found 184.1285.

*4.2.5. (trans-2,3-Dimethylcyclopropylidenemethoxymethyl)trimethylsilane (**4e**).* IR (neat) 2956, 1726, 1461, 1446, 1247, 1201, 1150,

841 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 3.69 (s, 3H), 1.20 (d, J=6.0 Hz, 3H), 1.14 (d, J=6.0 Hz, 3H), 1.03–0.97 (m, 1H), 0.93–0.88 (m, 1H), 0.14 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.8, 116.4, 56.0, 20.1, 19.9, 19.0, 16.2, −1.7. HRMS calcd for $C_{10}H_{20}OSi$ (M^+) 184.1283, found 184.1283.

*4.2.6. (trans-2,3-Dimethylcyclopropylidenemethoxymethyl)dimethylphenylsilane (**4f**).* IR (neat) 3065, 2955, 1723, 1455, 1253, 1143, 838 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.52–7.10 (m, 5H), 3.71 (s, 3H), 1.28 (d, J=6.0 Hz, 3H), 1.17 (d, J=6.0 Hz, 3H), 1.08–0.99 (m, 1H), 0.95–0.90 (m, 1H), 0.47 (s, 3H), 0.45 (s, 3H). HRMS calcd for $C_{15}H_{22}OSi$ (M^+) 246.1440, found 246.1441.

*4.2.7. (cis-2,3-Dimethylcyclopropylidenemethoxymethyl)trimethylsilane (**4g**).* IR (neat) 2963, 1718, 1453, 1255, 1148, 846 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 3.67 (s, 3H), 1.19 (d, J=5.9 Hz, 3H), 1.14 (d, J=5.9 Hz, 3H), 1.22–1.12 (m, 2H), 0.15 (s, 9H). HRMS calcd for $C_{10}H_{20}OSi$ (M^+) 184.1283, found 184.1289.

*4.2.8. (Bicyclo[4.1.0]heptan-7-ylidenemethoxymethyl)trimethylsilane (**4h**).* IR (neat) 2930, 1711, 1460, 1448, 1246, 1201, 1140, 840 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 3.65 (s, 3H), 1.95–1.85 (m, 2H), 1.82–1.76 (m, 1H), 1.73–1.66 (m, 1H), 1.64–1.54 (m, 2H), 1.38–1.28 (m, 2H), 1.28–1.15 (m, 2H), 0.15 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.4, 113.1, 56.1, 25.3, 24.6, 21.5, 21.1, 15.6, 11.4, −1.7. HRMS calcd for $C_{12}H_{22}OSi$ (M^+) 210.1440, found 210.1441.

*4.2.9. (Butoxy-2-phenylcyclopropylidenemethyl)trimethylsilane (**4i**).* Butyl dichloromethyl ether was used instead of dichloromethyl methyl ether to yield **4i**. IR (neat) 3033, 2956, 1718, 1601, 1493, 1451, 1252, 1201, 1151, 843 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.25–7.08 (m, 5H), 4.13–4.02 (m, 2H), 2.54 (dd, J=4.0, 8.0 Hz, 1H), 1.95 (t, J=7.6 Hz, 1H), 1.66 (dt, J=6.6, 15.0 Hz, 2H), 1.45 (ddd, J=5.6, 7.6, 15.0 Hz, 2H), 1.35 (dd, J=4.0, 7.4 Hz, 1H), 0.96 (t, J=7.4 Hz, 3H), −0.02 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.7, 144.2, 128.3, 125.9, 125.5, 107.8, 67.8, 31.9, 19.5, 18.9, 18.5, 14.1, −2.0. HRMS calcd for $C_{17}H_{26}OSi$ (M^+) 274.1753, found 274.1750.

4.3. Protonolysis of (methoxy-2-phenylcyclopropylidenemethyl)trimethylsilane 4a

*4.3.1. 2-Phenylcyclopropyl trimethylsilyl ketone (**2a**).* IR (neat) 3036, 2958, 1617, 1510, 1461, 1241, 1041, 834 cm^{-1}. HRMS calcd for $C_{13}H_{18}OSi$ (M^+) 218.1127, found 218.1123. *trans*-**2a**: ^1H NMR (500 MHz, $CDCl_3$): δ 7.28–7.10 (m, 5H), 3.00 (ddd, J=5.7, 6.9, 9.2 Hz, 1H), 2.77 (dd, J=8.6, 8.6 Hz, 1H), 2.01 (ddd, J=5.2, 6.3, 7.4 Hz, 1H), 1.22 (ddd, J=4.6, 7.4, 8.6 Hz, 1H), 0.05 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 242.8, 135.8, 128.8, 127.6, 126.2, 34.4, 29.8, 10.6, −3.7. *cis*-**2a**: ^1H NMR (500 MHz, $CDCl_3$): δ 7.32–7.10 (m, 5H), 2.51 (ddd, J=4.0, 6.3, 9.2 Hz, 1H), 1.34 (ddd, J=4.0, 6.9, 8.0 Hz, 1H), 1.70 (ddd, J=4.0, 5.1, 8.6 Hz, 1H), 0.24 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 244.4, 140.5, 128.8, 128.3, 126.0, 36.9, 29.5, 19.0, −3.4.

4.4. Isomerization of *cis*-2a with sulfuric acid into *trans*-2a

To a stirred solution of mixture of *cis* and *trans*-**2a** (36:64, 1 mmol) in THF (10 mL) at 20 °C was added slowly a sulfuric acid (1 mmol). After stirring for 2 h, the reaction mixture was poured into saturated $NaHCO_3$ aq. The aqueous layer was extracted with diethyl ether for three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on a silica gel using 20:1 hexane/ethyl acetate as eluent to give *trans*-**2a** in 97% yield.

4.5. General procedure for the one-pot synthesis of cyclopropyl silyl ketones

To a stirred solution of silylcyclopropyl bromide (1 mmol) in THF (20 mL) at −90 °C was added slowly a 1.6 M solution of *n*-BuLi (1.5 mL, 2.5 mmol) in hexane. The resulting reaction mixture was stirred at −90 °C for 0.3 h, and then dichloromethyl methyl ether (138 mg, 1.2 mmol) in THF (2 mL) was added. After stirring for 0.5 h, methanol (1 mL) and sulfuric acid (1 mmol) was sequentially added. The reaction mixture was stirred for 0.1 h and allowed to warm to ambient temperature and then poured into saturated $NaHCO_3$ aq. The aqueous layer was extracted with diethyl ether for three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on a silica gel using 20:1 hexane/ethyl acetate as eluent to give cyclopropyl silyl ketone derivatives.

*4.5.1. 2-Phenylcyclopropyl dimethylphenylsilyl ketone (**2b**).* IR (neat) 3086, 3063, 3030, 2959, 2900, 1705, 1640, 1496, 1250, 846 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.56–6.98 (m, 10H), 2.70 (ddd, J=3.4, 4.6, 8.6 Hz, 1H), 2.48 (ddd, J=3.1, 5.9, 9.6 Hz, 1H), 1.74–1.69 (m, 1H), 1.29 (ddd, J=2.6, 5.3, 9.3 Hz, 1H), 0.52 (s, 3H), 0.51 (s, 3H). HRMS calcd for $C_{18}H_{20}OSi$ (M^+) 280.1283, found 280.1284.

*4.5.2. 2-Phenylcyclopropyl triethylsilyl ketone (**2c**).* IR (neat) 3040, 2955, 1621, 1456, 1239, 1017, 735 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.90–7.30 (m, 5H), 2.74–2.70 (m, 1H), 2.54–2.49 (m, 1H), 1.75–1.70 (m, 1H), 1.35–1.30 (m, 1H), 1.02–1.96 (m, 9H), 0.80–0.74 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 244.6, 140.7, 128.4, 126.3, 126.1, 38.2, 29.5, 18.8, 7.3, 2.0. HRMS calcd for $C_{16}H_{24}OSi$ (M^+) 260.1596, found 260.1593.

*4.5.3. 2,2-Dimethylcyclopropyl trimethylsilyl ketone (**2d**).* IR (neat) 2952, 1728, 1621, 1379, 1250, 1103, 842 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.42 (dd, J=5.9, 7.3 Hz, 1H), 1.44 (dd, J=3.9, 5.6 Hz, 1H), 1.24 (s, 3H), 0.96 (s, 3H), 0.74 (dd, J=3.7, 7.3 Hz, 1H), 0.20 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 245.8, 40.6, 28.4, 27.3, 22.3, 18.3, −3.6. HRMS calcd for $C_9H_{18}OSi$ (M^+) 170.1127, found 170.1131.

*4.5.4. trans-2,3-Dimethylcyclopropyl trimethylsilyl ketone (**2e**).* IR (neat) 2955, 1716, 1618, 1456, 1249, 1069, 842 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.33 (dd, J=5.2, 8.6 Hz, 1H), 1.54 (dd, J=6.0, 11.2 Hz, 1H), 1.34–1.30 (m, 1H), 1.05 (d, J=5.7 Hz, 3H), 0.97 (d, J=5.7 Hz, 3H), 0.19 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 246.6, 40.3, 30.5, 23.5, 18.1, 11.6, −3.5. HRMS calcd for $C_9H_{18}OSi$ (M^+) 170.1127, found 170.1119.

*4.5.5. trans-2,3-Dimethylcyclopropyl dimethylphenylsilyl ketone (**2f**).* IR (neat) 3070, 2952, 1713, 1618, 1428, 1249, 1111, 834 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.58–7.36 (m, 5H), 2.30 (dd, J=4.9, 8.8 Hz, 1H), 1.57–1.51 (m, 1H), 1.32–1.22 (m, 1H), 0.99 (d, J=6.1 Hz, 3H), 0.92 (d, J=6.1 Hz, 3H), 0.49 (s, 3H), 0.46 (s, 3H). HRMS calcd for $C_{14}H_{20}OSi$ (M^+) 232.1284, found 232.1283.

*4.5.6. cis-2,3-Dimethylcyclopropyl trimethylsilyl ketone (**2g**).* IR (neat) 2958, 1644, 1618, 1410, 1249, 1076, 845 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.90 (t, J=4.3 Hz, 1H), 1.63–1.58 (m, 2H), 1.09 (d, J=5.7 Hz, 6H), 0.20 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 246.1, 43.6, 26.1, 12.1, −3.3. HRMS calcd for $C_9H_{18}OSi$ (M^+) 170.1127, found 170.1124.

*4.5.7. Bicyclo[4.1.0]hept-7-yl trimethylsilyl ketone (**2h**).* IR (neat) 2930, 2860, 1616, 1402, 1248, 1099, 846 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.30 (t, J=4.1 Hz, 1H), 1.90–1.85 (m, 2H), 1.75–1.71 (m, 2H), 1.69–1.66 (m, 1H), 1.64–1.62 (m, 1H), 1.35–1.22 (m, 4H), 0.22

(s, 9H). HRMS calcd for $C_{11}H_{20}OSi$ (M^+) 196.1284, found 196.1282.

4.6. General procedure for the one-pot synthesis of 1-substituted cyclopropyl silyl ketones

To a stirred solution of silylcyclopropyl bromide (1 mmol) in THF (20 mL) at −90 °C was added slowly a 1.6 M solution of *n*-BuLi (1.5 mL, 2.5 mmol) in hexane. The resulting reaction mixture was stirred at −90 °C for 0.3 h, and then dichloromethyl methyl ether (138 mg, 1.2 mmol) in THF (2 mL) was added. After stirring for 0.5 h, electrophilic reagent (1.5 mmol) in THF (2 mL) was added and stirred for 0.5 h. The reaction mixture allowed to warm to ambient temperature and then poured into saturated $NaHCO_3$ aq. The aqueous layer was extracted with diethyl ether for three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on a silica gel using 20:1 hexane/ethyl acetate as eluent to give cyclopropyl silyl ketone derivatives.

*4.6.1. 1-Chloro-2-phenylcyclopropyl trimethylsilyl ketone (**5a**).* IR (neat) 3042, 2961, 1621, 1514, 1453, 1254, 1046, 872 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.21–6.80 (m, 5H), 2.79 (dd, J=8.4, 10.0 Hz, 1H), 2.19 (dd, J=6.4, 8.4 Hz, 1H), 1.37 (dd, J=6.4, 10.0 Hz, 1H), −0.14 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 235.2, 133.6, 128.5, 128.1, 127.1, 57.0, 38.7, 18.8, −2.4. HRMS calcd for $C_{13}H_{17}ClOSi$ (M^+) 252.0737, found 252.0730.

*4.6.2. 1-Bromo-2-phenylcyclopropyl trimethylsilyl ketone (**5b**).* IR (neat) 3039, 2959, 1617, 1521, 1452, 1255, 1170, 1052, 846 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.21–6.74 (m, 5H), 2.74 (dd, J=8.4, 10.0 Hz, 1H), 2.15 (dd, J=7.2, 8.4 Hz, 1H), 1.31 (dd, J=6.8, 9.7 Hz, 1H), −0.24 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 234.2, 133.8, 128.2, 128.1, 127.0, 46.8, 36.7, 17.5, −2.2. $C_{13}H_{17}BrOSi$ (M^+) 296.0232, found 296.0240.

*4.6.3. 2-Phenyl-1-phenylthiocyclopropyl trimethylsilyl ketone (**5c**).* IR (neat) 3051, 2952, 1622, 1582, 1498, 1479, 1456, 1439, 1244, 843 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.23–7.06 (m, 10H), 2.99 (dd, J=8.0, 8.5 Hz, 1H), 2.67 (dd, J=5.6, 7.6 Hz, 1H), 1.45 (dd, J=5.6, 9.0 Hz, 1H), −0.11 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 238.0, 136.5, 134.0, 128.9, 128.4, 128.0, 127.0, 126.4, 125.5, 46.9, 37.0, 17.6, −2.5. HRMS calcd for $C_{19}H_{22}OSSi$ (M^+) 326.1161, found 326.1165.

*4.6.4. 2-Phenyl-1-phenylselenocyclopropyl trimethylsilyl ketone (**5d**).* IR (neat) 3059, 2957, 1616, 1580, 1497, 1479, 1452, 1439, 1248, 843 cm^{-1}. HRMS calcd for $C_{19}H_{22}OSeSi$ (M^+) 374.0605, found 374.0606. *cis*-**5d**: ^1H NMR (400 MHz, $CDCl_3$): δ 7.30–7.10 (m, 10H), 2.69 (dd, J=7.6, 9.0 Hz, 1H), 2.51 (dd, J=5.1, 9.3 Hz, 1H), 1.64 (dd, J=5.1, 7.3 Hz, 1H), 0.26 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 239.2, 136.3, 130.6, 129.4, 129.1, 129.0, 127.8, 127.1, 126.1, 45.6, 33.6, 19.8, −1.3. *trans*-**5d**: ^1H NMR (400 MHz, $CDCl_3$): δ 7.30–7.10 (m, 10H), 2.99 (dd, J=7.3, 8.8 Hz, 1H), 2.54 (dd, J=5.8, 7.1 Hz, 1H), 1.49 (dd, J=6.1, 8.8 Hz, 1H), −0.10 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 236.5, 135.1, 131.3, 129.2, 128.1, 128.0, 126.9, 126.8, 126.1, 44.4, 34.6, 16.9, −0.1.

*4.6.5. 2,2-Dimethyl-1-phenylselenocyclopropyl trimethylsilyl ketone (**5e**).* IR (neat) 3033, 2951, 1618, 1578, 1477, 1439, 1248, 843 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.29–7.13 (m, 5H), 1.93 (d, J=5.1 Hz, 1H), 1.52 (s, 3H), 1.03 (s, 3H), 0.86 (d, J=5.1 Hz, 1H), 0.23 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 237.7, 130.7, 130.2, 129.0, 126.4, 49.8, 27.8, 24.9, 24.1, 21.3, −1.9. HRMS calcd for $C_{15}H_{22}OSeSi$ (M^+) 326.0605, found 326.0607.

*4.6.6. trans-2,3-Dimethyl-1-phenylselenocyclopropyl trimethylsilyl ketone (**5f**).* IR (neat) 3059, 2957, 1617, 1479, 1247, 1077, 844 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.32–7.17 (m, 5H), 1.98 (dq, J=5.9, 6.3 Hz, 1H), 1.46 (dq, J=5.9, 6.3 Hz, 1H), 1.26 (d, J=6.3 Hz, 3H), 1.08 (d, J=6.3 Hz, 3H), 0.23 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 240.9, 132.0, 129.0, 128.3, 125.7, 49.0, 31.5, 22.5, 15.8, 13.3, −1.8. HRMS calcd for $C_{15}H_{22}OSeSi$ (M^+) 326.0605, found 326.0604.

*4.6.7. cis-2,3-Dimethyl-1-phenylselenocyclopropyl trimethylsilyl ketone (**5g**).* IR (neat) 3033, 2955, 1618, 1580, 1479, 1439, 1246, 845 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.25–7.09 (m, 5H), 1.78 (m, 2H), 1.17 (d, J=6.4 Hz, 6H), 0.18 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 239.7, 130.9, 129.0, 128.5, 125.7, 50.5, 23.4, 23.4, 10.2, 10.2, −1.4. HRMS calcd for $C_{15}H_{22}OSeSi$ (M^+) 326.0605, found 326.0603.

*4.6.8. 7-Phenylselenobicyclo[4.1.0]hept-7-yl trimethylsilyl ketone (**5h**).* IR (neat) 3032, 2937, 1618, 1577, 1479, 1460, 1439, 1246, 842 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.21–7.14 (m, 5H), 2.02–1.94 (m, 2H), 1.94–1.90 (m, 2H), 1.60–1.48 (m, 4H), 1.32–1.23 (m, 2H), 0.17 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 238.4, 130.6, 129.1, 128.4, 125.7, 50.6, 22.4, 21.5, 20.9, −1.3. HRMS calcd for $C_{17}H_{24}OSeSi$ (M^+) 352.0762, found 352.0759.

Acknowledgements

This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT), Japan.

References and notes

1. For recent reviews on synthesis and reaction of acylsilanes, see: (a) Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; Wiley: New York, NY, 2000; (b) Bonini, B. F.; Comes-Franchini, M.; Fochi, M.; Mazzanti, G.; Ricci, A. *J. Organomet. Chem.* **1998**, *567*, 181–189; (c) Qi, H.; Curran, D. P. In *Acyl Silicon, Germanium, or Boron Functions*; Katrizky, A. R., Meth-Cohn, O., Rees, C. W., Moody, C. J., Eds.; Comprehensive Organic Functional Group Transformations: Synthesis: Carbon with Two Attached Heteroatoms with at Least One Carbon-to-Heteroatom Multiple Link; Pergamon: Oxford, 1995; Vol. 5; Chapter 5.09, pp 409–433; (d) Cirillo, P. F.; Panek, J. S. *Org. Prep. Proced. Int.* **1992**, *24*, 553–582.
2. (a) Page, P. C. B.; Klair, S. S.; Rosenthal, S. *Chem. Soc. Rev.* **1990**, *19*, 147–195; (b) Ricci, A.; Degl'Innocenti, A. *Synthesis* **1989**, 647–660; (c) Fleming, I.; Barbero, A.; Walter, D. *Chem. Rev.* **1997**, *97*, 2063–2192; (d) Hau, C. S.; Jarvis, A. N.; Sweeney, J. B. *Contemp. Org. Synth.* **1996**, *3*, 65–91.
3. For reports about synthesis and reaction of cyclopropyl silyl ketones, see: (a) Danheiser, R. L.; Fink, D. M. *Tetrahedron Lett.* **1985**, *26*, 2513–2516; (b) Scheller, M. E.; Frei, B. *Helv. Chim. Acta* **1986**, *69*, 44–52; (c) Kang, J.; Lee, J. H.; Kim, K. S.; Jeong, J. U.; Ryun, C. *Tetrahedron Lett.* **1987**, *28*, 3261–3262; (d) Nowick, J. S.; Danheiser, R. L. *Tetrahedron* **1988**, *44*, 4113–4134; (e) Clayden, J.; Watson, D. W.; Chambers, M. *Tetrahedron* **2005**, *61*, 3195–3203.
4. Nakajima, T.; Tanabe, M.; Ohno, K.; Segi, M.; Suga, S. *Chem. Lett.* **1986**, 177–180.
5. Honda, M.; Yamamoto, Y.; Tsuchida, H.; Segi, M.; Nakajima, T. *Tetrahedron Lett.* **2005**, *46*, 6465–6468.
6. Nakajima, T.; Segi, M.; Sugimoto, F.; Hioki, R.; Yokota, S.; Miyashita, K. *Tetrahedron* **1993**, *49*, 8343–8358.
7. Honda, M.; Naitou, T.; Hoshino, H.; Takagi, S.; Segi, M.; Nakajima, T. *Tetrahedron Lett.* **2005**, *46*, 7345–7348.
8. The moderate yields denoted in Ref. 4 are determined by G.C. The attempt to isolate the cyclopropyl silyl ketones **2** actually affords lower yields.
9. Nishizawa, T.; Nakae, K.; Honda, M.; Kunimoto, K.-K.; Segi, M. *Tetrahedron Lett.* **2010**, *51*, 1294–1297.
10. Skell, P. S.; Garner, A. Y. *J. Am. Chem. Soc.* **1956**, *78*, 3409–3411.
11. Kitatani, K.; Hiyama, T.; Nozaki, H. *J. Am. Chem. Soc.* **1975**, *97*, 949–951.
12. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09 Revision B.01*; Gaussian: Wallingford, CT, 2010.
13. Hine, J.; Rosscup, R. J.; Duffey, D. C. *J. Am. Chem. Soc.* **1960**, *82*, 6120–6123.
14. Closs, G. L. *J. Am. Chem. Soc.* **1962**, *84*, 809–813.

15. (a) Creary, X.; Wang, Y.-X. *Tetrahedron Lett.* **1989**, *30*, 2493–2496; (b) Creary, X.; Butchko, M. A. *J. Org. Chem.* **2001**, *66*, 1115–1121; (c) Creary, X.; Butchko, M. A. *J. Org. Chem.* **2002**, *67*, 112–118.
16. The reaction of **2a** with HCl proceeded to afford the corresponding 4-chloro-4-phenyl-1-trimethylsilylbutanone. This result suggests that the product generates via homoallyl cation **D**; Nakajima, T.; Miyaji, H.; Segi, M.; Suga, S. *Chem. Lett.* **1986**, 181–182.
17. For review, see: Wiberg, K. B.; Hess, B. A., Jr.; Ashe, A. J., III. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, NY, 1972; Vol. 3, pp 1295–1345.
18. (a) Wierschke, S. G.; Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496–1500; (b) Lambert, J. B.; Wang, G.-T.; Finzel, R. B.; Teramura, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 7838–7845.
19. Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77–84.