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Stereoselective Synthesis of Cyclopropanone Ketals via Silyl Chloride Promoted Cyclization of β-Zinciopropionates

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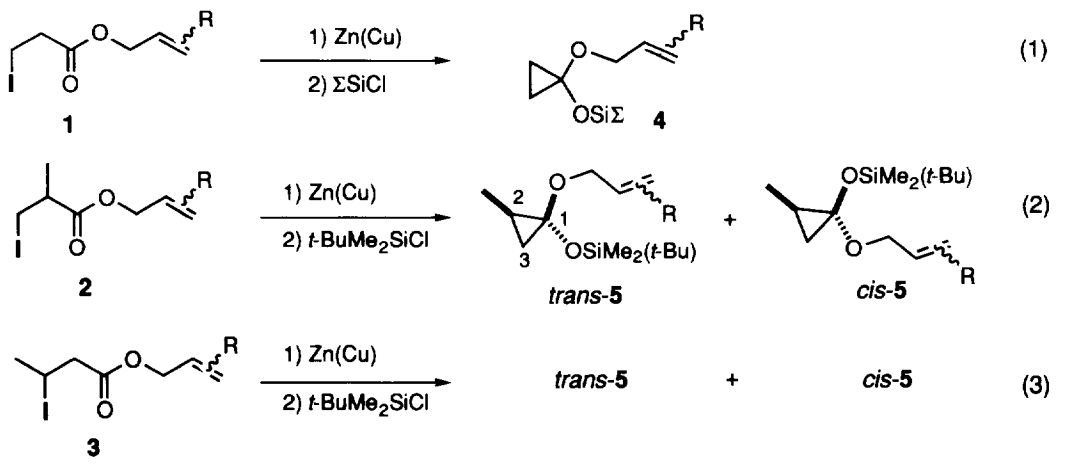
Abstract: Alkyl, allyl, and propargyl β-iodopropionates undergo a cyclopropanation by the reaction with zinc-copper couple and TBDMSCl in THF to give 1-alkoxy-, 1-allyloxy-, and 1-propargyloxy-1-*tert*-butyldimethylsiloxycyclopropanes in moderate or good yields. β-Iodo-α-methylpropionates **2** and **6** provide *trans*-**5** and *trans*-**8** selectively, while β-iodobutyrates **3** and **7** furnish *cis*-**5** and *cis*-**8** selectively.

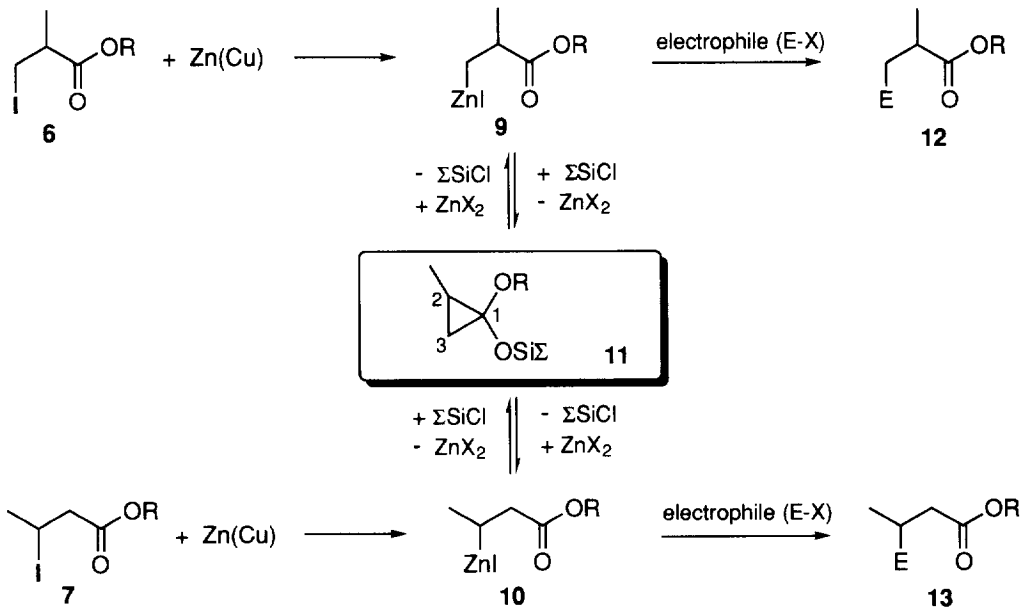
Cyclopropane derivatives have received much attention from synthetic and theoretical organic chemists,[1] because they possess uniquely hybridized strained bonds and rigid, compact structures as well as the physiological activities. As a part of our project to clarify a through-space interaction between the strained σ-bonds of cyclopropane ring and a π-bond assembled in the same molecule,[2] we required a variety of 1-allyloxy-1-siloxycyclopropanes **4**. At first, the preparation of **4** seemed to be straightforward, since the saturated hydrocarbon analogs, e.g., 1-ethoxy-1-siloxycyclopropane, were prepared by Salaün *et al.*[3] (from ethyl β-halopropionate, sodium metal, and trimethylsilyl chloride) and these cyclopropanone ketals have been utilized as useful synthetic intermediates.[4] Application of the Salaün's method to the cyclopropanation of allylic β-chloropropionates (e.g., allyl and cinnamyl β-chloropropionates), however, turned out to be unsuccessful; no expected **4** were detected, instead only intractable mixtures of polymeric products were recovered. This is probably due to side reactions involving intra-[5] and intermolecular addition reactions of β-allyloxycarbonylethyl radical species to the allylic double bonds.



We report here a modification of the Salaün's cyclopropanation method of allyl β-iodoesters **1**, which utilizes zinc metal in place of sodium metal as a reducing agent.[6] By this simple exchange of metals, a variety of **4** could be prepared in reasonable yields (in most cases in 40-60% isolated yields, eq 1). Furthermore, this method displayed an interesting stereoselectivity for the cyclopropanation of methyl substituted derivatives **2** and **3** (eqs 2 and 3): both of the stereoisomers, *trans*-**5** and *cis*-**5**, were obtained with high stereoselectivity starting from **2** (eq 2) and **3** (eq 3), respectively. The alkyl ester derivatives **6** and **7** showed the similar stereoselectivity to provide *trans*-**8** and *cis*-**8** preferably over the other isomers, respectively (eqs 4 and 5). The present method was also applicable to the preparation of 1-propargyloxy-1-siloxycyclopropanes **15** (eq 6).

RESULTS AND DISCUSSION

As β-zinciopropionates, generated from β-iodopropionates and zinc-copper couple, display a very poor nucleophilic reactivity, they do not react with even some reactive electrophiles, such as aldehydes[7] and acid chlorides.[8] However, with the help of some transition metals and/or Lewis acids these organozincs enjoy reactions with various electrophiles to form C-C bonds . For example, a combination of trimethylsilyl chloride (TMSCl) and a catalytic amount of Cu(I) salts effectively promotes a Michael addition reaction of α-methyl-β-



Scheme 1. Silyl Chloride Promoted Isomerization of 9 and 10 via 11.

zinciopropionate **9** and β-methyl-β-zinciopropionate **10** to a variety of unsaturated carbonyl compounds (at around 0 - 25°C, Scheme 1).[9] Similarly, TMSCl is essential to accomplish the addition reaction of **9** and **10** to aldehydes (at around 60°C).[7] For the Michael addition reaction, two types of products **12** and **13** (e.g., E = CH_2CH_2CHO, with acrolein) are obtained selectively from **9** and **10**, respectively, whereas for the addition

reaction to aldehydes only the single type of products **12** (e.g., E = PhCHOH, with benzaldehyde) is obtained from both **9** and **10**.

In these two types of addition reactions, TMSCl seems to serve as a Lewis acid to activate carbonyl compounds toward nucleophilic addition of **9** and **10** by the coordination to the carbonyl oxygen atoms of these electrophiles. Furthermore, as suggested from the above mentioned results for the reactions of **9** and **10** with aldehydes,[7] TMSCl seems to catalyze the isomerization of **10** to **9** at the elevated temperatures, whereby TMSCl accelerates an intramolecular addition of the C-Zn bond to the ester carbonyl of **10** to generate iodozinc 1-alkoxy-2-methylcyclopropanolate (or 1-alkoxy-1-siloxy-2-methylcyclopropane **11**). Concerning on the processes involved in the isomerization between **9** and **10**, it has been verified by Nakamura and Kuwajima[10] that **11** undergoes a regioselective ring opening (> 98%) at the C_1-C_3 bond to give **9**, when exposed to $ZnCl_2$ in ether. However, it is uncertain whether the methyl substituted β-zinciopropionates **9** and **10** are able to undergo an intramolecular addition to form **11** in the presence of silylating reagents .

Table 1. Preparation of 1-Allyloxy-1-siloxycyclopropanes 4 from Allyl β-Iodopropionates 1[a, b]

run		allyl group of 1	silylating agent[c]	% isolated yield of 4[d]	
1	**1a**:	$CH_2CH{=}CH_2$	TBDMSCl	**4a**:	56
2	**1b**:	*trans*-$CH_2CH{=}CHCH_3$	TBDMSCl	**4b**:	58
3	**1c**:	$CH_2C(CH_3){=}CH_2$	TBDMSCl	**4c**:	66
4	**1d**:	$CH(Me)CH{=}CH_2$	TBDMSCl	**4d**:	42
5	**1e**:	$CH_2CH{=}C(CH_3)_2$	TBDMSCl	**4e**:	33
6	**1f**:	*trans*-$CH_2CH{=}CHPh$	TBDMSCl	**4f**:	50
7	**1f**:	*trans*-$CH_2CH{=}CHPh$	TMSCl	**4g**:	30

a) For the structures of **1** and **4**, see eq 1.
b) Reaction conditions: **1** (5 mmol) and Zn(Cu) (5.5 mmol) in THF (5 ml) at reflux for 4 - 5 h, then silyl chloride (7.5 mmol) at 35 °C for 13 - 15 h under N_2.
c) TBDMSCl and TMSCl stand for *tert*-butyldimethylsilyl chloride and trimethylsilyl chloride, respectively.
d) The yields refer to the isolated yields for the spectroscopically homogeneous materials.

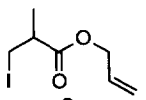
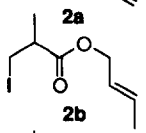
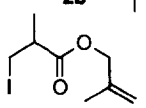
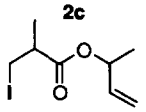
In order not only to settle this question, but also to overcome the difficulties associated with Salaün's method (see Introduction), we examined a silyl chloride promoted cyclization of β-zinciopropionates. Here we disclose that a variety of β-iodopropionates **1** - **3**, **6**, **7**, and **14** undergo the silyl chloride promoted cyclization via the corresponding β-zinciopropionates to provide 1-allyloxy- (**4**, **5**), 1-alkoxy- (**8**), and 1-propargyloxy-1-siloxycyclopropanes (**15**) in reasonable yields (eqs 1 - 6).

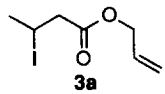
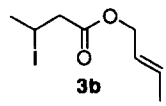
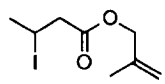
Throughout this study, cyclopropanation was undertaken under the following conditions: a β-iodopropionate **1** - **3**, **6**, **7**, or **14** was treated with 1.1 equivalents of zinc-copper couple in dry THF at reflux for 4 - 5 h

and then the resultant mixture was treated with 1.5 equivalents of TMSCl or *tert*-butyldimethylsilyl chloride (TBDMSCl) at 35°C overnight (13 - 19 h).

The results for the cyclization of allyl β-iodopropionates **1** are summarized in Table 1. Since TBDMS derivatives showed the better yields than the TMS derivatives (cf. runs 6 and 7, Table 1), most reactions were undertaken with TBDMSCl as the silylating agent. In all cases examined, the expected 1-allyloxy-1-siloxycyclopropanes **4** were obtained in moderate to good isolated yields (33-66%). The results in run 1 (Table 1) was reproducible in a larger scale experiment [**1a** (100 mmol), zinc-copper couple (110 mmol), TBDMSCl (150 mmol) in 150 ml of THF] and **4a** was isolated in almost the same yield (60%). No increase in the yield of **4a** was observed for the reaction with the increased amount of TBDMSCl (3 equivalents to **1a**). All of the products **4** were purified by distillation under reduced pressure and/or by column chromatography over silica gel (for the cases of TBDMS derivatives **4a-f**) or basic alumina (grade III, for the case of TMS derivative **4g**, which readily decomposed during purification over silica gel). The products **4** withstand without noticeable decomposition over a few years in shelf-storage at an ambient temperature.

Table 2. Stereoselective Preparation of *cis*- and *trans*-1-Allyloxy-1-(*tert*-butyldimethylsiloxy)-2-methylcyclopropanes 5 from Allyl β-Iodopropionates 2 and β-Iodobutyrates 3[a,b]

run	starting iodide **2**	time[b] (h)	% yield[c] of **5**	*cis*-**5**:*trans*-**5**[d]
1	 **2a**	15	**5a**: 54	1 : 12
2	 **2b**	15	**5b**: 66	1 : 4.8
3	 **2c**	16	**5c**: 60	1 : 7.9
4	 **2d**	10	**5d**: 41	1 : 2.4[e]

run	starting iodide **3**	time[b] (h)	% yield[c] of **5**	*cis*-**5**:*trans*-**5**[d]
5	 **3a**	14	**5a**: 47	2.5 : 1
6	 **3b**	19	**5b**: 32	4.5 : 1
7	 **3c**	18	**5c**: 50	3.6 : 1

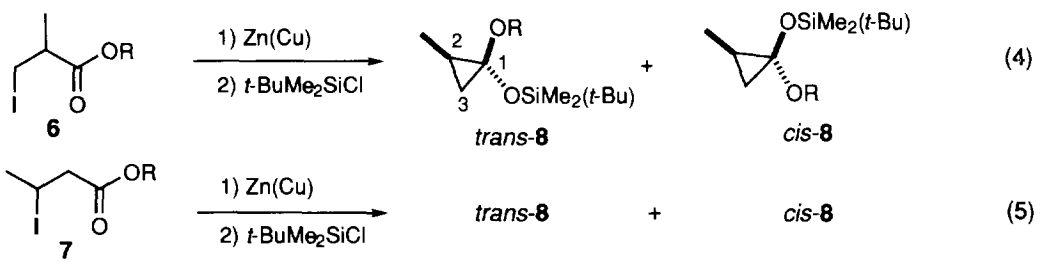
a) For the structure of **5**, see eqs 2 and 3.
b) Reaction conditions: **2** or **3** (5 mmol) and Zn(Cu) (5.5 mmol) in THF (5 ml) at reflux for 4 - 5 h, then TBDMSCl (7.5 mmol) at 35 °C for the indicated period of time under N_2.
c) The yields refer to the isolated yields for the spectroscopically homogeneous materials.
d) The ratios were determined by 400 MHz ^{1}H NMR.
e) *cis*- and *trans*-**5d** consist of two diastereomers in the ratio of 1 : 1.3 and 1 : 1.7, respectively.

The results obtained for the cyclopropanation of allyl β-iodo-α-methylpropionates **2** and β-iodobutyrate **3** are summarized in Table 2 (eqs 2 and 3). Interestingly, these cyclizations showed contrasting stereo-

selectivity; **2** provided *trans*-**5** predominantly over *cis*-**5** (runs 1-4, Table 2), while **3** gave rise to *cis*-**5** selectively over *trans*-**5** (runs 5-7, Table 2). We were unable to separate *cis*- and *trans*-**5a-c** by column chromatography over silica gel, thus the corresponding ratios listed in Table 2 were determined from the 400 MHz ^{1}H NMR spectra of the distillates. The stereoisomers of *cis*-**5d** and *trans*-**5d** could be separated by column chromatography and the ratio was determined from the isolated yields.

In order to test the generality of the stereoselectivity observed for the cyclopropanation of **2** and **3**, we next examined the cyclization of some alkyl β-iodo-α-methylpropionates **6a-d** and β-iodobutyrates **7b-e**, varying the steric bulk of the alkyl groups (R) from methyl to *tert*-butyl groups (eqs 4 and 5). The results are listed in Table 3. As apparent from this Table, the stereoselectivity turned out to be general for the cyclization of these alkyl iodoester derivatives; the primary iodides **6** provided *trans*-**8** with high selectivity, whereas the secondary iodides **7** furnished *cis*-**8** preferably over *trans*-**8**. Among the products listed in Table 3, the stereoisomers of **8a,c** were not separable and those of **8b,d,e** could be separated into each stereoisomers by column chromatography over silica gel.

Throughout Tables 2 and 3, the stereoselectivity with which β-iodo-α-methylpropionates provide the *trans* isomers is generally higher than the one with which the corresponding β-iodobutyrates furnish the *cis* isomers. However, there seems to be no apparent correlation between the stereoselectivity and the steric bulk of the alcoholic parts R of the iodoesters **2**, **3**, **6** and **7**.



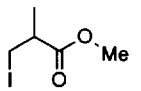
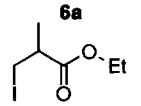
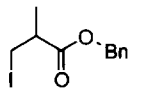
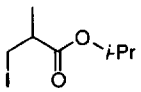
The stereoselective formation of either *trans*-**5** (and *trans*-**8**) from primary iodides **2** (and **6**) or *cis*-**5** (and *cis*-**8**) from secondary iodides **3** (and **7**) clearly indicates that these cyclopropanations are controlled kinetically, i. e., the isomerization between **9** and **10**, as shown in Scheme 1, is prohibited when TBDMSCl is used as a silylating reagent. Indeed, benzyl α-methylpropionate and benzyl butyrate were obtained as the by-products in the reactions of runs 3 and 6 (Table 3), respectively, without contamination with each other.

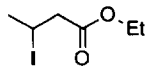
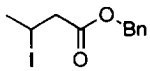
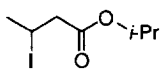
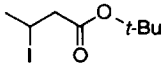
Making sharp contrast to these, the cyclopropanations of **6c** and **7c** with TMSCl, under the same conditions as those of runs 3 and 6 (Table 3), provided the mixtures of benzyl α-methylpropionate and benzyl butyrate in the ratios of 20:1 (11% isolated) and 1:6 (15% isolated), respectively, together with the TMS derivative of **8c** in low yields (15% from **6c** and 3% from **7c**). The cyclopropanation of **6c** with trimethylsilyl trifluoromethanesulfonate (TMSOTf) provided a mixture of *cis*-**8c** and *trans*-**8c** (as TMS derivatives) in 30% isolated yield. The ratio of *cis*-**8c** to *trans*-**8c** (1.9/1, TMS derivatives from TMSOTf), however, was quite different from that of *cis*-**8c** to *trans*-**8c** (1/6.8, TBDMS derivatives, run 3, Table 3).

These results clearly indicate that the ring opening process of **11** is operating for the TMS derivatives (Scheme 1) and under our conditions the ring opening is not regioselective, occurring both at the C_1-C_2 and C_1-

C_3 bonds. Furthermore, these results suggest that the main cause for the low yield of **8c** (the TMS derivative prepared from TMSCl, but not from TMSOTf) is this ring opening, the ease of which seemingly depends on both the C_2 substituents of **11** (cf. run 7, Table 1 for the C_2 non-substituted derivative) and the counter ions of Zn^{2+} (I^-, Cl^-, OTf^-).

Table 3. Stereoselective Preparation of *cis*- and *trans*- 1-Alkoxy-1-(*tert*-butyldimethylsiloxy)-2-methylcyclopropanes 8 from Alkyl β-Iodopropionates 6 and β-Iodobutyrates 7[a,b]

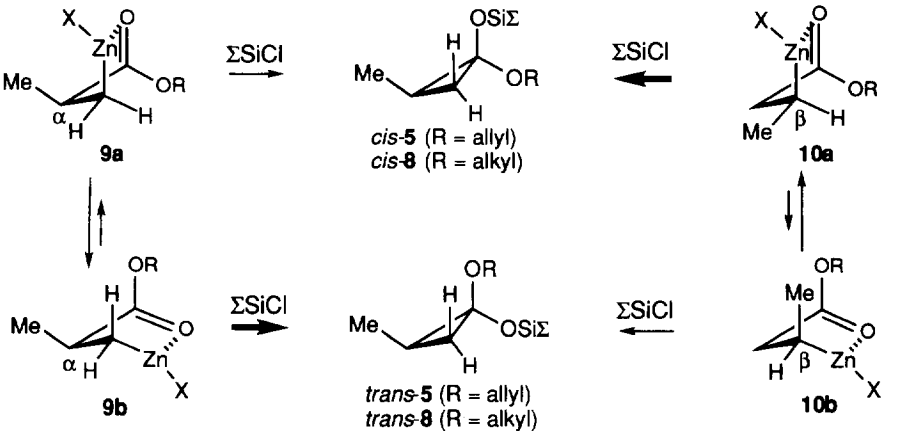
run	starting iodide **6**	time[b] (h)	% yield[c] of **8**	*cis*-**8**:*trans*-**8**[d]
1	 **6a**	15	**8a**: 54	1 : 5.6
2	 **6b**	14	**8b**: 58	1 : 5.5
3	 **6c**	15	**8c**: 61	1 : 6.8
4	 **6d**	16	**8d**: 59	1 : 2.2

run	starting iodide **7**	time[b] (h)	% yield[c] of **8**	*cis*-**8**:*trans*-**8**[d]
5	 **7b**	17	**8b**: 60	2.2 : 1
6	 **7c**	13	**8c**: 39	4.2 : 1
7	 **7d**	13	**8d**: 48	4.3 : 1
8	 **7e**	14	**8e**: 9	2.2 : 1

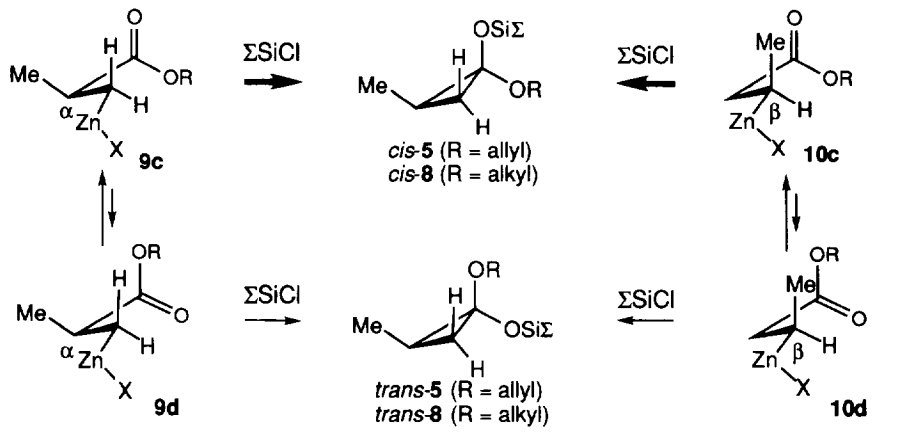
a) For the structure of **8**, see eqs 4 and 5.
b) Reaction conditions: **6** or **7** (5 mmol) and Zn(Cu) (5.5 mmol) in THF (5 ml) at reflux for 4 - 5 h, then TBDMSCl (7.5 mmol) at 35 °C for the indicated period of time under N_2.
c) The yields refer to the isolated yields for the spectroscopically homogeneous materials.
d) The ratios were determined from the isolated yields of each stereoisomers (**8b**,**d**,**e**) or from the 400 MHz ^1H NMR spectra of the mixtures (**8a**,**c**).

The contrasting stereochemical outcomes observed for the cyclopropanation of primary iodoesters (**2** and **6**) and secondary ones (**3** and **7**) (Tables 2 and 3) might be rationalized by supposing that (1) carbonyl oxygen atom coordinates to Zn^{2+} and (2) the intramolecular addition of the C-Zn bonds of **9** and **10** to their ester carbonyls proceeds with retention of configuration at the carbanionic stereocenters (Scheme 2).[11] For the cyclopropanation of **9**, two conformers **9a** and **9b** seem to be responsible. Of these, **9b** seems to be favored and would provide the *trans*-isomer selectively, since the other conformer **9a** suffers from a gauche repulsion between the C_α-Me and $ZnXL_2$ (L= ligand, omitted in Schemes 2 and 3 for simplicity) groups. For the

cyclization of **10**, the C_β-Me group of **10a** is free from the quasi diaxial repulsion against the ester group that **10b** suffers from, and hence **10a** would favorably undergo the cyclization to provide the *cis*-isomer selectively.



Scheme 2. Cyclopropanation of α-Methyl-β-zinciopropionate (9) and β-Zinciobutyrate (10) with Retention of Configuration at C-Zn Bond.

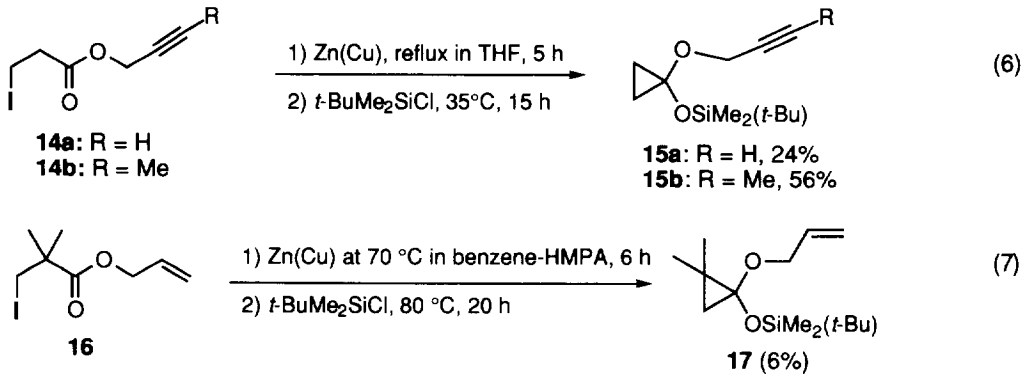


Scheme 3. Cyclopropanation of α-Methyl-β-zinciopropionate (9) and β-Zinciobutyrate (10) (10) with Inversion of Configuration at C-Zn Bond.

On the other hand, the mechanism involving an inversion of configuration outlined in Scheme 3 seems to be unlikely, since this mechanism predicts that both **9** and **10** would selectively provide the same *cis* isomers, i.e., **9c** seems to be favored over **9d**, since the C_α-Me in **9c** experiences a smaller repulsion against carbonyl oxygen atom than the C_α-Me of **9d** does against OR. On the same ground, **10c** may be favored over **10d** and would furnish the *cis* isomer selectively. According to this mechanism, the stereoselectivity is expected to be

affected largely by the steric bulk of the OR groups; in both cases of **9** and **10**, the larger the steric bulk of OR, the higher would be the *cis* selectivity. This differs entirely from what we have observed (Tables 2 and 3).

On one side, the low reactivity of organozinc halides is beneficial, as demonstrated by the successful cyclopropanation of such esters possessing acidic protons like **14a** (eq 6).[12] In this reaction, despite the presence of an acidic acetylenic proton, **15a** could be prepared according to the standard procedure. On the other side, this low reactivity poses some limitations to the present method; such cyclopropanone ketals with bulky substituents as **8e** (run 8, Table 3) and **17** (eq 7) were obtained only in very poor yields. Especially, **16** was too reluctant to undergo the cyclization. Usual treatment with TBDMSCl at 35 °C, or even at 60 °C overnight, only resulted in the quantitative formation of allyl pivalate, the reduction product of **16**. The expected product **17** could be obtained in 6% yield by the silylation with TBDMSCl in benzene-HMPA at reflux overnight.



Determination of Stereochemistry of 5 and 8. The chemical shifts and coupling patterns of cyclopropane ring protons as well as the TBDMS protons are summarized in Table 4. The ^{1}H NMR spectra (400 MHz) of **5** and **8** are rather complex, not only because all of the resonances of cyclopropane ring protons

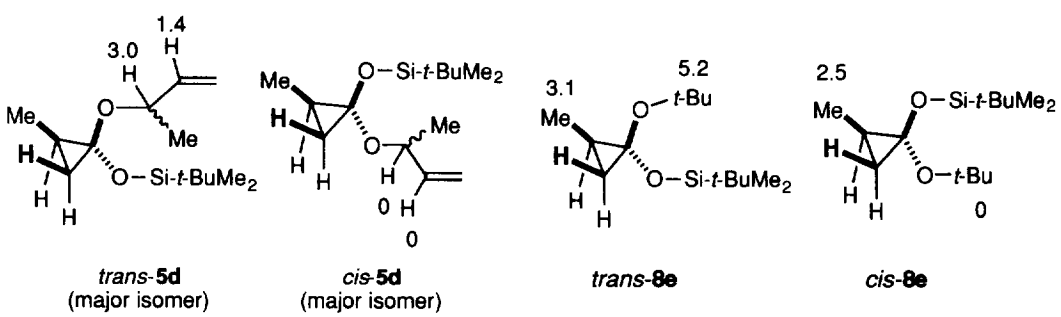


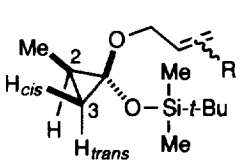
Fig. 1. NOE (%) Observed by the Irradiation at the Protons Indicated in Boldface.

appear in a narrow range of chemical shift, but also because these resonances are generally broadened owing to the restricted rotation of the substituents.[13] However, the C_3-H_{cis} protons of **5** and **8**, *cis* with respect to the C_2-Me group, can be assigned easily, since they appear separately from the other ring protons; they resonate

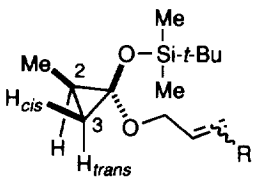
Table 4. Chemical Shifts (in ppm) and Coupling Patterns of Cyclopropane Ring Protons and TBDMS Protons of 5 and 8 Determined by 400 MHz ^{1}H NMR Spectra in $CDCl_3$[a]

	C_3H_{cis}	C_3H_{trans}	C_2H	$SiMe_2$	Si-*t*-Bu
trans-**5a**	0.43 (dd, J = 5.1, 5.9 Hz)	0.89 (m)	1.09 (m)	0.14 (s)	0.87 (s)
cis-**5a**	0.34 (m)	0.82-1.12 (m)		0.16(s), 0.18 (s)	0.90 (s)
trans-**5b**	0.43 (t, J = 5.5 Hz)	0.89 (m)	1.09 (m)	0.14 (s)	0.87 (s)
cis-**5b**	0.32 (m)	0.90 (m)	1.08 (m)	0.15 (s), 0.18 (s)	0.90 (s)
trans-**5c**	0.42 (dd, J = 5.5, 5.9 Hz)	0.90 (m)	1.10 (m)	0.14 (s)	0.87 (s)
cis-**5c**	0.35 (dd, J = 4.0, 4.4 Hz)	0.90 (m)	1.10 (m)	0.16 (s), 0.18 (s)	0.90 (s)
trans-**5d** (major)	0.51 (dd, J = 5.1, 6.2 Hz)	0.80-1.10 (m)		0.12(s)	0.87 (s)
trans-**5d** (minor)	0.45 (t, J = 5.5 Hz)	0.80-1.10 (m)		0.15 (s)	0.86 (s)
cis-**5d** (major)	0.31 (dd, J = 5.1, 5.9 Hz)	0.87-1.16 (m)		0.18 (s), 0.20 (s)	0.89 (s)
cis-**5d** (minor)	0.28 (dd, J = 5.5, 6.2 Hz)	0.87-1.16 (m)		0.14 (s)	0.91 (s)
trans-**8a**	0.38 (dd, J = 5.5, 5.9 Hz)	0.90 (m)	1.09 (m)	0.13 (s), 0.14 (s)	0.88 (s)
cis-**8a**	0.33 (m)	0.89 (m)	1.07 (m)	0.15 (s), 0.18 (s)	0.91 (s)
trans-**8b**	0.39 (dd, J = 5.1, 5.9 Hz)	0.88 (m)	1.08 (m)	0.13 (s)	0.87 (s)
cis-**8b**	0.32 (m)	1.03-1.07 (m)		0.15 (s), 0.17 (s)	0.87 (s)
trans-**8c**	0.47 (t, J = 5.7 Hz)	0.96 (m)	1.17 (m)	0.16 (s)	0.90 (s)
cis-**8c**	0.39 (dd, J = 4.8, 5.5 Hz)	0.92 (m)	1.15 (m)	0.18 (s), 0.21 (s)	0.93 (s)
trans-**8d**	0.43 (t, J = 5.5 Hz)	0.92 (m)	1.06 (m)	0.12 (s), 0.14 (s)	0.86 (s)
cis-**8d**	0.31 (dd, J = 4.8, 5.9 Hz)	0.96 (m)	1.07 (m)	0.14 (s), 0.19 (s)	0.90 (s)
trans-**8e**	0.62 (t, J = 5.1 Hz)	0.81-0.99 (m)		0.10 (s), 0.14 (s)	0.85 (s)
cis-**8e**	0.27 (dd, J = 5.5, 6.2 Hz)	0.89 (m)	1.26 (m)	0.13 (s), 0.21 (s)	0.89 (s)

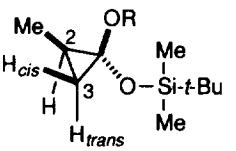
a) C_3H_{cis}, C_3H_{trans}, and C_2H are defined as follows.



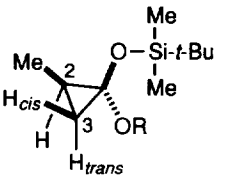
trans-**5**



cis-**5**



trans-**8**



cis-**8**

characteristically at the higher fields by ca. 0.5 ppm than the geminal C_3-H_{trans} protons, owing to the shielding effect of the methyl group.[14]

Nuclear Overhauser effects[15] turned out to be very effective to diagnose the stereochemistry of **5** and **8**. In Fig. 1 are indicated the results observed for the pairs of stereoisomers of **5d** and **8e** by irradiation at the protons (C_3-H_{cis}) indicated in boldface. In the major isomer of *trans*-**5d**, the allylic proton and the internal olefinic proton showed NOEs, while the corresponding protons of the major isomer of *cis*-**5d** showed no NOE. The NOEs of the methyl protons in these isomers were obscured owing to the overlap of the resonances with C_2-H protons. Fortunately all of the ring protons of *trans*-**8e** and *cis*-**8e** are well resolved and appear separately. In *trans*-**8e**, apparent increments in the area intensity were observed for the methyl and *t*-butyl groups, whereas in *cis*-**8e** NOE was observed only for the methyl protons.

As apparent from Table 4, the C_3-H_{cis} protons of *cis*-**5** and *cis*-**8** isomers generally appear at the higher fields than those of the corresponding *trans*-**5** and *trans*-**8** isomers. In the *cis*-isomers of **5** and **8**, the diastereotopic two methyl groups of TBDMS are exposed close to an unsymmetrical environment (C_2-Me, C_3-H, rather than C_2-H, C_3-H), and this seems to be reflected in the larger differences in the chemical shifts of these two methyl groups in the *cis* isomers of **5** and **8** than those of the corresponding *trans* isomers.

CONCLUSION

A variety of β-zinciopropionates, generated from allyl, propargyl, and alkyl β-iodopropionates as well as α-methyl- and β-methyl-β-iodopropionates by treatment with zinc-copper couple, undergo a cyclization by the use of silylating reagents (TBDMSCl, TMSCl, TMSOTf) to give cyclopropanone ketals (**4**, **5**, **8**, **15**) in the preparatively useful yields. When cyclization suffers from the steric repulsion of the substituents, the corresponding ketals such as **8e** (run 8, Table 3) and **17** (eq 7) are obtained only in low yields. The reaction displays pronounced stereoselectivity; both the *trans*- and the *cis*-isomers of **5** and **8** can be prepared with high stereoselectivity starting from primary iodoesters (**2** and **6**) and secondary ones (**3** and **7**), respectively.

Stereoselective generation of enolates has been a subject of strong concern for synthetic organic chemists, since the stereochemical homogeneity of enolates is crucial to bring about the desired stereochemistry in the products in many C-C bond formation reactions.[16] In this context, the present method may find wide applications in organic synthesis, because it enables us to stereoselectively prepare substituted 1-alkoxy-1-siloxycyclopropanes, a synthetic equivalent of a homoenolate.[4]

Finally, it should be pointed out that the alkali metal mediated cyclization of the chloro derivatives of **6** provides mixtures of *trans*- and *cis*-**8** non-stereoselectively and this method is not applicable to the cyclization of the secondary haloesters **7** (chloro and bromo derivatives).[3,14]

Acknowledgment: Support from the Japanese Ministry of Education, Science and Culture is gratefully acknowledged. We thank Mr. Y. Ohhama for his splendid assistance with the NMR experiments.

EXPERIMENTAL

Melting points were not corrected. Unless otherwise specified, short-path (bulb-to-bulb) distillation was carried out in a kugelrohr apparatus. In this case, boiling points refer to the oven temperatures. Microanalysis was performed by the Microanalysis Center of Nagasaki University. Analysis agreed with the calculated values within ± 0.3 %. Proton magnetic resonance spectra were determined either at 60, 90, or 400 MHz with tetramethylsilane as an internal standard. ^{13}C NMR spectra were determined at 100 MHz with tetramethylsilane as an internal standard. Chemical shift values were given in ppm downfield from the internal standard. High-resolution mass spectra were determined with perfluorokerosene as an internal standard (EI, 70 eV). R_f values were measured over Merck Kiesel gel $60F_{254}$.

Solvents and Reagents. THF and ether were dried and distilled from benzophenone ketyl immediately before use under N_2. Hexamethylphosphoric triamide (HMPA), dimethylformamide (DMF), and *N,N*-dimethylaniline were distilled over CaH_2 under reduced pressure. Pyridine and benzene were distilled over CaH_2. Acetone was distilled from K_2CO_3. TMSCl was distilled from Na and kept over pieces of Na under N_2. Zinc powder (reagent grade), $CuSO_4$, NaI, β-chloropropionyl chloride, β-chloropivaloyl chloride, *tert*-butyldimethysilyl chloride (TBDMSCl), and trimethylsilyl trifluoromethanesulfonate were purchased and used without further purification. Zinc-copper couple was prepared according to the literature[17] and kept under N_2. The following β-iodoesters (**1a-f**, **2a-d**, **6a-d**, **14a,b**) were prepared according to the literature[18] and used after purification by distillation under reduced pressure.

Allyl β–iodopropionate (1a): bp 85 °C/6.0 mmHg; IR (neat film) 3080 (w), 2950 (m), 1730 (s), 1650 (w) cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 2.85 - 3.13 (m, 2 H), 3.16 - 3.50 (m, 2 H), 4.60 (d, *J*= 6.3 Hz, 2 H), 5.10 - 5.50 (m, 2 H), 5.69 - 6.13 (m, 1H).

***trans*-Crotyl β–iodopropionate (1b)**: bp 80 °C/3.6 mmHg; IR (neat film) 3030 (w), 2950 (m), 1730 (s) cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 1.73 (d, *J* = 6.3 Hz, 3 H), 2.86 - 3.06 (m, 2 H), 3.23 - 3.43 (m, 2 H), 4.55 (d, *J* = 7.2 Hz, 2 H), 5.37 - 6.05 (m, 2 H).

β–Methylallyl β–iodopropionate (1c): bp 77 °C/3.3 mmHg; IR (neat film) 3090 (w), 2975 (m), 1740 (s), 1660 (m) cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 1.77 (s, 3 H), 3.02 (t, *J*= 7.2 Hz, 2 H), 3.34 (t, *J*= 7.2 Hz, 2 H), 4.56 (s, 2 H), 4.95 - 5.13 (m, 2).

α–Methylallyl β–iodopropionate (1d): bp 82 °C/5.5 mmHg; IR (neat film) 3100 (w), 2900 (m), 1735 (s), 1643 (m) cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 1.34 (d, *J*= 6.3 Hz, 2 H), 2.97 (t, *J*= 5.8 Hz, 2 H), 3.33 (t, *J*= 5.8 Hz, 2 H), 5.02 - 5.57 (m, 3 H), 5.63 - 6.06 (m, 1 H).

Prenyl β–iodopropionate (1e): bp 83 °C/1.8 mmHg; IR (neat film) 2980 (m), 1738 (s), 1645 (w) cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 1.73 (d, *J*= 4.5 Hz, 6 H), 2.96 (t, *J*= 7.2 Hz, 2 H), 3.32 (t, *J*= 7.2 Hz, 2 H), 4.62 (d, *J*= 8.1 Hz, 2 H), 5.52 - 5.46 (m, 1 H).

***trans*-Cinnamyl β–iodopropionate (1f)**: bp 160 °C/1.2 mmHg; IR (neat film) 3030 (w), 2950 (w), 1730 (s) cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 3.10 (t, *J*= 8.1 Hz, 2 H), 3.47 (t, *J*= 8.1 Hz, 2 H), 4.87 (d, *J*= 7.2 Hz, 2 H), 6.20 - 6.97 (m, 2 H).

Allyl β–iodo-α–methylpropionate (2a): bp 52 °C/0.4 mmHg; IR (neat film) 3060 (w), 1722 (s), 1640 (w), 1190 (s), 1136 (s), 967 (m) cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 1.27 (d, *J*= 6.6 Hz, 3 H), 2.70 (sextet, *J*= 6.6 Hz, 1 H), 3.00 - 3.66 (m, 2 H), 4.50 (d, *J*= 5.2 Hz, 2 H), 5.00 - 5.43 (m, 2 H), 5.86 (m, 1 H).

***trans*-Crotyl β-iodo-α-methylpropionate (2b)**: bp 80 °C/0.4 mmHg; IR (neat film) 3020 (w), 1735 (s), 1456 (m), 1380 (m), 1260 (m), 1206 (s), 1155 (s), 1041 (w), 1015 (w), 965 (s) cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 1.26 (d, *J*= 6.6 Hz, 3 H), 1.72 (br d, *J*= 5.6 Hz, 3 H), 2.68 (sextet , *J*= 6.6 Hz, 1 H), 2.97 - 3.69 (m, 2 H), 4.46 (br d, *J*= 4.6 Hz, 2 H), 5.17 - 6.08 (m, 2 H).

β-Methylallyl β-iodo-α-methylpropionate (2c): bp 76 °C/0.42 mmHg; IR (neat film) 3078 (w), 2972 (m), 2932 (m), 2976 (w), 1738 (s), 1661 (w), 1465 (m), 1331 (m), 1260 (m), 1205 (s), 1152 (s), 1043 (m), 1018 (w), 990 (w), 956 (w), 908 (m) cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 1.28 (d, *J*= 6.6 Hz, 3 H), 1.76 (s, 3 H), 2.73 (sextet , *J*= 6.6 Hz, 1 H), 3.02 - 3.72 (m, 2 H), 4.47 (s, 2 H), 4.82 - 5.00 (m, 2 H).

α-Methylallyl β-iodo-α-methylpropionate (2d): bp 52 °C/0.4 mmHg; IR (neat film) 2974 (m), 2928 (m), 1728 (s), 1649 (w), 1372 (m), 1206 (s), 1153 (s), 1111 (m), 1084 (m), 1040 (m), 1010 (w), 986 (m), 925 (m) cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 1.27 (d, *J*= 7.2 Hz, 3 H), 1.34 (d, *J*= 6.6 Hz, 3 H), 2.70 (sextet, *J*= 6.6 Hz, 1 H), 3.03 - 3.53 (m, 2 H), 5.00 - 5.43 (m, 3 H), 5.87 (m, 1 H).

Methyl β-iodopropionate (6a): bp 60 °C/3.0 mmHg; IR (neat film) 2970 (m), 2870 (w), 1738 (s), 1431 (s), 1359 (m), 1210 (s), 1155 (s), 1117 (m), 1094 (m), 1043 (m), 1016 (w), 980 (w), 900 (w) cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 1.27 (d, *J*= 6.6 Hz, 3 H), 2.73 (sextet, *J*= 6.6 Hz, 1 H), 3.03 -3.53 (m, 2 H), 3.70 (s, 3 H).

Ethyl β-iodo-α-methylpropionate (6b): bp 60 °C/3.0 mmHg; IR (neat film) 2976 (s), 2932 (m), 1732 (s), 1456 (m), 1330 (m), 1277 (m), 1206 (s), 1151 (s), 1091 (m), 1040 (m), 1021 (m), 930 (w) cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 1.23 (d, *J*= 6.6 Hz, 3 H), 1.26 (t, *J*= 7.0 Hz, 3 H), 2.68 (sextet, 6.6 Hz, 1 H), 3.00 - 3.51 (m, 2 H), 4.13 (q, *J*= 7.0 Hz, 2 H).

Benzyl β-iodo-α-methylpropionate (6c): bp 110 °C/0.01 mmHg; IR (neat film) 3050 (w), 3022 (w), 2963 (m), 1732 (s), 1450 (m), 1328 (m), 1260 (m), 1200 (s), 1148 (s), 1084 (w), 1012 (m), 959 (w), 900 (w), 690 (s) cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 1.29 (d, *J*= 6.6 Hz, 3 H), 2.76 (sextet, *J*= 6.6 Hz, 1 H), 3.03 - 3.54 (m, 2 H), 5.11 (s, 2 H), 7.31 (s, 5 H).

Isopropyl β-iodo-α-methylpropionate (6d): bp 58 °C/0.01 mmHg; IR (neat film) 2970 (s), 2924 (m), 1730 (s), 1452 (m), 1374 (m), 1270 (m), 1212 (s), 1160 (m), 1109 (s), 1039 (w), 1012 (w), 947 (w), 905 (w) cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 1.26 (d, *J*= 6.4 Hz, 9 H), 2.16 (sextet, *J*= 6.4 Hz, 1 H), 3.03 - 3.51 (m, 2 H), 5.00 (septet, 6.4 Hz, 1 H).

Propargyl β-iodopropionate (14a): bp 95 °C/0.8 mmHg; IR (neat film) 3272 (s), 2920 (w), 2200 (w), 1735 (s), 1370 (m), 1231 (m), 1191 (s), 1140 (s), 1114 (s), 1030 (w), 987 (m) cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 2.36 (t, *J* = 2.6 Hz, 1 H), 2.82 - 3.49 (m, 4 H), 4.68 (d, *J*= 2.6 Hz, 2 H).

2-Butynyl β-iodopropionate (14b): bp 77 °C/1.3 mmHg; IR (neat film) 2240 (m), 1740 (s) cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 1.86 (s, 3 H), 2.90 - 3.17 (m, 2 H), 3.27 - 3.50 (m, 2 H), 4.65 - 4.72 (m, 2 H).

General Procedure for the Preparation of β-Iodobutyrates: β-Iodobutyrates (**3a-c** and **7b-e**) were prepared as follows as typified with benzyl β-iodobutyrate (**7c**): Benzyl acetate (15.0 g, 100 mmol) was added at - 78°C over a period of 30 min via a syringe into a solution of LDA in THF-hexane, prepared from diisopropylamine (10.1 g, 100 mmol in 100 ml of THF) and n-butyllithium (105 mmol, 65 ml of 1.6 N hexane solution) at - 78°C for 30 min and at 0 °C for 1 h. Into this solution was added freshly distilled acetaldehyde (6.7 ml, 120 mmol) in one portion at the same temperature. The mixture was stirred for 2-3 min and then 2 N HCl (50ml) was added at - 78°C. After evaporation of the organic solvents, the residue was extracted with ethyl

acetate (2 x 150 ml). The combined extracts were washed with sat. $NaHCO_3$, dried ($MgSO_4$), and concentrated and the residue was distilled (100 °C/0.6 mmHg) to give benzyl β-hydroxybutyrate (10.7 g, 55 mmol) in 55% yield. The solution of the distillate (10.7 g) and *p*-toluenesulfonyl chloride (12.6 g, 66 mmol) in dry pyridine (7 ml) was stirred at 0 °C for 4 h under N_2 and then kept in a refrigerator for 2 days. The mixture was dissolved into ethyl acetate (200 ml) and washed successively with 2 M HCl (18 ml) and sat. NaCl, dried ($MgSO_4$), and concentrated. Then the residue was dissolved in dry acetone (55 ml) and into this solution was added NaI (24.7 g, 165 mmol). This heterogeneous mixture was refluxed for 2 days under N_2. After distilling off the solvent, the residue was diluted with water and extracted with ethyl acetate (100 ml + 50 ml). The organic extracts were successively washed with 1 M $Na_2S_2O_3$ and sat. $NaHCO_3$, dried ($MgSO_4$), concentrated, and distilled (98 °C/0.35 mmHg) to give **7c** (9.83 g) in 59% overall yield from β-hydroxybutyrate.

Allyl β–iodobutyrate (3a): bp 85 °C/0.40 mmHg; IR (neat film) 3078 (w), 2978 (w), 2950 (w), 2918 (w), 1739 (s), 1654 (w), 1416 (m), 1380 (m), 1290 (s), 1198 (s), 1140 (s), 1071 (m), 989 (s), 930 (m) cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 1.94 (d, *J*= 7.0 Hz, 3 H), 2.92 (dd, *J*= 7.0, 1.8 H, 2 H), 4.00 - 4.65 (m, 3 H), 5.00 - 5.45 (m, 2 H), 5.78 (m, 1 H).

***trans*-Crotyl β–iodobutyrate (3b)**: bp 95 °C/0.50 mmHg; IR (neat film) 3020 (w), 2920 (w), 1738 (s), 1445 (m), 1379 (m), 1286 (m), 1193 (s), 1139 (s), 1070 (m), 1000 (m), 963 (s), 906 (w) cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 1.73 (br d, *J*= 5.0 Hz, 3 H), 1.92 (d, *J*= 7.0 Hz, 3 H), 2.77 - 3.00 (m, 2 H), 4.07 - 4.70 (m, 3 H), 5.07 - 5.97 (m, 2 H).

β–Methylallyl β–iodobutyrate (3c): bp 90 °C/0.40 mmHg; IR (neat film) 3074 (w), 2966 (w), 2914 (w), 1737 (s), 1663 (w), 1451 (m), 1378 (m), 1260 (m), 1193 (s), 1140 (s), 1070 (m), 1001 (m), 960 (w), 905 (m) cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 1.75 (s, 3 H), 1.93 (d, *J*= 7.0 Hz, 3 H), 2.93 (dd, *J*= 7.0, 1.8 Hz, 2 H), 4.40 (sextet, *J*= 7.0, 1 H), 4.44 (s, 2 H), 4,77 - 4.98 (m, 2 H).

Ethyl β–iodobutyrate (7b): bp 75 °C/0.40 mmHg; IR (neat film) 2980 (m), 2924 (m), 2862 (w), 1736 (s), 1443 (m), 1350 (m), 1373 (s), 1288 (s), 1201 (s), 1140 (s), 1069 (m), 1029 (s), 998 (w), 938 (w), 905 (w) cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 1.27 (t, *J*= 7.2 Hz, 3 H), 1.93 (d, *J*= 6.7 Hz, 3 H), 2.86 (dd, *J*= 6.7, 1.8 Hz, 2 H), 4.09 (q, *J*= 7.2 Hz, 2 H), 4.36 (sextet, *J*= 6.7 Hz, 1 H).

Benzyl β–iodobutyrate (7c): bp 98 °C/0.35 mmHg; IR (neat film) 3052 (w), 3022 (w), 2944 (m), 1732 (s), 1451 (m), 1410 (m), 1355 (m), 1286 (s), 1190 (s), 1137 (s), 1070 (m), 1001 (m), 970 (m), 906 (w), 690 (s) cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 1.92 (d, *J*= 7.0 Hz, 3 H), 2.93 (d, *J*= 7.0 Hz, 1 H), 2.96 (d, *J*= 7.0 Hz, 1 H), 4.43 (sextet, *J*= 7.0 Hz, 1 H), 5.09 (s, 2 H), 7.28 (s, 5 H).

Isopropyl β–iodobutyrate (7d): bp 70 °C/0.80 mmHg; IR (neat film) 2974 (s), 2870 (w), 1729 (s), 1450 (m), 1313 (s), 1289 (s), 1209 (s), 1140 (s), 1106 (s), 1070 (m), 997 (w), 959 (m), 909 (w) cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 1.23 (d, *J*= 6.2 Hz, 6 H), 1.93 (d, *J*= 6.8 Hz, 3 H), 2.86 (br d, *J*= 6.8 Hz, 2 H), 4.40 (sextet, *J*= 6.8 Hz, 1 H), 4.97 (septet, *J*= 6.2 Hz, 1 H).

***tert*-Butyl β–iodobutyrate (7e)**: bp 41 °C/0.39 mmHg; IR (neat film) 2980 (w), 2938 (m), 1732 (s), 1459 (m), 1370 (s), 1297 (s), 1221 (m), 1167 (s), 1138 (s), 1060 (m), 1000 (w), 951 (w), 909 (w) cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 1.43 (s, 9 H), 1.91 (d, *J*= 7.0 Hz, 3 H), 2.79 (dd, *J*= 7.0, 2.0 Hz, 2 H), 4.35 (sextet, *J*= 7.0 Hz, 1 H).

Preparation of Allyl β-Iodopivalate (16): Into a solution of β-chloropivaloyl chloride (7.75 g, 50 mmol) in ether (50 ml) was added a mixture of allyl alcohol (3.2 g, 55 mmol, dried over molecular sieves 4A)

and *N,N*-dimethylaniline (6.7 g, 55 mmol) over a period of 20 min at 0 °C under N_2. The mixture was stirred at 0 °C for 3 h then at rt overnight. A mixture of allyl alcohol (20 mmol) and *N,N*-dimethylaniline (20 mmol) was added into this reaction mixture over a period of 10 min at 0 °C under N_2 and the resultant mixture was stirred at rt overnight. The mixture was diluted with ether (100 ml) and washed successively with 2 N HCl and sat. NaCl, dried ($MgSO_4$), concentrated, and distilled (64 °C/0.8 mmHg) to give allyl β-chloropivalate (2.47 g, 14 mmol) in 28% yield. The mixture of β-chloropivalate (2.47 g, 14 mmol) and NaI (6.25 g, 42 mmol) in dry DMF (13 ml) was stirred and heated at 100 °C under N_2 for 2 days. The mixture was diluted with ethyl acetate (100 ml) and then with hexane (100 ml) and successively washed with 1 M $Na_2S_2O_3$ and water (5 x 10 ml), dried ($MgSO_4$), concentrated, and distilled under reduced pressure to give **16** in 47% yield. **16**: bp 80°C/0.50 mmHg; 2944 (m), 2900 (w), 1725 (s), 1640 (w), 1460 (m), 1288 (s), 1254 (m), 1220 (m), 1160 (s), 1122 (s), 1072 (w), 975 (m), 922 (m) cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 1.28 (s, 6 H), 3.30 (s, 2 H), 4.50 (br d, J= 5.2 Hz, 2 H), 5.03 - 5.40 (m, 2 H), 5.84 (m, 1 H).

General Procedure for Cyclopropanation: 1-Allyloxy-1-siloxycyclopropanes **4a-g**, 1-allyloxy-2-methyl-1-siloxycyclopropanes **5a-d**, 1-alkoxy-2-methyl-1-siloxycyclopropanes **8a-e**, and 1-propargyloxy-1-siloxycyclopropanes **15a,b** were prepared as follows as typified with 1-allyloxy-1-*tert*-butyldimethylsiloxycyclopropane (**4a**): a mixture of **1a** (1.2 g, 5.0 mmol) and zinc-copper couple (362 mg, 5.5 mmol) in dry THF (5 ml) was stirred and refluxed under N_2 for 5 h. The reaction temperature was allowed to cool to 35 °C, and then a solution of TBDMSCl (1.13 g, 7.5 mmol) in THF (1.5 ml) was added into this mixture via a syringe. The mixture was stirred at the same temperature for 15 h. After being allowed to cool to rt, the mixture was diluted with ether (40 ml) and washed with water [20 ml, containing K_2CO_3 (2.1 g, 15 mmol)]. The water layer was extracted with ether (2 x 10 ml). The combined extracts were dried ($MgSO_4$), concentrated, and distilled (71 °C/6.0 mmHg) to give **4a** in 56% yield.

The synthesis of **17** (eq 7) was unsuccessful according to the procedure described here and **17** was prepared under somewhat different conditions [zincation in benzene (10 ml) and HMPA (1.3 ml) at 70 °C for 6 h and silylation at 80°C for 20 h].

It is recommended to undertake the extractive work-up and distillation as promptly as possible. We occasionally experienced serious drops in yields, when distillation was delayed next day. Generally TBDMS derivatives could be purified further by the column chromatography over silica gel without noticeable decomposition, while TMS derivatives decomposed over silica gel, therefore further purification of these derivatives was undertaken over basic alumina (grade III). The *cis*- and *trans*-isomers of **5d**, **8b**, **8d**, and **8e** were separated each other by the column chromatography over silica gel. Generally the cyclopropanone ketals described here, after purification by distillation and/or column chromatography, were stable at ambient temperature under N_2 and kept over a few years without noticeable decomposition.

1-Allyloxy-1-(*tert*-butyldimethylsiloxy)cyclopropane (4a): R_f = 0.86 (benzene:hexane = 5:2, v/v); bp 71 °C/6.0 mmHg; IR (neat film) 3095 (w), 3010 (w), 2920 (s), 1649 (w), 1254 (m), 1220 (s), 1040 (m), 1007 (s), 995 (s), 918 (m) cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 0.16 (s, 6 H), 0.88 (s, 9 H), 0.82 - 0.91 (m, 4 H), 4.07 - 4.22 (m, 2 H), 5.01 - 5.37 (m, 2 H), 5.69 - 6.16 (m, 1 H). High-resolution MS, Calcd for $C_{12}H_{24}O_2Si$ - *t*-Bu: 171.0841. Found m/e (relative intensity): 171.0813 (M^+- *t*-Bu), 73 (100).

1-*trans*-Crotyloxy-1-(*tert*-butyldimethylsiloxy)cyclopropane (4b): R_f = 0.75 (benzene : hexane = 5:2, v/v); bp 100 °C/13.2 mmHg; IR (neat film) 3075 (w), 2900 (s), 1675 (w), 1252 (s), 1210 (s), 1082 (m), 1015 (s), 990 (s), 935 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.16 (s, 6 H), 0.88 (s, 9 H), 0.82 - 0.91 (m, 4 H), 1.69 (d, *J*= 4.5 Hz, 3 H), 3.99 - 4.15 (m, 2 H), 5.49 - 5.79 (m, 2 H). High-resolution MS, Calcd for $C_{13}H_{26}O_2Si$: 242.1702. Found m/e (relative intensity): 242.1616 (M^+, 1), 185.1063 (M^+ - *t*-Bu, 28), 131 (49), 68 (100)

1-(β-Methylallyloxy)-1-(*tert*-butyldimethylsiloxy)cyclopropane (4c): R_f = 0.68 (benzene: hexane = 1:2, v/v); bp 77 °C/3.3 mmHg; IR (neat film) 3078 (w), 3060 (w), 2990 (s), 2916 (s), 2842 (s), 1655 (w), 1448 (s), 1307 (s), 1249 (s), 1218 (s), 1071 (m), 1042 (m), 1006 (s), 996 (s), 925 (w) cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 0.14 (s. 6 H), 0.87 (s, 9 H), 0.73 - 0.93 (m, 4 H), 1.68 (s, 3 H), 3.94 (s, 2 H), 4.81 (s, 1 H), 4.83 (s, 1 H). High-resolution MS, Calcd for $C_{13}H_{26}O_2Si$: 242.1702. Found m/e (relative intensity): 242.1612 (M^+, <1), 185.1039 (M^+ - *t*-Bu), 131 (16), 75 (100).

1-(α-Methylallyloxy)-1-(*tert*-butyldimethylsiloxy)cyclopropane (4d): R_f = 0.84 (benzene: hexane = 5:2, v/v); bp 91 °C/8.0 mmHg; IR (neat film) 3066 (w), 2984 (w), 2926 (s), 2900 (s), 1639 (w), 1451 (m), 1296 (s), 1213 (s), 1052 (m), 1007 (s), 997 (s), 971 (m), 953 (m), 909 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.15 (s, 3 H), 0.17 (s, 3 H), 0.72 - 0.98 (m, 4 H), 0.88 (s, 9 H), 1.26 (dd, *J*= 6.6, 1.5 Hz, 3 H), 4.47 (quintet, *J*= 6.6 Hz, 1 H), 5.03 (dt, *J*= 10.4, 1.5 Hz, 1 H), 5.15 (dt, *J*= 17.2, 1.5 Hz, 1 H), 5.83 (ddd, *J*= 17.2, 10.4, 6.6 Hz, 1 H). High-resolution MS, Calcd for $C_{13}H_{26}O_2Si$: 242.1702. Found m/e (relative intensity): 242.1681 (M^+, <1), 185.1025 (M^+ - *t*-Bu, 31), 131 (54), 75 (100).

1-Prenyloxy-1-(*tert*-butyldimethylsiloxy)cyclopropane (4e): R_f = 0.43 (benzene:hexane = 1:2, v/v); bp 90 °C/0.5 mmHg; IR (neat film) 3076 (w), 3000 (w), 2940 (s), 2918 (s), 2872 (m), 1671 (w), 1470 (m), 1448 (m), 1303 (s), 1218 (s), 1005 (s), 990 (s), 923 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 0.14 (s, 6 H), 0.72 - 0.97 (m, 4 H), 0.88 (s, 9 H), 1.65 (s, 3 H), 1.72 (s, 3 H), 4.06 (d, *J*= 6.4 Hz, 2 H), 5.22 (m, 1 H). High-resolution MS, Calcd for $C_{14}H_{28}O_2Si$ - *t*-Bu: 199.1154. Found m/e (relative intensity): 199.1156 (M^+ - *t*-Bu, 12), 131 (48), 69 (100).

1-*trans*-Cinnamyloxy-1-(*tert*-butyldimethylsiloxy)cyclopropane (4f): R_f = 0.44 (benzene: hexane = 1:2, v/v); bp 120 °C/0.008 mmHg; IR (neat film) 3050 (w), 3000 (w), 2920 (s), 2958 (m), 1481 (w), 1300 (s), 1240 (m), 1208 (s), 1056 (w), 1000 (s), 951 (m), 762 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.19 (s, 6 H), 0.83 - 0.87 (m, 2 H), 0.90 (s, 9 H), 0.94 - 0.99 (m, 2 H), 4.33 (dd, *J*= 6.0, 1.5 Hz, 2 H), 6.27 (dt, *J*= 15.9, 6.0 Hz, 1 H), 6.58 (d, *J*= 15.9 Hz, 1 H), 7.20 - 7.38 (m, 5 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ -3.97 (Si<u>Me</u>$_2$), 14.13 ($C_{2,3}$), 17.75 (Si-<u>C</u>Me$_3$), 25.69 (Si-C<u>Me</u>$_3$), 67.02 (allylic CH_2), 86.72 (C_1), 126.18, 126.45, 127.54, 128.47, 131.79, 136.92. Anal. Calcd for $C_{18}H_{28}O_2Si$: C, 71.00; H, 9.27. Found: C, 70.89; H, 9.23.

1-*trans*-Cinnnamyloxy-1-(trimethylsiloxy)cyclopropane (4g): R_f = 0.33 (benzene:hexane = 1:2, v/v); bp 152 °C/0.70 mmHg; IR (neat film) 3050 (w), 3030 (w), 3000 (w), 2926 (m), 2832 (w), 1440 (m), 1300 (s), 1239 (s), 1207 (s), 1080 (w), 1018 (s), 993 (s), 950 (m), 853 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.21 (s, 9 H), 0.85 - 0.89 (m, 2 H), 0.97 - 1.00 (m, 2 H), 4.32 (dd, *J*= 6.0, 1.5 Hz, 2 H), 6.28 (dt, *J*=

15.9, 6.0 Hz, 1 H), 6.58 (d, *J*= 15.9 Hz, 1 H), 7.20 - 7.39 (m, 5 H). Anal. Calcd for $C_{15}H_{22}O_2Si$: C, 68.66; H, 8.45. Found: C, 68.43; H, 8.47.

1-Allyloxy-1-(*tert*-butyldimethylsiloxy)-2-methylcyclopropane (5a): R_f = 0.79 (benzene: hexane = 2:1, v/v); bp 84 °C/2.0 mmHg; IR (neat film) 3052 (w), 2984 (w), 2920 (s), 2900 (s), 2824 (s), 1639 (w), 1428 (w), 1261 (s), 1240 (s), 1189 (s), 1020 (m), 1000 (m), 931 (m), 905 (m), 821 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) *trans*-**5a** δ 0.14 (s, 6 H), 0.43 (dd, *J*= 5.1, 5.9 Hz, 1 H), 0.89 (m, 1 H), 0.87 (s, 9 H), 1.09 (m, 1 H), 1.10 (br d, *J*= 1.5 Hz, 3 H), 4.11 (ddt, *J*= 12.6, 5.5, 1.5 Hz, 1 H), 4.18 (ddt, *J*= 12.6, 5.5, 1.5 Hz, 1 H), 5.13 (dq, *J*= 10.6, 1.7 Hz, 1 H), 5.27 (dq, *J*=17.2, 1.7 Hz, 1 H), 5.93 (ddt, *J*= 17.2, 10.6, 5.5 Hz, 1 H); *cis*-**5a** δ 0.16 (s, 3 H), 0.18 (s, 3 H), 0.34 (m, 1 H), 0.82 - 1.12 (m, 2 H), 0.90 (s, 9 H), 1.09 (m, 3 H), 3.99 (ddt, *J*= 12.5, 5.5, 1.5 Hz, 1 H), 4.21 (ddt, *J*= 12.5, 5.5, 1.5 Hz, 1 H), 5.13 (dq, *J*= 10.3, 1.5 Hz, 1 H), 5.24 (dq, *J*=17.2, 1.5 Hz, 1 H), 5.90 (ddt, *J*= 17.2, 10.3, 5.5 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz) *trans*-**5a** δ - 4.20 (Si<u>Me</u>), - 3.93 (Si<u>Me</u>), 13.19 (C_2-<u>Me</u>), 17.71 (Si-<u>C</u>Me$_3$), 19.81 (C_3), 21.10 (C_2), 25.73 (Si-C<u>Me</u>$_3$), 67.57 (allylic CH_2), 88.97 (C_1), 116.06, 134.94; *cis*-**5a**: δ - 3.78 (Si<u>Me</u>), 13.35 (C_2-<u>Me</u>), 25.96 (Si-C<u>Me</u>$_3$), 67.14 (allylic CH_2). High-resolution MS, Calcd for $C_{13}H_{26}O_2Si$: 242.1702. Found m/e (relative intensity): 242.1692 (M^+, 1), 185.0986 (14), 73 (100).

1-*trans*-Crotyloxy-1-(*tert*-butyldimethylsiloxy)-2-methylcyclopropane (5b): R_f = 0.89 (benzene:hexane = 2:1, v/v); bp 102 °C/1.9 mmHg; IR (neat film) 3076 (w), 3016 (w), 2950 (s), 2924 (s), 2880 (m), 2854 (m), 1460 (m), 1440 (m), 1360 (m), 1270 (s), 1250 (s), 1190 (s), 1159 (m), 1028 (s), 960 (m), 950 (m), 936 (m), 924 (m), 834 (s), 772 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) *trans*-**5b** δ 0.14 (s, 6 H), 0.43 (t, *J*= 5.5 Hz, 1 H), 0.89 (m, 1 H), 0.87 (s, 9 H), 1.09 (m, 1 H), 1.11 (br d, *J*= 2.6 Hz, 3 H), 1.70 (br d, *J*= 6.2 Hz, 3 H), 4.01 - 4.13 (m, 2 H), 5.50 - 5.76 (m, 2 H); *cis*-**5b** δ 0.15 (s, 3 H), 0.18 (s, 3 H), 0.32 (m, 1 H), 0.90 (m, 1 H), 0.90 (s, 9 H), 1.08 (m, 1 H), 1.06 (br s, 3 H), 1.70 (br d, *J*= 6.2 Hz, 3 H), 3.90 (ddt, *J*= 11.4, 6.6, 1.1 Hz, 1 H), 4.14 (ddt, *J*= 11.4, 6.6, 1.1 Hz, 1 H), 5.47 - 5.84 (m, 2 H). High-resolution MS, Calcd for $C_{14}H_{28}O_2Si$: 256.1859. Found m/e (relative intensity): 256.1845 (M^+, 3), 241 (10), 199 (34), 145 (43), 73 (100).

1-(β-Methallyloxy)-1-(*tert*-butyldimethylsiloxy)-2-methylcyclopropane (5c): R_f = 0.79 (benzene:hexane = 2:1, v/v); bp 105 °C/1.5 mmHg; IR (neat film) 3068 (w), 2944 (m), 2922 (m), 2878 (m), 2850 (m), 1660 (w), 1461 (m), 1360 (m), 1273 (m), 1200 (s), 1160 (s), 1088 (m), 949 (m), 936 (m), 836 (s), 773 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) *trans*-**5c** δ 0.14 (s, 6 H), 0.42 (dd, *J*= 5.9, 5.5 Hz, 1 H), 0.90 (m, 1 H), 0.87 (s, 9 H), 1.10 (m, 1 H), 1.11 (br d, *J*= 1.5 Hz, 3 H), 1.73 (s, 3 H), 3.99 (d, *J*= 12.5 Hz, 1 H), 4.09 (d, *J*= 12.5 Hz, 1 H), 4.83 (br s, 1 H), 4.97 (br s, 1 H); *cis*-**5c** δ 0.16 (s, 3 H), 0.18 (s, 3 H), 0.35 (dd, *J*= 4.4, 4.0 Hz,1 H), 0.90 (m, 1 H), 0.90 (s, 9 H), 1.07 (br s, 3 H), 1.10 (m, 1 H), 1.71 (br s, 3 H), 3.87 (d, *J*= 12.5 Hz, 1 H), 4.11 (d, *J*= 12.5 Hz, 1 H), 4.83 (br s, 1 H), 4.93 (br s, 1 H). High-resolution MS, Calcd for $C_{14}H_{28}O_2Si$ - Me: 241.1624. Found m/e (relative intensity): 241.1648 (4). MS, Found m/e (relative intensity): 256 (<1), 241 (2), 213 (5), 199 (39), 143 (18), 73 (100).

1-(α-Methallyloxy)-1-(*tert*-butyldimethylsiloxy)-2-methylcyclopropane (5d): bp 90°C/5.5 mmHg. *trans*-**5d** (R_f = 0.69, benzene:hexane = 1:2, v/v, consisting of two diastereomers in a ratio of 1.7:1); IR (neat film) 2930 (s), 2900 (s), 2884 (m), 1635 (w), 1450 (w), 1350 (w), 1258 (m), 1178 (s), 1095 (w), 1005

(m), 975 (w), 936 (s), 908 (m), 821 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) the major isomer δ 0.12 (s, 6 H), 0.51 (dd, *J*= 5.1, 6.2 Hz, 1 H), 0.80 - 1.10 (m, 2 H), 0.87 (s, 9 H), 1.07 (br s, 3 H), 1.29 (d, *J*= 6.6 Hz, 3 H), 4.44 (quintet. t, *J*=6.6, 1.1 Hz, 1 H), 5.01 (ddd, *J*= 10.3, 1.8, 1.1 Hz, 1 H), 5.15 (dt, *J*= 17.2, 1.5 Hz, 1 H), 5.80 (ddd, *J*= 17.2, 10.3, 6.6 Hz, 1 H); the minor isomer δ 0.15 (s, 6 H), 0.45 (t, *J*= 5.5 Hz, 1 H), 0.80 - 1.10 (m, 2 H), 0.86 (s, 9 H), 1.08 (br s, 3 H), 1.24 (d, *J*= 6.2 Hz, 3 H), 4.39 (qdt, *J*=6.2, 6.6, 1.1 Hz, 1 H), 5.03 (ddd, *J*= 10.4, 1.8, 1.1 Hz, 1 H), 5.16 (dt, *J*= 17.2, 1.5 Hz, 1 H), 5.94 (ddd, *J*= 17.2, 10.4, 6.6 Hz, 1 H). *cis*-**5d** (R_f = 0.63, benzene:hexane = 1:2, v/v, consisting of two diastereomers in a ratio of 1.3:1); IR (neat film) 2924 (s), 2900 (s), 2864 (m), 1637 (w), 1450 (w), 1350 (w), 1260 (s), 1240 (m), 1188 (s), 1092 (m), 1049 (m), 1005 (s), 985 (s), 931 (w), 906 (m), 820 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) the major isomer δ 0.18 (s, 3 H), 0.20 (s, 3 H), 0.31 (dd, *J*= 5.1, 5.9 Hz, 1 H), 0.87 - 1.16 (m, 2 H), 0.89 (s, 9 H), 0.99 (br d, *J*= 6.2 Hz, 3 H), 1.21 (d, *J*=6.2 Hz, 3 H), 4.38 (m, 1 H), 5.03 (m, 1 H), 5.14 (dt, *J*= 17.2, 1.5 Hz, 1 H), 5.89 (ddd, *J*=17.2, 10.3, 6.5 Hz, 1 H); the minor isomer δ 0.14 (s, 6 H), 0.28 (dd, *J*= 6.2, 5.5 Hz, 1 H), 0.87 - 1.16 (m, 2 H), 0.91 (s, 9 H), 1.07 (br s, 3 H), 1.24 (d, *J*= 6.6 Hz, 3 H), 4.38 (m, 1 H), 5.03 (m, 1 H), 5.14 (dt, *J*= 17.2, 1.4 Hz, 1 H), 5.74 (ddd, *J*= 17.2, 10.3, 7.3 Hz, 1 H). High-resolution MS, Calcd for $C_{14}H_{28}O_2Si$: 256.1859. Found m/e (relative intensity): 256.1865 (M^+, <1), 199.1164 (12), 171 (3), 145 (26), 73 (100).

1-Methoxy-1-(*tert*-butyldimethylsiloxy)-2-methylcyclopropane (8a): R_f = 0.68 (benzene: hexane = 2:1, v/v); bp 65 °C/16 mmHg; IR (neat film) 2920 (s), 2900 (s), 2860 (m), 1448 (m), 1370 (w), 1350 (m), 1260 (m), 1197 (s), 1166 (s), 1096 (m), 1002 (m), 941 (m), 921 (m), 820 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) *trans*-**8a** δ 0.13 (s, 3 H), 0.14 (s, 3 H), 0.38 (dd, *J*= 5.5, 5.9 Hz, 1 H), 0.90 (m, 1 H), 0.88 (s, 9 H), 1.09 (m, 1 H), 1.09 (br s, 3 H), 3.39 (s, 3 H); *cis*-**8a** δ 0.15 (s, 3 H), 0.18 (s, 3 H), 0.33 (m, 1 H), 0.89 (m, 1 H), 0.91 (s, 9 H), 1.07 (m, 1 H), 1.09 (m, 3 H), 3.32 (s, 3 H). High-resolution MS, Calcd for $C_{11}H_{24}O_2Si$: 216.1546. Found m/e (relative intensity): 216.1518 (M^+, 17), 201 (44), 159 (100).

1-Ethoxy-1-(*tert*-butyldimethylsiloxy)-2-methylcyclopropane (8b): bp 60 °C/1.2 mmHg; IR (neat film) 3050 (w), 2930 (s), 2904 (s), 1465 (m), 1351 (w), 1268 (s), 1244 (s), 1195 (s), 1100 (m), 1048 (s), 1010 (s), 940 (s), 900 (m), 830 (s) cm^{-1}. *trans*-**8b**: R_f = 0.77 (benzene:hexane = 2:1, v/v); ^1H NMR ($CDCl_3$, 400 MHz) δ 0.13 (s, 6 H), 0.39 (dd, *J*= 5.1, 5.9 Hz, 1 H), 0.88 (m, 1 H), 0.87 (s, 9 H), 1.08 (m, 1 H), 1.08 (br d, *J*= 1.5 Hz, 3 H), 1.19 (t, *J*= 7.1 Hz, 3 H), 3.63 (dq, *J*=9.4, 7.1 Hz, 1 H), 3.70 (dq, *J*= 9.4, 7.1 Hz, 1 H). *cis*-**8b**: R_f = 0.73 (benzene:hexane = 2:1, v/v); ^1H NMR ($CDCl_3$, 400 MHz) δ 0.15 (s, 3 H), 0.17 (s, 3 H), 0.32 (m, 1 H), 0.90 (s, 9 H), 1.03 - 1.07 (m, 2 H), 1.05 (br s, 3 H), 1.15 (t, *J*= 7.1 Hz, 3 H), 3.49 (dq, *J*= 9.4, 7.1 Hz, 1 H), 3.74 (dq, *J*= 9.4, 7.1 Hz, 1 H). High-resolution MS, Calcd for $C_{12}H_{26}O_2Si$: 230.1702. Found m/e (relative intensity): 230.1711 (M^+, 5), 215 (9), 173 (7), 73 (100).

1-Benzyloxy-1-(*tert*-butyldimethylsiloxy)-2-methylcyclopropane (8c): R_f = 0.66 (benzene:hexane = 1:1, v/v); bp 100 °C/0.3 mmHg; IR (neat film) 2924 (s), 2900 (s), 2856 (m), 1485 (w), 1350 (w), 1239 (m), 1182 (s), 1142 (w), 1070 (w), 1011 (w), 940 (w), 820 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz), *trans*-**8c** δ 0.16 (s, 6 H), 0.47 (t, *J*= 5.7 Hz, 1 H), 0.90 (s, 9 H), 0.96 (m 1 H), 1.15 (br s, 3 H), 1.17 (m, 1 H), 4.66 (d, *J*= 11.4 Hz, 1 H), 4.72 (d, *J*= 11.4 Hz, 1 H), 7.25 - 7.36 (m, 5 H); *cis*-**8c** δ 0.18 (s, 3 H), 0.21 (s, 3 H), 0.39 (dd, *J*= 4.8, 5.5 Hz, 1 H), 0.92 (m, 1 H), 0.93 (s, 9 H), 1.09 (br s, 3 H), 1.15 (m, 1 H),

4.50 (d, *J*= 11.7 Hz, 1 H), 4.77 (d, *J*= 11.7 Hz, 1 H), 7.24 - 7.33 (m, 5 H). High-resolution MS, Calcd for $C_{17}H_{28}O_2Si$: 292.1859. Found m/e (relative intensity): 292.1868 (M^+, 3), 235 (36), 91 (100).

1-Benzyloxy-1-trimethylsiloxy-2-methylcyclopropane (**8c**, the TMS derivative): bp 90 °C/0.38 mmHg; IR (neat film) 3060 (w), 1500 (w), 1456 (m), 1365 (m), 1253 (s), 1199 (s), 1112 (m), 1010 (s), 930 (m), 865 (m) cm^{-1}; ^1H NNR ($CDCl_3$, 400 MHz) ***trans*-8c** δ 0.19 (s, 9 H), 0.48 (dd, J = 4.8, 6.2 Hz, 1 H), 0.99 (m, 1 H), 1.16 (m, 1 H), 1.16 (br s, 3 H), 4.64 (d, J = 11.5 Hz, 1 H), 4.71 (d, J = 11.5 Hz, 1 H), 7.27 - 7.35 (m, 5 H); *cis*-**8c** δ 0.22 (s, 9 H), 0.39 (dd, J = 4.4, 5.5 Hz, 1 H), 4.71 (d, J = 11.5 Hz, 1 H). High-resolution MS, Calcd for $C_{14}H_{22}O_2Si$: 250.1389. Found m/e (relative intensity): 250.1392 (4), 160 (3), 91 (100).

1-Isopropyloxy-1-(*tert*-butyldimethylsiloxy)-2-methylcyclopropane (**8d**): bp 65°C/2.8 mmHg; IR (neat film) 2920 (s), 2898 (s), 2822 (m), 1449 (m), 1349 (w), 1259 (m), 1185 (s), 1108 (m), 1093 (m), 1004 (m), 939 (s), 820 (s) cm^{-1}. ***trans*-8d**: R_f = 0.82 (benzene:hexane = 2:1, v/v); ^1H NMR ($CDCl_3$, 400 MHz) δ 0.12 (s, 3 H), 0.14 (s, 3 H), 0.43 (t, *J*= 5.5 Hz, 1 H), 0.86 (s, 9 H), 0.92 (m, 1 H), 1.06 (m, 1 H), 1.06 (br s, 3 H), 1.15 (d, *J*= 6.2 Hz, 3 H), 1.24 (d, *J*= 6.2 Hz, 3 H), 4.05 (quintet, *J*= 6.2 Hz, 1 H). *cis*-**8d**:R_f = 0.72 (benzene:hexane = 2:1, v/v); ^1H NMR ($CDCl_3$, 400 MHz) δ 0.14 (s, 3 H), 0.19 (s, 3 H), 0.31 (dd, *J*= 4.8, 5.9 Hz, 1 H), 0.90 (s, 9 H), 0.96 (m, 1 H), 1.07 (m, 1 H), 1.07 (br s, 3 H), 1.13 (d, *J*= 6.2 Hz, 3 H), 1.19 (d, *J*= 6.2 Hz, 3 H), 4.07 (quintet, *J*= 6.2 Hz, 1 H). High-resolution MS, Calcd for $C_{13}H_{28}O_2Si$: 244.1859. Found m/e (relative intensity): 244.1836 (M^+, 3), 187 (12), 145 (100).

***trans*-1-*tert*-Butyloxy-1-(*tert*-butyldimethylsiloxy)-2-methylcyclopropane** (*trans*-**8e**): R_f = 0.81 (benzene:hexane = 1:1, v/v); IR (neat film) 3088 (w), 2958 (s), 2936 (s), 2900 (m), 2860 (m), 1480 (m), 1465 (m), 1363 (m), 1255 (s), 1210 (s), 1171 (s), 1163 (s), 1106 (m), 1017 (m), 986 (m), 951 (s), 920 (m), 836 (s), 774 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.10 (s, 3 H), 0.14 (s, 3 H), 0.62 (t, *J*= 5.1 Hz, 1 H), 0.81 - 0.99 (m, 2 H), 0.85 (s, 9 H), 1.03 (d, *J*= 5.9 Hz, 3 H), 1.30 (s, 9 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ - 4.01 (Si<u>Me</u>), - 3.04 (Si<u>Me</u>), 13.35 (C_2-<u>Me</u>), 17.79 (Si-<u>C</u>Me_3), 19.19 (C_2), 20.78 (C_3), 25.92 (Si-C<u>Me</u>$_3$), 29.93 (O-C<u>Me</u>$_3$), 76.28 (O-<u>C</u>Me_3), 85.04 (C_1). High-resolution MS, Calcd for $C_{14}H_{30}O_2Si$ - C_4H_8:202.1389. Found m/e (relative intensity): 202.1398 (44), 171 (17), 145 (100), 75 (29), 56 (15).

***cis*-1-*tert*-Butyloxy-1-(*tert*-butyldimethylsiloxy)-2-methylcyclopropane** (*cis*-**8e**): Rf = 0.63 (benzene:hexane = 1:1, v/v); bp 65 °C/1.5 mmHg; IR (neat film) 3074 (w), 2946 (s), 2922 (s), 2888 (m), 2850 (m), 1477 (m), 1462 (m), 1363 (m), 1260 (s), 1218 (m), 1169 (s), 1104 (m), 1014 (s), 994 (s), 950 (m), 920 (m), 832 (s), 772 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.13 (s, 3 H), 0.21 (s, 3 H), 0.27 (dd, *J*= 5.5, 6.2 Hz, 1 H), 0.89 (m, 1 H), 0.89 (s, 9 H), 1.07 (d, *J*= 6.2 Hz, 3 H), 1.26 (m, 1 H), 1.28 (s, 9 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ - 3.66 (Si<u>Me</u>), - 2.29 (Si<u>Me</u>), 12.84 (C_2-<u>Me</u>), 18.02 (Si-<u>C</u>Me_3), 19.42 (C_2), 20.24 (C_3), 26.04 (Si-C<u>Me</u>$_3$), 30.13 (O-C<u>Me</u>$_3$), 76.13 (O-<u>C</u>Me_3), 85.31 (C_1). High-resolution MS, Calcd for $C_{14}H_{30}O_2Si$ - C_4H_8: 202.1389. Found m/e (relative intensity): 202.1332 (39), 171 (14), 145 (100), 75 (18), 56 (10).

1-Propynyloxy-1-(*tert*-butyldimethylsiloxy)cyclopropane (**15a**): Rf = 0.43 (benzene:hexane = 1:2, v/v); bp 90 °C/1.5 mmHg; IR (neat film) 3288 (m), 3070 (w), 2932 (s), 2906 (s), 2862 (m), 2836 (s), 1463 (m), 1441 (s), 1301 (s), 1241 (s), 1207 (s), 1031 (s), 1001 (s), 991 (s), 919 (m), 880 (m), 770 (s) cm^{-1};

^{1}H NMR ($CDCl_3$, 60 MHz) δ 0.16 (s, 6 H), 0.85 (s, 9 H), 0.90-1.02 (m, 4 H), 2.20 (t, J = 2.4 Hz, 1 H), 4.21 (d, J = 2.4 Hz, 1 H). High-resolution MS, Calcd for $C_{12}H_{22}O_2Si$: 226.1389. Found m/e (relative intensity): 226.1388 (M^+, <1), 169.0688 (M^+- *t*-Bu, 31), 131 (12), 75 (100).

1-(2-Butynyloxy)-1-(*tert*-butyldimethylsiloxy)cyclopropane (15b): bp 77 °C/1.3 mmHg; IR (neat film) 2900 (s), 2220 (w), 1250 (s), 1205 (s), 1030 (s), 1002 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 0.18 (s, 6 H), 0.89 (s, 9 H), 0.78-1.05 (m, 4 H), 1.85 (t, J = 1.8 Hz, 1 H), 4.25 (q, J = 1.8 Hz, 1 H). High-resolution MS, Calcd for $C_{13}H_{24}O_2Si$: 240.1546. Found m/e (relative intensity): 240.1544 (M^+, 1), 183 (M^+- *t*-Bu, 12), 73 (100).

1-Allyloxy-1-(*tert*-butyldimethylsiloxy)-2,2-dimethylcyclopropane (17): IR (neat film) 3050 (w), 2928 (s), 2862 (m), 1641 (w), 1454 (m), 1247 (m), 1175 (s), 1168 (s), 1016 (s), 971 (m), 910 (m), 830 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.14 (s, 3 H), 0.16 (s, 3 H), 0.52 (d, J= 5.5 Hz, 1 H), 0.68 (d, J= 5.5 Hz, 1 H), 0.90 (s, 9 H), 1.12 (s, 3 H), 1.15 (s, 3 H), 3.96 (ddt, J= 12.5, 5.5, 1.5 Hz, 1 H), 4.23 (ddt, J= 12.5, 5.5, 1.5 Hz, 1 H), 5.13 (dq, J= 10.3, 1.5 Hz, 1 H), 5.26 (dq, J= 17.2, 1.5 Hz, 1 H), 5.92 (ddt, J= 17.2, 10.3, 5.5 Hz, 1 H). High-resolution MS, Calcd for $C_{14}H_{28}O_2Si$: 256.1859. Found m/e (relative intensity): 256.1838 (M^+, 5).

REFERENCES AND NOTES

1) (a) Davies, H. M. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I., Eds.; Pergamon: Oxford, U. K., 1991; Vol. 4, Chapter 4.8. (b) Hudlicky, T.; Reed, J. W. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I., Eds.; Pergamon: Oxford, U. K., 1991; Vol. 5, Chapter 8.1. (c) Charette, A. B.; Juteau, H. *J. Am. Chem. Soc.* **1994**, *116*, 2651. (d) Lautens, M.; Delanghe, P. H. M. *J. Am. Chem. Soc.* **1994**, *116*, 8526.
2) Yasui, K.; Fugami, K.; Tanaka, S.; Ii, A.; Yoshida, Z.; Tamaru, Y. *Tetrahedron Lett.* **1992**, *33*, 631.
3) (a) Rühlman, K. *Synthesis* **1971**, 236. (b) Salaün, J.; Marguerite, J. *Org. Synth.* **1985**, *63*, 147. (c) Salaün, J. *Chem. Rev.* **1983**, *83*, 619.
4) Kuwajima, I.; Nakamura, E. *Topics in Current Chem.* **1990**, *155*, 1.
5) Yasui, K.; Fugami, K.; Tanaka, S.; Ii, A.; Yoshida, Z.; Saidi, M. R.; Tamaru, Y. *Tetrahedron Lett.* **1992**, *33*, 785.
6) (a) Curran, D. P.; Chang, C. -T. *Tetrahedron Lett.* **1987**, *28*, 2477. (b) Curran, D. P.; Chang, C. -T. *J. Org. Chem.* **1989**, *54*, 3140.
7) Tamaru, Y.; Nakamura, T.; Sakaguchi, M.; Ochiai, H.; Yoshida, Z. *J. Chem. Soc., Chem. Commun.* **1988**, 610.
8) (a) Tamaru, Y.; Ochiai, H.; Nakamura, T.; Yoshida, Z. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1157. (b) Tamaru, Y.; Ochiai, H.; Nakamura, T.; Yoshida, Z. *Org. Synth.* **1988**, *67*, 98.
9) Tamaru, Y.; Tanigawa, H.; Yamamoto, T.; Yoshida, Z. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 351.

10) (a) Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1984**, *106*, 3368. (b) Nakamura, E.; Aoki, S.; Sekiya, K.; Oshino, H.; Kuwajima, I. *J. Am. Chem. Soc.* **1987**, *109*, 8056.

11) (a) Duddu, R.; Eckhardt, M.; Furlong, M.; Knoess, H. P.; Berger, S.; Knochel, P. *Tetrahedron* **1994**, *50*, 2415. (b) Tamaru, Y.; Tanaka, A.; Yasui, K.; Goto, S.; Tanaka, S. *Angew. Chem.* in press.

12) (a) Jackson, R. F. W.; Wishart, N.; Wood, A.; James, K.; Wythes, M. J. *J. Org. Chem.* **1992**, *57*, 3397. (b) Dunn, M. J.; Jackson, R. F. W.; Pietruszka, J.; Wishart, N.; Ellis, D.; Wythes, M. J. *Synlett* **1993**, 499.

13) No significant changes in the 400 MHz ^{1}H NMR spectra of **8b** were observed at a wide range of temperature (20 - 120°C in d_6-DMSO).

14) Nakamura, E.; Oshino, H.; Kuwajima, I. *J. Am. Chem. Soc.* **1986**, *108*, 3745.

15) Breitmaier, E. *Structure Elucidation by NMR in Organic Chemistry*, Wiley, 1993.

16) (a) Heathcock, C. H. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I., Eds.; Pergamon: Oxford, U. K., 1991; Vol. 2, Chapter 1.6. (b) Kim, B. M.; Williams, S. F.; Masamune, S. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I., Eds.; Pergamon: Oxford, U. K., 1991; Vol. 2, Chapter 1.7.

17) Smith, R. D.; Simmons, H. E. *Org. Synth.* **1973**, Collect. Vol. 5, 855.

18) Yasui, K.; Fugami, K.; Tanaka, S.; Tamaru, Y. *J. Org. Chem.* **1995**, *60*, 1365.

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