# Synthesis of New Alkenyl-Substituted 2-(*tert*-Butyldimethylsiloxy)-cyclopropanecarboxylates and Their Diastereoselective Conversion into (Hydroxymethyl)cyclopropanes

**Bernhard Hofmann[a][1] and Hans-Ulrich Reißig*[b]**

Institut für Organische Chemie der Technischen Hochschule Darmstadt[a], Petersenstraße 22, D-64287 Darmstadt, Germany

Institut für Organische Chemie der Technischen Universität Dresden[b], Mommsenstraße 13, D-01062 Dresden, Germany

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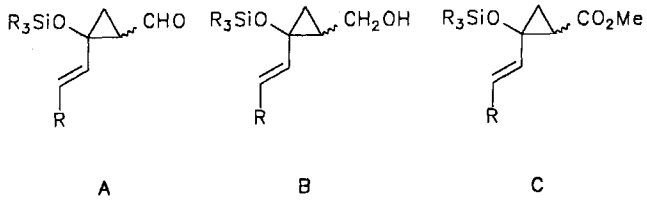
Various new 2-alkenyl-substituted methyl 2-(*tert*-butyldimethylsiloxy)cyclopropanecarboxylates **8**–**14** were synthesized from siloxy dienes and methyl diazoacetate. Further substitution by deprotonation and reactions with electrophiles provided derivatives **15**–**19** in good yields. Reduction of *trans*-configurated cyclopropanecarboxylates with $LiAlH_4$ afforded the corresponding *trans*-2-(*tert*-butyldimethylsiloxy)-1-(hydroxymethyl)cyclopropanes in excellent yields. The related *cis*-compounds were not formed, but ring-opened products derived thereof were isolated. This unexpected influence of the configuration of the starting material on the type of the product formed is discussed.

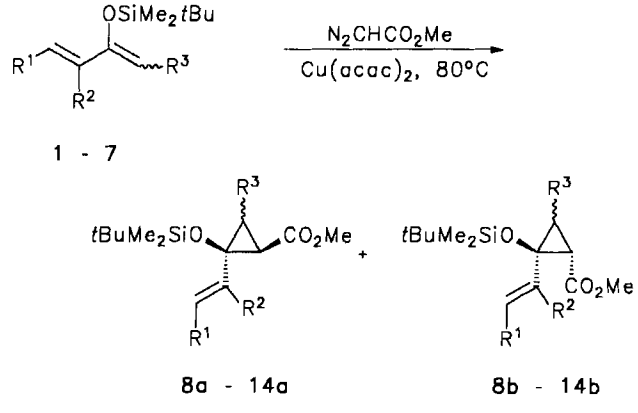
To further explore the synthetic potential of donor-acceptor substituted cyclopropanes[2] we required an efficient route to 2-siloxycyclopropanecarboxaldehydes **A**, in particular those with additional alkenyl substituents. These are of interest because they may undergo rearrangements[3], or they could be starting materials for olefination reactions. The most apparent way to generate the aldehydes would be the chemoselective oxidation of the corresponding alcohols **B** which should be available from methyl 2-siloxycyclopropanecarboxylates **C**. These are known in great variety and are easily prepared – even on a moderately large scale – from silyl enol ethers and methyl diazoacetate[4]. However, earlier experiments[5] with trimethylsiloxy-substituted cyclopropane derivatives have demonstrated that attempts to reduce these compounds with $LiAlH_4$ also cause cleavage of the silicon oxygen bond and thus (partial) ring opening of the three-membered ring. In this paper we report on our experience with the more stable[6] *tert*-butyldimethylsiloxy-substituted cyclopropanecarboxylates which in most cases lead to the desired alcohols, but which give also ring-opened products in singular examples.




A B C

## Synthesis of Alkenyl-Substituted Methyl 2-(*tert*-Butyldimethylsiloxy)cyclopropanecarboxylates

Methyl 2-siloxycyclopropanecarboxylates **8**–**14** were conveniently prepared by regioselective cyclopropanation of siloxy dienes **1**–**7**[4]. In all examples the standard catalyst $Cu(acac)_2$ was sufficient to obtain moderate to very good yields (Table 1). Use of $Rh_2(OAc)_4$ did not improve yields and *cis*:*trans* selectivity. Formation of the second regioisomer or of the double adduct was not observed in these examples.




Further diastereoselective substitution of these cyclopropanes is easily possible by deprotonation/alkylation[7]. Thus, **8**, **10**, and **11** were deprotonated with LDA at −78°C and the anion then treated with electrophiles. Substitution products **15**–**19** (Table 2) were isolated in good yield and with more than 97% *trans* selectivity (*cis* and *trans* define the arrangement of the siloxy group with respect to the methoxycarbonyl function).

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Table 1. Cu(acac)$_2$-catalyzed syntheses of methyl 2-(*tert*-butyldimethylsiloxy)cyclopropanecarboxylates **8**–**14**

| Starting Material | $R^1$ | $R^2$ | $R^3$ | Product | a : b | Yield |
|---|---|---|---|---|---|---|
| **1** | H | H | H | **8** | 33 : 67 | 64 % |
| **2** | H | H | Me | **9** | [a] | 52 % |
| **3** | H | Me | H | **10** | 47 : 53 | 63 % |
| **4** | Ph | H | H | **11** | 28 : 72 | 80 % |
| **5** | [b] | H | H | **12** | 28 : 72 | 84 % |
| **6** | Me | H | H | **13** | 35 : 65 | 76 % |
| **7** | MeO | H | H | **14** | 25 : 75 | 72 % |

[a] Compound **9** was obtained as a mixture of all four possible diastereomers (**9a**:**9b**:**9c**:**9d** = 24:27:32:17); an exact determination of configuration could not be achieved by $^1$H-NMR spectroscopical means. – [b] $R^1$ = *p*-$F_3CC_6H_4$.

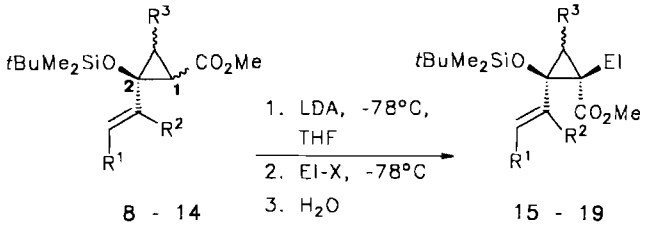


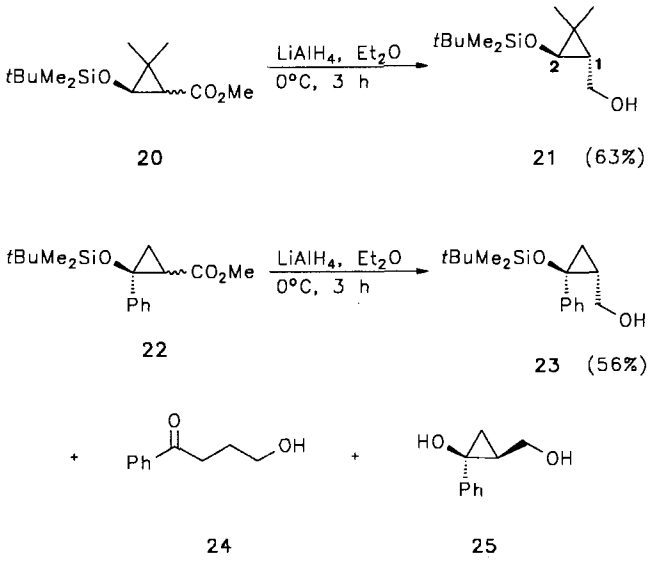

Table 2. Alkylation of methyl 2-siloxycyclopropanecarboxylates **8**, **10**, and **11**

| Starting Material | a : b | $R^1$ | $R^2$ | El-X | Product[a] | Yield |
|---|---|---|---|---|---|---|
| **8** | 33 : 67 | H | H | $CH_3$-I | **15** | 69 % |
| **8** | 33 : 67 | H | H | Allyl-Br | **16** | 80 % |
| **10** | 47 : 53 | H | $CH_3$ | $CH_3$-I | **17** | 81 % |
| **11** | 28 : 72 | Ph | H | $CH_3$-I | **18** | 74 % |
| **8** | 33 : 67 | H | H | Acetone | **19** | 55 % |

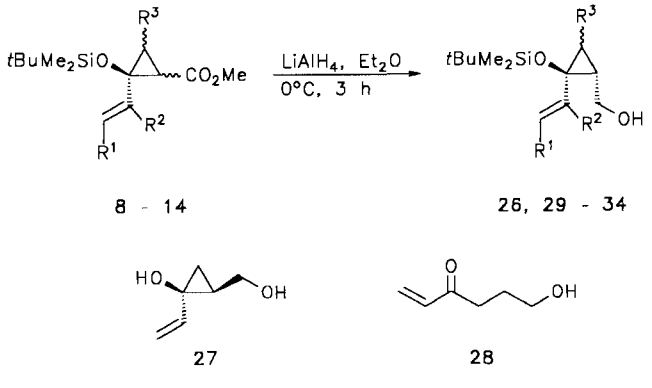
[a] All compounds were obtained as purely *trans*-configurated compounds (*cis*:*trans* < 3:97 according to $^1$H NMR, 300 MHz).

## Reduction of Methyl 2-(*tert*-Butyldimethylsiloxy)-cyclopropanecarboxylates

To test the stability of 2-(*tert*-butyldimethylsiloxy)cyclopropanes toward $LiAlH_4$ we first reduced compounds **20** and **22** which do not bear an alkenyl group. When we started with cyclopropane derivative **20** (*trans*:*cis* = 77:23), reduction and chromatography provided the expected (hydroxymethyl)cyclopropane **21** in 63% yield, surprisingly as the pure *trans* isomer. Similarly, siloxycyclopropane **22** (*trans*:*cis* = 60:40) gave *trans*-alcohol **23** in 56% yield together with desilylated *cis*-(hydroxymethyl)cyclopropane **25** and ring cleavage product **24**. With respect to the amount of *trans*-cyclopropane in starting materials **20** and **22** the yields of products **21** and **23** are excellent (82 and 93%). We assume that **25** is formed from *cis*-**22** and **24** arises by ring opening of this compound (see discussion).




Vinylcyclopropane derivative **8** (*trans*:*cis* = 67:33) was similarly reduced, and after chromatography we obtained the expected (hydroxymethyl)cyclopropane **26** in 66% yield with exclusive *trans* configuration. In addition, we isolated *cis*-diol **27** and the vinyl ketone **28** in very low yield (approximately 2% overall yield). The reduction products **29**–**34** were obtained by starting from cyclopropane derivatives **9**–**14** (Table 3). In these experiments eventually formed diols or ring-opened products were probably removed or destroyed during distillation. Again the yields of (hydroxymethyl)cyclopropanes were excellent (approximately 90%) based on the content of *trans*-cyclopropanes in the starting materials.

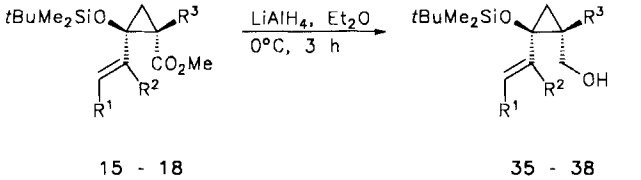



Not surprisingly, the $LiAlH_4$ reductions of 1-alkylated cyclopropane derivatives **15**–**18**, which are available as pure *trans* compounds, very efficiently and exclusively provided the desired *trans* products **35**–**38** with no indication of side products (Table 4). In contrast, reaction of 1-hydroxyalkylated cyclopropanecarboxylate **19** with $LiAlH_4$ gave a mixture of the expected reduction product **39** (31%) and the acyclic diol **40** (21%).

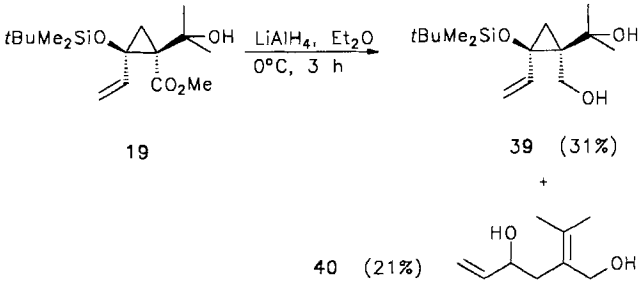
Table 3. Reduction of methyl 2-siloxycyclopropanecarboxylates **8**–**14**

| Starting Material | $R^1$ | $R^2$ | $R^3$ | a : b | Product | Yield |
|---|---|---|---|---|---|---|
| **8** | H | H | H | 33 : 67 | **26** | 66 % |
| **9** | H | H | Me | [a] | **29** | 32 %[b] |
| **10** | H | Me | H | 47 : 53 | **30** | 43 % |
| **11** | Ph | H | H | 28 : 72 | **31** | 42 % |
| **12** | *p*-$F_3CC_6H_4$ | H | H | 28 : 72 | **32** | 65 % |
| **13** | Me | H | H | 38 : 62 | **33** | 65 % |
| **14** | MeO | H | H | 34 : 66 | **34** | 65 % |

[a] **9a**:**9b**:**9c**:**9d** = 24:27:32:17. – [b] *c*-3/*r*-1 **29**:*t*-3/*r*-1 **29** = 45:55.




15 - 18 35 - 38




19 39 (31%) + 40 (21%)

Table 4. Reduction of C-1-alkylated methyl 2-siloxycyclopropanecarboxylates **15**–**19**

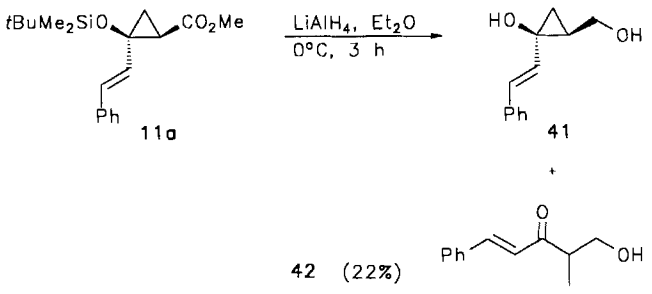
| Starting Material[a] | $R^1$ | $R^2$ | $R^3$ | Product | Yield |
|---|---|---|---|---|---|
| **15** | H | H | Me | **35** | 74 % |
| **16** | H | H | Allyl | **36** | 92 % |
| **17** | H | Me | Me | **37** | 89 % |
| **18** | Ph | H | Me | **38** | 89 % |

[a] Starting materials were used as diastereomerically pure *trans* compounds.

## Discussion

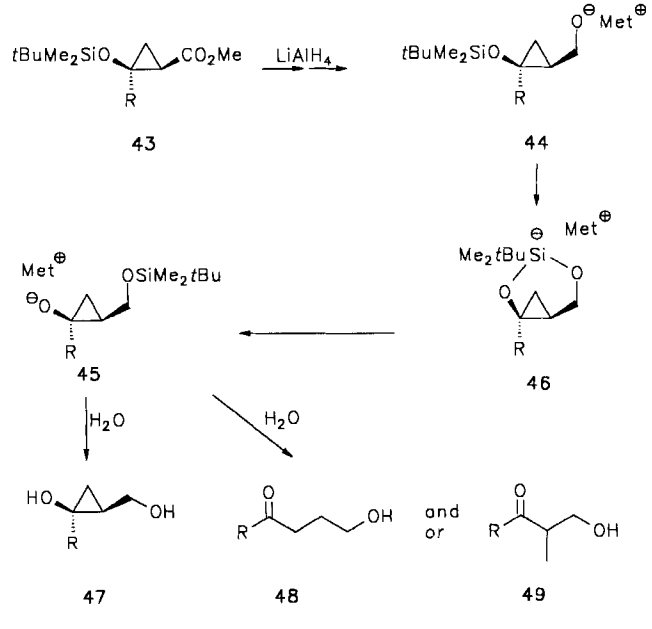
Our experiments illustrate that *trans*-configurated methyl (*tert*-butyldimethylsiloxy)cyclopropanecarboxylates may be reduced with $LiAlH_4$ without interference of the siloxy group. They provide *trans*-1-(hydroxymethyl)-2-siloxycyclopropanes in excellent yields. The corresponding *cis* compounds could not be isolated in any of the cases investigated. Either the related diols (**25**, **27**) or ring-opened products such as **24**, **28**, and **40** were found. The proximity of the *tert*-butyldimethylsilyloxy group to the methoxycarbonyl substituent and the function formed after the reduction must be responsible for this different behavior.

In order to confirm this dependence on the configuration of the starting material, we separated cyclopropane **11** into the two diastereomers by HPLC. While the reduction of *trans* isomer **11b** provided the expected product **31** with *trans* configuration, the corresponding *cis* isomer **11a** was converted by $LiAlH_4$ into *cis*-diol **41** and ring-cleaved compound **42**. Thus, it was proven that the unexpected products were actually derived from the *cis*-configurated cyclopropanes.




11a 41 + 42 (22%)

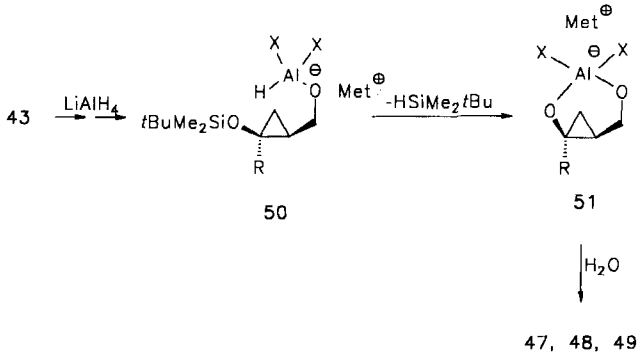
The *cis*-diols **47** might be formed by 1,5-migration of the silyl group from the 2-oxygen to the oxy anion of **44** generated during reduction of **43**. Intermediates such as **46** with a pentavalent silicon are plausible for the transformation **44** → **45**. *O*,*O*′-migrations of silyl groups under basic conditions are well-known[8]. Furthermore, there is ample precedence for the ring cleavage of cyclopropanols under basic conditions with formation of acyclic ketones[9]. Linear ring-opened ketones (e.g. **24**, **28**, **40**) were formed from most cyclopropanols while the branched acyclic ketone **42** surprisingly results from the ring cleavage of **41**.



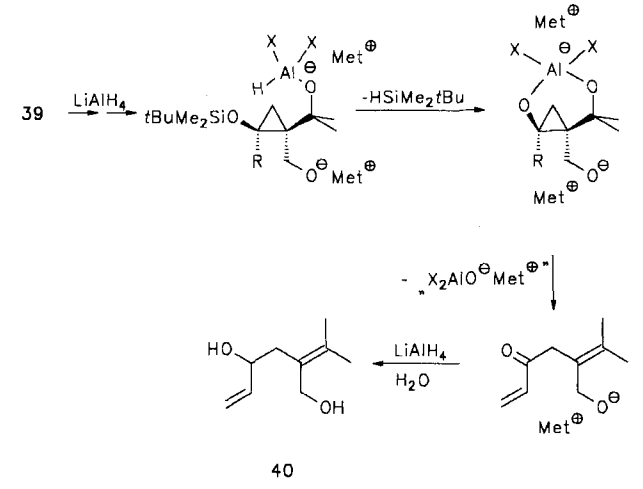

43 44 45 46 47 48 49

However, the reaction conditions employed should lead to structures as **47**, **48**, and **49** bearing however *silylated* primary alcohol groups; desilylation during the workup procedure is rather unlikely[6]. Therefore, we prefer an alternative mechanistic scheme. Reductions of *cis*-cyclopropanecarboxylates **43** afford aluminates which still contain

active hydrides, e.g. **50**. By intramolecular hydride attack on silicon the Si–O bond is reductively cleaved[10] and an intermediate such as **51** should arise. Hydrolysis gives diol **47** whereas ring opening provides acyclic ketones **48** and **49**. This mechanism requires that *tert*-butyldimethylsilane is liberated. No attempts to provide evidence for its formation have been undertaken.




In accordance with this mechanism, reduction of cyclopropane derivative **19** provides **39** and **40**. Although **39** also contains a *cis*-hydroxy function, only partial desilylation and ring cleavage were observed, demonstrating that a tertiary alcohol undergoes the processes discussed above less readily. Compound **40** is probably formed by the reaction sequence reductive desilylation, ring opening, elimination, and subsequent reduction of the ketone function as illustrated.




We have demonstrated that *trans*-(*tert*-butyldimethylsiloxy)(hydroxymethyl)cyclopropanes are conveniently accessible in diastereomerically pure form. The corresponding *cis* isomers are not isolable and undergo subsequent reactions affording different products which allow their simple removal from the reaction mixture. The use of the desired alcohols for further synthetic applications are described in the succeeding report[11].

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## Experimental

For general remarks see ref.[12]. Siloxydienes **1**–**7** were prepared according to known procedures[13]. For synthesis of **20** and **22** see ref.[4]. – NMR: in $CDCl_3$, 300 MHz ($^1H$) and 75.5 MHz ($^{13}C$).

*Methyl 2-Siloxycyclopropanecarboxylates* **8**–**14** (Table 5) were prepared according to the general procedure described in the literature[4] using $Cu(acac)_2$ as catalyst. Instead of benzene, ethyl acetate was used as solvent. Purification was achieved by kugelrohr distillation. Analytical data are given in Tables 6–9, for analytical data for **8** see ref.[14]. – Spectroscopical data of cyclopropanes **9a**–**d**: $^1H$ NMR: δ = 6.13, 4.91, 4.85 (ABX system, $J_{AX}$ = 17.1, $J_{BX}$ = 10.8, $J_{AB}$ = 1.6 Hz, CH=$CH_2$, **9a**), 6.12, 5.33, 5.11 (ABX system, $J_{AX}$ = 17.1, $J_{BX}$ = 11.0, $J_{AB}$ = 2.1 Hz, CH=$CH_2$, **9b**), 5.77, 5.20, 4.96 (ABX system, $J_{AX}$ = 17.1, $J_{BX}$ = 10.4, $J_{AB}$ = 1.0 Hz, CH=$CH_2$, **9c**), 5.70, 5.25, 5.06 (ABX system, $J_{AX}$ = 17.0, $J_{BX}$ = 10.7, $J_{AB}$ = 1.5 Hz, CH=$CH_2$, **9d**), 3.51 (s, $CO_2Me$, **9c**), 3.50 (s, $CO_2Me$, **9d**), 3.49 (s, $CO_2Me$, **9b**), 3.48 (s, $CO_2Me$, **9a**), 2.04–1.21, 0.95 (m, d, *J* = 6.5 Hz, 1,3-H, **9a**–**d**, 3-Me **9a**, **d**), 1.15 (d, *J* = 6.7 Hz, 3-Me, **9b**), 1.05 (d, *J* = 6.2 Hz, 3-Me, **9c**), 0.78 (s, *t*BuSi, **9c**), 0.76 (s, *t*BuSi, **9d**), 0.75 (s, *t*BuSi, **9b**), 0.74 (s, *t*BuSi, **9a**), 0.02, 0.00, −0.03, −0.04, −0.05, −0.07, −0.10, −0.13 (8 s, $Me_2Si$, **9a**–**d**); (further assignments were not possible, integrals corresponded to expected values and showed a distribution of **9a**:**9b**:**9c**:**9d** = 24:27:32:17). – $^{13}C$ NMR: δ = 173.8, 51.5 (s, q, $CO_2Me$, **9c**), 171.1, 51.1 (s, q, $CO_2Me$, **9b**), 169.4, 51.4 (s, q, $CO_2Me$, **9d**), 168.9, 50.8 (s, q, $CO_2Me$, **9a**), 140.4, 113.0 (d, t, CH=$CH_2$, **9a**), 136.6, 115.3 (d, t, CH=$CH_2$, **9c**), 136.4, 111.4 (d, t, HC=$CH_2$, **9d**), 133.4, 113.8 (d, t, CH=$CH_2$, **9b**), 66.8 (s, C-2, **9c**), 66.4 (s, C-2, **9d**), 65.7 (s, C-2, **9b**), 64.8 (s, C-2, **9a**), 36.4, 34.4, 33.4, 30.1, 28.5, 27.5, 26.7, 26.6, (8 d, C-1,3, **9a**–**d**), 25.7, 25.6, 25.5, 25.2, 18.1, 18.0, 17.9, (4 q, 3 s, *t*BuSi, **9a**–**d**), 12.7, 10.6, 7.9, 7.1 (4 q, 3-Me, **9c**, **d**, **b**, **a**), −3.1, −3.2, −3.5, −3.8, −4.1 (6 q, $Me_2Si$, **9a**–**d**). – Elemental analyses and IR data see Table 8.

Table 5. Preparation of methyl 2-siloxycyclopropanecarboxylates **8**–**14**

| Siloxy diene | g (mmol) | Cat. g (mmol) | Methyl Diazo-acetate g (mmol) | Pro-duct | Yield g (%) | a:b | b.p. [°C/ Torr][a] |
|---|---|---|---|---|---|---|---|
| **1** | 15.0 (79.9)[b] | 0.42 (1.60) | 9.68 (88.0)[c] | **8** | 13.2 (64) | 33:67 | 50-70/ 0.02 |
| **2**[d] | 3.83 (19.3) | 0.166 (0.643) | 2.28 (22.3) | **9** | 2.70 (52) | [e] | 100-110/1 |
| **3** | 5.68 (28.2) | 0.148 (0.564) | 3.10 (31.0) | **10** | 4.83 (62) | 47:53 | 68/0.1 |
| **4** | 5.06 (19.4) | 0.112 (0.428) | 2.24 (22.4) | **11** | 5.19 (80) | 28:72 | 140-160/ 0.01 |
| **5** | 2.81 (8.55) | 0.045 (0.172) | 1.02 (10.2) | **12** | 2.89 (84) | 28:72 | 165-170/ 0.01 |
| **6** | 3.20 (16.1) | 0.084 (0.321) | 1.74 (17.4) | **13** | 3.28 (76) | 35:65 | 70-130/ 0.01 |
| **7** | 2.14 (10.0) | 0.054 (0.206) | 1.10 (11.0) | **14** | 2.08 (72) | 25:75 | 100-125/ 0.01 |

[a] Kugelrohr distillation. – [b] Contains 7% of siloxane. – [c] 91% by weight. – [d] *E*:*Z* = 35:65. – [e] Compound was obtained as a mixture of all four possible diastereomers **9a**:**9b**:**9c**:**9d** = 24:27:32:17.

*Alkylations of Methyl 2-Siloxycyclopropanecarboxylates* **8**, **10**, *and* **11**: The general procedure is described in the literature[7]. Purification of the crude products was achieved by kugelrohr distil-

Table 6. $^1$H-NMR data (δ values, *J* in Hz) of methyl 2-siloxycyclopropanecarboxylates **10**–**14** (integrals correspond to the expected values)

| Compound | 2'-H | 2'-H | 1'-H | $CO_2Me$ | ABX system of ring protons | | | | | | *t*BuMe$_2$Si | Other Signals |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | 1-H | 3-H[a] | 3-H[b] | $J_{cis}$ | $J_{trans}$ | $J_{gem}$ | | |
| | | | | | | | | [c] | [c] | [c] | | |
| **10a** | 4.79 (s, long-range coupling) | 4.68 (quint., $J$=1.4) | -- | 3.55 (s) | 1.57-1.34 (m) | | | | | | 0.72 (s)<br>-0.01 (s)<br>-0.06 (s) | 1.71 (s, long-range coupling, 3H, 1'-Me) |
| **10b** | 4.98 (bs) | 4.95 ($m_c$) | -- | 3.61 (s) | 1.96 | 1.67 | 1.29 | 9.1 | 7.0 | 5.8 | 0.82 (s)<br>0.06 (s)<br>0.05 (s) | 1.74 (d, $J$<1, 3H, 1'-Me) |
| **11a** | -- | 6.70, 6.16 (2d, $J$=15.8) | | 3.78 (s) | 2.05-1.96 (m) | | 1.49 | [c] | 7.3 | 4.4 | 1.04 (s)<br>0.29 (s)<br>0.25 (s) | 7.45-7.28 (m, Ph) |
| **11b** | -- | 6.87, 6.46 (2d, $J$=15.9) | | 3.76 (s) | 2.33 | 1.76 | 1.71 | 9.3 | 7.5 | 5.9 | 1.04 (s)<br>0.29 (s)<br>0.25 (s) | 7.46-7.26 (m, Ph) |
| **12a** | -- | 6.65, 6.12 (2d, $J$=15.8) | | 3.70 (s) | 1.99 | 1.93 | 1.43 | 8.2 | 6.9 | 5.4 | 0.94 (s)<br>0.15 (s)[d] | 7.57-7.52, 7.44-7.40 (2m, $C_6H_4$) |
| **12b** | -- | 6.80, 6.48 (2d, $J$=15.9) | | 3.69 (s) | 2.27 | 1.69 | 1.66 | 9.2 | 7.7 | 5.9 | 0.95 (s)<br>0.18 (s)<br>0.17 (s) | 7.57-7.52, 7.44- 7.40 (2m, $C_6H_4$) |
| **13a** | -- | 5.63 (dq, $J$=15.0, $J$=7.0) | 5.45 (dd, $J$=15.0, $J$=1.5) | 3.62 (s) | 1.92 | [e] | 1.32 | 9.0 | 7.2 | 5.9 | 0.78 (s)<br>0.09 (s)<br>0.04 (s) | 1.64 (dd, 3H, $J$=6.4, $J$=1.5, 2'-Me) |
| **13b** | -- | 5.79 (dq, $J$=15.3, $J$=6.6) | 5.53 (dd, $J$=15.3, $J$=1.5) | 3.65 (s) | 2.05 | 1.47 | 1.41 | 9.3 | 7.4 | 5.8 | 0.86 (s)<br>0.11 (s)<br>0.10 (s) | 1.69 (dd, 3H, $J$=6.6, $J$=1.5, 2'-Me) |
| **14a** | -- | 6.46, 4.93 (d, $J$=12.6) | | 3.58 (s)[f] | 1.65 -1.56 (m) | | 1.17 | [c] | 7.4 | 4.5 | 0.77 (s)<br>0.04 (s)[d] | 3.43 (s, OMe) |
| **14b** | -- | 6.53, 4.83 (d, $J$=12.6) | | 3.62 (s)[g] | 1.95 | 1.38 | 1.30 | 9.4 | 7.0 | 5.9 | 0.78 (s)<br>0.05 (s)[d] | 3.42 (s, OMe) |

[a] *cis* with respect to 1-H. – [b] *trans* with respect to 1-H. – [c] Coupling not determinable. – [d] Intensity of signal is 6H. – [e] Hidden signal. – [f] Long-range coupling ca. 0.6 Hz. – [g] Signals broadened by long-range coupling.

lation or chromatography (Table 9). Analytical data are given in Tables 10–12.

*Reductions of Methyl 2-Siloxycyclopropanecarboxylates. – General Procedure:* To a cooled suspension (0°C) of $LiAlH_4$ (1.2 equivalents) in dry diethyl ether (2 ml/mmol) a solution of the methyl cyclopropanecarboxylate in diethyl ether (2 ml/mmol) was added dropwise, and the mixture was stirred for 3 h. After hydrolysis with sodium hydrogencarbonate solution (5%) and addition of 2 N NaOH the layers were separated, and the aqueous phase was extracted with diethyl ether for several times. The combined organic layers were dried ($MgSO_4$), and the solvent was evaporated in vacuo. The crude products were worked up as described.

*Reduction of Methyl 2-(tert-Butyldimethylsiloxy)-3,3-dimethylcyclopropanecarboxylate* (**20**): According to the general procedure 0.474 g (12.5 mmol) of $LiAlH_4$ in 10 ml of diethyl ether was stirred with a solution of 2.58 g (10.0 mmol) of **20** (**20a**:**20b** = 23:77) in 10 ml of diethyl ether. After workup 1.90 g (83%) of crude product was obtained. Purification by chromatography (alumina, hexane/ethyl acetate, 1:1) afforded 1.44 g (63%, 82% regarding the amount of **20b**) of **21** as a colorless oil. Analytical data are given in Tables 13–15.

*Reduction of Methyl 2-(tert-Butyldimethylsiloxy)-2-phenylcyclopropanecarboxylate* (**22**): According to the general procedure 0.191 g (5.03 mmol) of $LiAlH_4$ in 10 ml of diethyl ether was stirred with 1.24 g (4.04 mmol) of **22** (**22a**:**22b** = 40:60) in 8 ml of diethyl ether to afford 1.00 g of crude product. Further purification by chromatography (silica gel, hexane/ethyl acetate, 1:2) yielded 0.628 g (56%, 93% regarding the amount of **20b**) of **23** as a pale yellow oil, 0.041 g (6%) of **25** (colorless oil), and 0.162 g (24%) of a mixture of **24** and **25** (**24**:**25** = 4:96). Compound **23** slowly crystallized to furnish a colorless solid (m.p. 65–67°C). Analytical data of **23** are given in Tables 13–15. – **24**: $^1$H NMR: δ = 7.86–7.83, 7.41–7.38 (2 m, 5H, Ph), 3.48 (t, $J$ = 6.4 Hz, 2H, 4-H), 2.88 (t, $J$ = 7.0 Hz, 2H, 2-H), 1.81 (quint., $J$ = 6.5 Hz, 2H, 3-H), signal for OH not detected. – $^{13}$C NMR: δ = 133.0, 128.4, 128.0 (3 d, Ph), 34.8 (t, C-2), 26.5 (t, C-3), signals of *ipso*-C, C-1 and C-4 are not detected. For further characterization see ref.[5]. – **25**: $^1$H NMR: δ = 7.25–7.10 (m, 5H, Ph), 5.0–3.6 (bs, ca. 2H, OH), 3.86, 3.55 (2 dd, $J_{vic}$ = 9.2, $J_{vic}$ = 4.7, $J_{gem}$ = 11.6 Hz, 1H each, $CH_2OH$), 1.43–1.13 (m, 1H, 1-H), 1.01, 0.88 (2 dd, $J_{vic}$ = 9.6, $J_{vic}$ = 6.8, $J_{gem}$ = 5.9 Hz, 1H each, 3-H), signal for OH not detected. – $^{13}$C NMR: δ = 144.2, 128.0, 126.1, 124.2 (s, 3 d, Ph), 61.5 (t, $CH_2OH$), 58.5 (s, C-2), 29.1 (d, C-1), 20.3 (t, C-3).

*Reduction of Methyl 2-(tert-Butyldimethylsiloxy)-2-vinylcyclopropanecarboxylate* (**8**): According to the general procedure 0.685 g (18.0 mmol) of $LiAlH_4$ in 38 ml of diethyl ether was stirred with 3.84 g (15.0 mmol) of **8** (**8a**:**8b** = 33:67) in 30 ml of diethyl ether to afford 2.59 g (76%) of crude product. Further purification by chromatography (silica gel, hexane/ethyl acetate, 1:1) furnished

Table 7. $^{13}$C-NMR data (δ values) of methyl 2-siloxycyclopropanecarboxylates **10**–**14**

| Compound | $CO_2Me$ | C-1' | C-2' | C-2 | C-1 | C-3 | *t*BuSi | $Me_2Si$ | Other signals |
|---|---|---|---|---|---|---|---|---|---|
| **10a** | 169.7 (s)<br>51.5 (q) | 145.5 (s) | 111.2 (t) | 64.9 (s) | 27.9 (d) | 17.8 (t) | 25.4 (q)[a] | -4.2 (q)<br>-4.3 (q) | 18.2 (q, 1'-Me) |
| **10b** | 171.0 (s)<br>51.5 (q) | 141.1 (s) | 114.7 (t) | 67.0 (s) | 28.8 (d) | 19.7 (t) | 25.5 (q)<br>17.7 (s) | -4.1 (q)<br>-4.2 (q) | 19.6 (q, 1'-Me) |
| **11a** | 169.3 (s)<br>51.8 (q) | [b] | [b] | 62.5 (s) | 29.6 (d) | 20.5 (t) | 25.9 (q)<br>18.2 (s) | -3.3 (s)<br>-3.6 (s) | 136.4 (s, C-*i*-Ph)[b] |
| **11b** | 171.4 (s)<br>52.0 (q) | [c] | [c] | 63.7 (s) | 31.2 (d) | 23.1 (t) | 26.1 (q)<br>15.8 (s) | -2.9 (q)<br>-3.2 (q) | 137.1 (s, C-*i*-Ph)[c] |
| **12a** | 168.9 (s)<br>51.5 (q) | [d] | [d] | 62.1 (s) | 29.5 (d) | 20.6 (t) | 25.6 (q)<br>18.0 (s) | -3.5 (q)<br>-3.7 (q) | 139.9 (s, C-*i*-Ph), 124.3 (q, $J_{CF}$=272 Hz, p-$CF_3$)[d] |
| **12b** | 171.1 (s)<br>51.8 (q) | [e] | [e] | 63.3 (s) | 31.7 (d) | 23.2 (t) | 25.7 (q)<br>18.0 (s) | -3.2 (q)[f] | 140.3 (s, C-*i*-Ph), 124.3 (q, $J_{CF}$=272 Hz, p-$CF_3$)[e] |
| **13a** | 169.5 (s)<br>51.5 (q) | 133.3 (d) | 124.5 (d) | 62.0 (s) | 28.8 (d) | 19.6 (t) | 25.5 (q)<br>17.9 (s) | -3.7 (q)<br>-4.1 (q) | 17.2 (q, 2'-Me) |
| **13b** | 171.2 (s)<br>51.5 (q) | 128.8 (d) | 126.3 (d) | 63.1 (s) | 30.1 (d) | 21.6 (t) | 25.7 (q)<br>17.8 (s) | -3.7 (q)<br>-4.0 (q) | 17.6 (q, 2'-Me) |
| **14a** | 169.4 (s)<br>51.3 (q) | 105.5 (d) | 149.4 (d) | 60.0 (s) | 28.7 (d) | 19.0 (t) | 25.4 (q)<br>17.6 (s) | -3.4 (q)<br>-4.9 (q) | 55.8 (q, OMe) |
| **14b** | 170.9 (s)<br>51.3 (q) | 101.1 (d) | 150.2 (d) | 61.3 (s) | 29.6 (d) | 21.0 (t) | 25.5 (q)<br>17.6 (s) | -3.4 (q)<br>-4.9 (q) | 55.8 (q, OMe) |

[a] Signal for quaternary C-atom not detected. – [b] Signals at δ = 132.2, 129.1, 128.6, 127.7, 126.5 (5 d, PhCH=CH). – [c] Signals at δ = 130.1, 128.9, 128.4, 127.5, 126.5 (5 d, PhCH=CH). – [d] Signals at δ = 131.1, 128.4, 126.3, 125.6 (4 d, $C_6H_4CH$=CH, *p*-C atom not detected). – [e] Signals at δ = 135.2, 127.3, 126.3, 125.5 (4 d, $C_6H_4CH$=CH, *p*-C atom not detected). – [f] Signal of double intensity.

Table 8. Elemental analyses and IR data (ṽ in $cm^{-1}$, film) of methyl 2-siloxycyclopropanecarboxylates **9**–**14** (mixture of diastereomers)

| Compound | Formula | Molecular weight | | C | H | IR data |
|---|---|---|---|---|---|---|
| **9** | $C_{14}H_{26}O_3Si$ | 270.4 | Calcd.<br>Found | 62.19<br>59.65[a] | 9.69<br>9.34 | 2980-2820 (=CH,-CH), 1730 (C=O), 1460, 1250, 1160, 830 |
| **10** | $C_{14}H_{26}O_3Si$ | 270.4 | Calcd.<br>Found | 62.19<br>62.50 | 9.69<br>9.83 | 3050-2780 (=CH,-CH), 1740 (C=O), 1440, 1370, 1250, 840 |
| **11** | $C_{19}H_{28}O_3Si$ | 332.5 | Calcd.<br>Found | 68.63<br>68.75 | 8.48<br>8.71 | 3120-3020 ($CH_{arom}$,=CH), 3000-2780 (-CH), 1725 (C=O), 1430, 1160, 830 |
| **12** | $C_{20}H_{27}F_3O_3Si$ | 400.5 | Calcd.<br>Found | 59.98<br>59.97 | 6.79<br>6.72 | 2990-2820 ($CH_{arom}$,=CH,-CH), 1720 (C=O), 1610 (C=C), 1435, 1370, 1160, 830 |
| **13** | $C_{14}H_{26}O_3Si$ | 270.4 | Calcd.<br>Found | 62.19<br>61.86 | 9.69<br>9.78 | 3000-2920 (=CH,-CH), 1730 (C=O), 1665 (C=C), 1430, 1370, 1250, 1160, 830 |
| **14** | $C_{14}H_{26}O_4Si$ | 286.4 | Calcd.<br>Found | 58.71<br>58.71 | 9.14<br>9.31 | 3060-2800 (=CH, -CH), 2850 ($OCH_3$), 1665 (C=C), 1455, 1365, 1250, 1230, 1195, 830 |

[a] Despite several attempts, a correct elemental analysis could not be obtained.

2.09 g (61%, 91% regarding the amount of **8b**) of **26** as a colorless oil and 0.033 g (2%) of **27** and **28** (**27**:**28** = 84:16). Analytical data of **26** are given in Tables 13–15. – **27**: $^1$H NMR: δ = 5.56, 5.25, 5.02 (ABX system, $J_{AB}$ = 1.4, $J_{AX}$ = 17.1, $J_{BX}$ = 10.6 Hz, 1H each, 1',2'-H), 3.99, 3.63 (2 dd, $J_{vic}$ = 9.4, $J_{vic}$ = 4.6, $J_{gem}$ = 11.6 Hz, 1H each, C*H*$_2$OH), 1.31–1.20 (m, 1H, 1-H), 0.90, 0.85 (2 dd, $J_{vic}$ = 9.3, $J_{vic}$ = 6.8, $J_{gem}$ = 5.8 Hz, 1H each, 3-H), signal for OH is not detected. – $^{13}$C NMR: δ = 142.6 (d, C-1'), 110.5 (t, C-2'), 61.9 (t, $CH_2OH$), 58.9 (s, C-2), 28.2 (d, C-1), 19.9 (t, C-3). – **28**: $^1$H NMR: δ = 6.35, 6.25, 5.85 (ABX system, $J_{AB}$ = 1.6, $J_{AX}$ = 17.7, $J_{BX}$ = 10.1 Hz, 1H each, 1,2-H), 3.63 ($m_c$, 2H, 6-H), 2.72 (t, *J* = 7.0 Hz, 2H, 4-H), 1.86 (quint., *J* = 6.5 Hz, 2H, 5-H), signal of OH is not detected. – $^{13}$C NMR: δ = 201.7 (s, C-3), 136.5 (d, C-2), 128.9 (t, C-1), 62.1 (t, C-6), 36.4 (t, C-4), 26.7 (t, C-5).

*Reduction of Methyl 2-(tert-Butyldimethylsiloxy)-3-methyl-2-vinylcyclopropanecarboxylate* (**9**): According to the general procedure 0.230 g (6.06 mmol) of $LiAlH_4$ in 10 ml of diethyl ether was stirred with 1.35 g (4.99 mmol) of **9** (**9a**:**9b**:**9c**:**9d** = 24:27:32:17) in 10 ml of diethyl ether. Purification of the crude product by kugelrohr distillation (80°C/0.01 Torr) afforded 0.759 g (63%) of **29**. 0.588 g was purified by chromatography (silica gel, hexane/ethyl acetate, 1:1) to furnish 0.304 g (32%) of pure **29** (*c*-3/*r*-1-**29**:*t*-3/*r*-1-**29** = 45:55). – $^1$H NMR: δ = 5.74, 5.44, 5.22 (ABX system, $J_{AX}$ = 17.1,

Table 9. Synthesis of methyl 2-siloxycyclopropanecarboxylates **15**–**19**

| Starting Material | a:b | g (mmol) | El-X | g or ml (mmol) | Product | g (%) | b.p. [°C/Torr][a] |
|---|---|---|---|---|---|---|---|
| **8** | 33:67 | 0.571 (2.23) | MeI[b] | 0.3 ml (4.8) | **15** | 0.415 (69) | 100-105/0.135 |
| **8** | 33:67 | 1.11 (4.33) | Allyl-Br | 1.16 g (13.3) | **16** | 1.02 (80) | 90-100/0.015 |
| **10** | 47:53 | 2.70 (10.0) | MeI[b] | 1.6 ml (26) | **17** | 2.31 (81) | 50-85/0.1 |
| **11** | 28:72 | 1.66 (4.99) | MeI[b] | 0.8 ml (13) | **18** | 1.28 (74) | [c] |
| **8** | 33:67 | 1.28 (5.00) | Acetone | 0.76 g (13.1) | **19** | 0.868 (55) | [d] |

[a] Kugelrohr distillation. – [b] Freshly filtered through basic alumina. – [c] Purification by chromatography (alumina, hexane/ethyl acetate, 20:1). – [d] Purification by chromatography (silica gel, hexane/ethyl acetate, 4:1).

$J_{BX}$ = 10.7, $J_{AB}$ = 1.9 Hz, HC=$CH_2$, *c*-3/*r*-1-**29**), 5.70, 5.23, 5.06 (ABX system, $J_{AX}$ = 17.1, $J_{BX}$ = 10.7, $J_{AB}$ = 1.5 Hz, HC=$CH_2$, *t*-3/*r*-1-**29**), 3.71–3.57 (m, 2H of *c*-3/*r*-1-**29**, 1H of *t*-3/*r*-1-**29**, $CH_2OH$), 3.43 (dd, $J_{gem}$ = 11.7, $J_{vic}$ = 8.2 Hz, 1H of *t*-3/*r*-1-**29**, $CH_2OH$), 1.81 (bs, 1H, OH), 1.61–1.40 (m, 1H, 1-H, *c*-3/*r*-1-**29**, *t*-3/*r*-1-**29**), 1.14 (d, *J* = 6.1 Hz, 3-Me, *t*-3/*r*-1-**29**), 1.06 (d, *J* = 6.6 Hz, 3-Me, *c*-3/*r*-1-**29**), 0.90 (s, t-BuSi, *t*-3/*r*-1-**29**), 0.85 (s, *t*BuSi, *c*-3/*r*-1-**29**), 0.14, 0.11 (2 s, $Me_2Si$, *t*-3/*r*-1-**29**), 0.07, 0.06 (2 s, $Me_2Si$, *c*-3/*r*-1-**29**), integrals corresponded to expected values and showed a distribution of *c*-3/*r*-1-**29**:*t*-3/*r*-1-**29** = 45:55. – Further analytical data are given in Tables 14 and 15.

*Reduction of Methyl 2-(tert-Butyldimethylsiloxy)-2-isopropenylcyclopropanecarboxylate* (**10**): According to the general procedure 0.239 g (6.29 mmol) of $LiAlH_4$ in 12 ml of diethyl ether was stirred with 1.38 g (5.10 mmol) of **10** (**10a**:**10b** = 47:53) in 10 ml of diethyl ether to provide 0.933 g (75%) of crude product. Further purification by chromatography (silica gel, hexane/ethyl acetate, 2:1) yielded 0.531 g (43%, 81% regarding the amount of **10b**) of **30** as a colorless oil. Analytical data are given in Tables 13–15.

Table 10. $^1$H-NMR data (δ values, *J* in Hz) of C-1-substituted methyl 2-siloxycyclopropanecarboxylates **15**–**19** (integrals correspond to expected values)

| Compound | 1'-H | 2'-H | 2'-H | $CO_2Me$ | 3-H[a] | 3-H[b] | $J_{gem}$ | *t*BuSi | $Me_2Si$ | Other Signals |
|---|---|---|---|---|---|---|---|---|---|---|
| **15** | ABX-system: $\delta_X$=5.82, $\delta_A$=5.25, $\delta_B$=5.08, $J_{AX}$=17.0, $J_{BX}$=10.7, $J_{AB}$=1.6 | | | 3.60 (s) | 1.85 (s) | 0.96 (s) | 6.2 | 0.89 (s) | 0.09 (s) 0.06 (s) | 1.39 (s, 3H, 1-Me) |
| **16** | ABX-system: $\delta_X$[c], $\delta_A$=5.25, $\delta_B$=5.08, $J_{AX}$=17.2, $J_{BX}$=10.5, $J_{AB}$=1.4 | | | 3.60 (s) | 1.83 (d) | 1.02 (d) | 6.3 | 0.89 (s) | 0.10 (s) 0.07 (s) | [d] |
| **17** | -- | 4.90 ($m_c$) | 4.89 ($m_c$) | 3.56 (s) | 1.92 (d) | 0.78 (d) | 5.9 | 0.85 (s) | 0.06 (s) 0.05 (s) | 1.67[e](s, 3H, 1-Me) |
| **18** | 6.64 and 6.27 (2d, *J*=15.9) | | -- | 3.58 (s) | 1.98 (d) | 1.09 (d) | 6.1 | 0.96 (s) | 0.15 (s) 0.11 (s) | 7.40-7.21(m, Ph), 1.47 (s, 1-Me) |
| **19** | 5.95 (dd, *J*= 17.2, *J*=10.3) | 5.03 (m) | 4.98 (2m) | 3.54 (s) | 1.72 (d) | 1.68 (d)[f] | 6.7 | 0.87 (s) | 0.11 (s) 0.10 (s) | 3.08 (bs, OH), 1.64, 1.22 (2s, je 3H, Me) |

[a] *trans* with respect to ester group. – [b] *cis* with respect to ester group. – [c] 5.88–5.75 (m, 2H, 1'-H, 2''-H). – [d] 5.04 (dd, *J* = 15.7/1.5, 1H, 3''-H), 4.98 (dd, *J* = 11.0/1.5, 1H, 3''-H), 2.98, 2.22 (2 ddd, *J* = 15.6/6.4/1.1, 1H each, 1''-H). – [e] Line broadening by allyl coupling. – [f] Signal with long-range coupling.

Table 11. $^{13}$C-NMR data (δ values) of C-1-substituted methyl 2-siloxycyclopropanecarboxylates **15**–**19**

| Compound | $CO_2Me$ | C-1' | C-2' | C-2 | C-1 | C-3 | *t*BuSi | $Me_2Si$ | Other Signals |
|---|---|---|---|---|---|---|---|---|---|
| **15** | 173.1 (s) 51.9 (q) | 139.9 (d) | 115.1 (t) | 64.9 (s) | 32.6 (s) | 25.7 (t) | 25.8 (q) 18.3 (s) | -3.5 (s) -3.6 (q) | 15.1 (q, 1'-Me) |
| **16** | 171.9 (s) 51.7 (q) | [a] | [b] | 65.0 (s) | 37.1 (s) | 23.6 (t) | 25.8 (q) 18.1 (s) | -3.5 (q) -3.7 (q) | 32.8 (t, C-1''), [a,b] |
| **17** | 173.0 (s) 51.9 (q) | 142.3 (s) | 114.1 (d) | 68.3 (s) | 30.9 (s) | 24.3 (t) | 25.6 (q) 18.1 (s) | -3.0 (q) -4.2 (q) | 19.3 (q, 1'-Me), 14.9 (q, 1-Me) |
| **18** | 173.0 (s) 52.0 (q) | [c] | [c] | 65.0 (s) | 33.2 (s) | 26.9 (t) | 26.0 (q) 18.4 (s) | -3.4 (q) -3.7 (q) | 137.0 (s, C-*i*-Ph), 15.3 (q, 1-Me)[c] |
| **19** | 170.0 (s) 51.5 (q) | 136.4 (d) | 114.6 (t) | 65.0 (s) | 45.3 (s) | 16.4 (t) | 25.5 (q) 17.5 (s) | -3.2 (q) -4.1 (q) | 70.6 (s, C-1''), 28.4, 27.8 (2q, Me) |

[a] Signals at δ = 136.7 and 135.7 (2 d, C-1', C-2). – [b] Signals at δ = 115.7 and 115.1 (2 t, C-2', C-3''). – [c] Signals at δ = 130.4, 129.0, 128.7, 127.7, 126.4 (5 d, PhCH=CH).

Table 12. Elemental analyses and IR data ($\tilde{\nu}$ in $cm^{-1}$, film) of C-1-substituted methyl 2-siloxycyclopropanecarboxylates **15**–**19**

| Compound | Formula | Molecular weight | | C | H | IR data |
|---|---|---|---|---|---|---|
| **15** | $C_{14}H_{26}O_3Si$ | 270.4 | Calcd. | 62.19 | 9.69 | 3060-2880 (=$CH_2$-CH), 1725 (C=O), 1630 (C=C), 1460, 1250, 860 |
| | | | Found | 61.82 | 9.93 | |
| **16** | $C_{16}H_{28}O_3Si$ | 296.5 | Calcd. | 64.82 | 9.52 | 3080-2860 (=$CH_2$-CH), 1720 (C=O), 1640 (C=C), 1250, 1210, 830 |
| | | | Found | 64.38 | 9.55 | |
| **17** | $C_{15}H_{28}O_3Si$ | 284.5 | Calcd. | 63.33 | 9.92 | 2980-2840 (=$CH_2$-CH), 1735 (C=O), 1645 (C=C), 1300, 1250, 1145, 830 |
| | | | Found | 62.72 | 10.19 | |
| **18** | $C_{20}H_{30}O_3Si$ | 346.5 | Calcd. | 69.32 | 8.72 | 3100-2980 ($CH_{arom}$,=CH), 2970-2700 (CH), 1720 (C=O), 1600 (C=C), 1310, 1250, 830 |
| | | | Found | 68.74 | 8.63 | |
| **19** | $C_{16}H_{30}O_4Si$ | 314.5 | Calcd. | 61.11 | 9.15 | 3520 (OH), 2980-2850 (=CH,-CH), 1730 (C=O), 1640 (C=C), 1280, 830 |
| | | | Found | 61.14 | 9.61 | |

Table 13. $^1$H-NMR data ($\delta$ values, $J$ in Hz) of (hydroxymethyl)cyclopropanes **21**, **23**, **26**, and **30**–**34** (integrals correspond to the expected values)

| Compound | $CH_2OH$ (2dd) $J_{vic}$ | $J_{vic}$ | $J_{gem}$ | OH (br.s) | 1-H | 3-H $J_{vic}$ | 3-H $J_{vic}$ | (2dd) $J_{gem}$ | *t*BuSi (s) | $Me_2Si$ (2s) | Other Signals |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **21** | 3.76<br>6.5 | 3.41<br>9.0 | 11.5 | 1.52 | 0.83 (ddd, $J$=9.0, $J$=6.5, $J$=3.0 | -- | -- | -- | 0.88 | 0.07[a] | 2.94 (d, $J$=3.0, 2-H), 1.12, 1.04 (2s, 3-Me) |
| **23** | 3.28<br>6.8 | 3.03<br>8.3 | 11.7 | [b] | [b] | 1.19-1.12 (m) [c] | | [c] | 0.82 | 0.04<br>-0.24 | 7.45-7.42, 7.35-7.26 (2m, Ph) |
| **26** | 3.60<br>6.8 | 3.41<br>8.6 | 11.7 | 1.76 | 1.62-1.51 | 1.13<br>10.0 | 0.75<br>6.9 | 5.9 | 0.86 | 0.10<br>0.08 | 5.82[d], 5.26, 5.14 (ABX system, $J_{AX}$=17.0, $J_{BX}$=10.6, $J_{AB}$= 1.6, $H_2C$=CH) |
| **30** | 3.43<br>7.7 | 3.24<br>7.4 | 11.3 | 2.53 | 1.41-1.30 (m) | 0.90<br>9.9 | [e] | 5.6 | 0.80[f] | 0.28<br>0.25 | 4.85, 4.80 (quint., $J_{gem}$=$J_{allyl}$=1.5, $m_c$, 2'-H), 1.82 (d, $J_{allyl}$=1.5, 1'-Me) |
| **31** | 3.64<br>6.9 | 3.53<br>8.1 | 11.7 | 2.29 | 1.74-1.64 (m) | 1.26<br>10.0 | [e] | 5.9 | 0.95 | 0.18<br>0.17 | 7.40-7.21 (m, Ph), 6.68, 6.23 (2d, $J$=15.8, HC=CH) |
| **32** | 3.69<br>6.7 | 3.52<br>8.2 | 11.7 | 2.46 | 1.77-1.66 (m) | 1.31<br>10.0 | [e] | 6.0 | 0.91[f] | 0.15<br>0.14 | 7.64-7.26 (2m, $F_3C$-$C_6H_4$), 6.70, 6.28 (2d, $J$=15.8, HC=CH) |
| **33** | 3.55<br>6.9 | 3.29<br>8.3 | 11.6 | 2.04 | 1.50-1.39 (m) | 0.99<br>9.8 | 0.65<br>6.5 | 5.9 | 0.82 | 0.06<br>0.05 | 5.64 (dq, $J$=15.3, $J$=6.3, 2'-H), 5.42 (d[g], $J$=15.3, 1'-H), 1.68 (dd, $J$=6.3, $J$=1.4, 2'-Me) |
| **34** | [h] | | | 2.05 | 1.43-1.32 (m) | 0.93 - 0.82 [i] | | [c] | 0.80 | 0.06<br>0.05 | 6.49, 4.97 (2d, $J$=12.6, HC=CH) |

[a] Signal of double intensity. – [b] Signal at $\delta$ = 1.75–1.51 (m, 2H, 1-H, OH). – [c] Coupling not determinable. – [d] Line broadened by long-range coupling. – [e] Signal hidden by *tert*-butyl group. – [f] Integral 10 H, *t*Bu and 3-H signal. – [g] Signal with fine coupling. – [h] Signals at $\delta$ = 3.62–3.41 (m) and 3.50 (s), together 5H, $CH_2OH$ and OMe. – [i] Integral 3H, 3-H and side product.

*Reduction of Methyl 2-(tert-Butyldimethylsiloxy)-2-styrylcyclopropanecarboxylate* (**11**): According to the general procedure 0.285 g (7.50 mmol) of $LiAlH_4$ in 10 ml of diethyl ether was combined with 2.49 g (7.49 mmol) of **11** (**11a**:**11b** = 28:72) in 10 ml of diethyl ether. After addition of the ester the mixture was refluxed for 1 h. Further workup was performed as described in the general procedure and provided 2.03 g (89%) of crude product. Purification by chromatography (alumina, hexane/ethyl acetate, 2:1) afforded 1.23 g (54%, 75% regarding the amount of **11b**) of **31** as a colorless oil. Analytical data are given in Tables 13–15. For further investigations the mixture of **11a** and **11b** was separated by HPLC (hygrosil column, 5 µm, hexane/ethyl acetate, 98:2; retention time of **11b**: 20.0 min, of **11a**: 24.8 min).

*Reduction of Diastereomerically Pure* **11b**: According to the general procedure 0.144 g (3.79 mmol) of $LiAlH_4$ in 10 ml of diethyl ether was stirred with 0.981 g (2.95 mmol) of **11b**. After hydrolysis, the reaction mixture was extracted with ethyl acetate. After evaporation of the solvent from the extract 0.852 g (95%) of crude **31** was obtained. Purification by kugelrohr distillation (175°C/0.015 Torr) yielded 0.810 g (90%) of **31**.

*Reduction of Diastereomerically Pure* **11a**: As described above 0.065 g (1.63 mmol) of $LiAlH_4$ in 5 ml of diethyl ether was stirred with 0.408 g (1.22 mmol) of **11a** in 5 ml of diethyl ether. After hydrolysis the crude mixture was extracted with ethyl acetate. Evaporation of the solvent from the extract furnished 0.270 g of crude product. Chromatography (silica gel, hexane/ethyl acetate, 1:7) furnished 0.052 g (22%) of **42** and 0.069 g of **41** containing small amounts of several unidentified side products. – **41**: $^1$H NMR: $\delta$ = 7.61–7.15 (m, ca. 28H, Ph and side products), 6.63, 5.93 (2 d, $J$ = 15.9 Hz, 1H each, 1',2'-H), 4.50–4.18 (bm, ca. 5H, 2-OH, $CH_2OH$

Table 14. $^{13}$C-NMR data (δ values) of (hydroxymethyl)cyclopropanes **21**, **23**, **26**, and **30**–**34**

| Compound | C-1' | C-2' | $CH_2OH$ | C-2 | C-1 | C-3 | *t*BuSi | $Me_2Si$ | Other Signals |
|---|---|---|---|---|---|---|---|---|---|
| **21** | -- | -- | 61.9 (t) | 61.7 (s) | 33.7 (d) | 21.1 (s) | 25.7 (q) 17.9 (s) | -5.1 (q) -5.2 (q) | 19.1, 18.0 (2q, 3-Me) |
| **23** | -- | -- | 62.9 (t) | 62.2 (s) | 28.7 (d) | 15.8 (t) | 25.6 (q) 17.6 (s) | -3.8 (q) -3.9 (q) | 139.8, 128.4, 128.1, 127.5 (s, 3d, Ph) |
| **26** | 137.7 (d) | 113.9 (t) | 62.4 (t) | 60.1 (s) | 29.5 (d) | 18.3 (t) | 25.5 (q) 17.6 (s) | -3.6 (q) -3.9 (q) | -- |
| **29**[a] | 139.0 (d) | 113.5 (t) | 63.0 (t) | 63.4 (s) | 36.5 (d) | 23.3 (d) | 26.2 (q) 18.5 (s) | -3.1 (q) -3.2 (q) | 11.9 (q, 3-Me) |
| **29**[b] | 135.5 (d) | 115.6 (t) | 59.1 (t) | 62.1 (s) | 33.4 (d) | 23.3 (d) | 26.0 (q) 18.1 (s) | -2.9 (q) -3.3 (q) | 8.9 (q, 3-Me) |
| **30** | 143.7 (s) | 112.8 (t) | 61.7 (t) | 63.8 (s) | 27.7 (d) | 15.1 (t) | 25.6 (q) 16.9 (s) | -3.9 (q) -4.0 (q) | 20.4 (q, 1'-Me) |
| **31** | [c] | [c] | 62.8 (t) | 60.4 (s) | 30.5 (d) | 19.5 (t) | 26.0 (q) 18.1 (s) | -3.1 (q) -3.4 (q) | 136.9 (s, C-*i*)[c] |
| **32** | [d] | [d] | 62.6 (t) | 60.2 (s) | 30.7 (d) | 19.9 (t) | 25.7 (q) 17.9 (s) | -3.3 (q) -3.4 (q) | 140.3 (s, C-*i*), 124.3 (q, $J_{CF}$ = 272 Hz, *p*-$CF_3$)[d] |
| **33** | 130.4 (d) | 126.0 (d) | 62.7 (t) | 59.9 (s) | 29.0 (d) | 17.8 (t) | 25.7 (q) 17.7 (s) | -3.3 (q) -3.4 (q) | 17.6 (q, 2'-Me) |
| **34** | 102.3 (d) | 150.4 (d) | 62.8 (t) | 57.6 (s) | 27.7 (d) | 16.6 (t) | 25.5 (q) 17.5 (s) | -3.4 (q) -3.8 (q) | 55.9 (q, OMe) |

[a] *t*-3-*r*-1-**29**. – [b] *c*-3-*r*-1-**29**. – [c] Signals at δ = 130.1, 129.7, 128.5, 127.4, 126.3 (5 d, PhCH=CH). – [d] Signals at δ = 133.1, 128.3, 126.2, 125.5 (4 d, $F_3CC_6H_4CH$=CH, C-*p* not detected).

Table 15. Elemental analyses and IR data ($\tilde{\nu}$ in $cm^{-1}$, film) of (hydroxymethyl)cyclopropanes **21**, **23**, **26**, **29**–**34**

| Compound | Formula | Molecular weight | | C | H | IR data |
|---|---|---|---|---|---|---|
| **21** | $C_{12}H_{26}O_2Si$ | 230.4 | Calcd. | 62.55 | 11.37 | 3340 (OH), 3000-2830 (CH), 1470, 1255, |
| | | | Found | 62.47 | 11.54 | 1160, 990 |
| **23** | $C_{16}H_{26}O_2Si$ | 278.5 | Calcd. | 69.01 | 9.41 | 3340 (OH), 3120-3000 ($CH_{arom}$), 3000-2680 |
| | | | Found | 68.97 | 9.42 | (=CH), 1680, 1610, 1460, 1440, 1250, 830 |
| **26** | $C_{12}H_{24}O_2Si$ | 228.4 | Calcd. | 63.01 | 10.59 | 3340 (OH), 3070 (=CH), 2990-2700 (-CH), |
| | | | Found | 62.81 | 10.73 | 1635 (C=C), 1250, 830, 780 |
| **29** | $C_{13}H_{26}O_2Si$ | 242.4 | Calcd. | 64.42 | 10.81 | 3360 (OH), 3010-2820 (=CH,-CH), 1685, |
| | | | Found | 64.29 | 10.79 | 1630 (C=C), 1460, 1250, 1030, 830 |
| **30** | $C_{13}H_{26}O_2Si$ | 242.4 | Calcd. | 64.42 | 10.81 | 3320 (OH), 3080-2800 (=CH,-CH), 1640 |
| | | | Found | 64.27 | 10.69 | (C=C), 1460, 1250, 1210, 1170, 830 |
| **31** | $C_{18}H_{28}O_2Si$ | 304.5 | Calcd. | 71.00 | 9.27 | 3340 (OH), 3180-3020 ($CH_{arom}$,=CH), 2980- |
| | | | Found | 70.78 | 9.44 | 2840 (-CH), 1680 (C=C), 1600, 1250, 830 |
| **32** | $C_{19}H_{27}F_3O_2Si$ | 372.5 | Calcd. | 61.26 | 7.26 | 3350 (OH), 3000-2810 ($CH_{arom}$,=CH,-CH), |
| | | | Found | 61.01 | 6.95 | 1640 (C=C), 1610, 1455, 1410, 1320 |
| **33** | $C_{13}H_{26}O_2Si$ | 242.4 | Calcd. | 64.42 | 10.81 | 3350 (OH), 3020-2840 (=CH,-CH), 1660 |
| | | | Found | 64.27 | 10.74 | (C=C), 1470-1430, 1250, 830 |
| **34** | $C_{13}H_{26}O_3Si$ | 258.4 | Calcd. | 60.43 | 10.14 | 3360 (OH), 3060-2800 (=CH,-CH), 1645 |
| | | | Found | 60.03 | 9.87 | (C=C), 1455, 1250, 1210, 830 |

and side products), 1.45–1.31, 1.05–0.80 (2 m, ca. 2H, ca. 3H, 1,3-H and side products). – $^{13}$C NMR: δ = 136.9, 134.3, 133.5, 130.1, 128.4, 127.0, 126.0 (s, 6 d, PhCH=CH-, one doublet could not be assigned), 61.9 (t, $CH_2OH$), 58.8 (s, C-2), 20.9 (d, C-1), 19.5 (t, C-3). – **42**: $^1$H NMR: δ = 7.64, 6.82 (2 d, *J* = 16.1 Hz, 1H each, 1,2-H), 7.59–7.53, 7.42–7.33 (2 m, 2H, 3H, Ph), 3.90, 3.79, 3.11, 1.21 ($ABMX_3$ system, $J_{AB}$ = 11.1, $J_{AM}$ = 4.3, $J_{BM}$ = 7.1, $J_{MX}$ = 7.2 Hz, 2H, 1H, 3H, 5,4-H, 4-Me), 2.71 (bs, 1H, OH). – $^{13}$C NMR: δ = 203.7 (s, C-3), 143.5, 134.4, 130.7, 129.0, 128.4, 124.8 (d, s, 4 d, Ph, C-1,2), 64.4 (t, C-5), 46.3 (d, C-4), 13.7 (q, Me).

Table 16. Reduction of C-1-substituted methyl 2-siloxycyclopropanecarboxylates **15–18**

| Starting Material[a] | g (mmol) | Diethyl ether (ml) | $LiAlH_4$ g (mmol) | Diethyl ether (ml) | Product | Yield g (%) | b.p. [°C/ Torr][b] |
|---|---|---|---|---|---|---|---|
| **15** | 1.08 (3.99) | 9 | 0.180 (4.74) | 10 | **35** | 0.72 (74) | 100-120/ 0.01 |
| **16** | 1.02 (3.44) | 10 | 0.183 (4.82) | 10 | **36** | 0.847 (92) | 100-150/ 0.02 |
| **17** | 1.42 (5.00) | 10 | 0.279 (7.29) | 12 | **37** | 1.14 (89) | 60-80/ 0.01 |
| **18** | 1.20 (3.47) | 10 | 0.160 (4.22) | 10 | **38** | 0.987 (89) | 165-170/ 0.1 |

[a] *cis:trans* < 3:97. – [b] Kugelrohr distillation.

*Reduction of Methyl 2-(tert-Butyldimethylsiloxy)-2-{2-[4-(trifluoromethyl)phenyl]ethenyl}cyclopropanecarboxylate* (**12**): As described in the general procedure 0.23 g (6.05 mmol) of $LiAlH_4$ in 12 ml of diethyl ether was stirred with 2.00 g (5.00 mmol) of **12** (**12a**:**12b** = 28:72) to afford 1.64 g (88%) of crude product. Kugelrohr distillation (150–170°C/0.01 Torr) furnished 1.42 g (76%) of still impure **32**. 1.39 g was subjected to chromatography (silica gel, hexane/ethyl acetate, 1:1) to yield 0.775 g (42%, 60% regarding the amount of **12b**) of pure **32**. Analytical data are given in Tables 13–15.

*Reduction of Methyl 2-(tert-Butyldimethylsiloxy)-2-(1-propenyl)cyclopropanecarboxylate* (**13**): According to the general procedure 0.230 g (6.06 mmol) of $LiAlH_4$ in 12 ml of diethyl ether was stirred with 1.35 g (5.00 mmol) of **13** (**13a**:**13b** = 38:62) in 10 ml of diethyl ether. 0.888 g (73%) of crude product was obtained, and further purification by kugelrohr distillation (120–135°C/0.03 Torr) provided 0.733 g (60%, 97% regarding the amount of **13b**) of **33** as a pale yellow oil. Analytical data are given in Tables 13–15.

*Reduction of Methyl 2-(tert-Butyldimethylsiloxy)-2-(2-methoxyvinyl)cyclopropanecarboxylate* (**14**): As described in the general procedure 0.089 g (2.35 mmol) of $LiAlH_4$ in 3 ml of diethyl ether was stirred with 0.502 g (1.75 mmol) of **14** (**14a**:**14b** = 34:66) in 4 ml of diethyl ether to provide 0.341 g (75%) of crude product. Kugelrohr distillation (140–150°C/0.01 Torr) furnished 0.294 g (65%, 98% regarding the amount of **14b**) of **34**. Analytical data are given in Tables 13–15.

*Reduction of C-1-Substituted Methyl 2-Siloxycyclopropanecarboxylates* **15–18** (Table 16) was performed as described in the general procedure. Workup by kugelrohr distillation. Analytical data are given in Tables 17–19..

Table 17. $^1$H-NMR data (δ values, *J* in Hz) of C-1-substituted (hydroxymethyl)cyclopropanes **35–38** (integrals correspond to the expected values)

| Compound | 1'-H | 2'-H | $CH_2OH$ | $J_{AB}$ | OH | 3-H (2d) | $J_{gem}$ | *t*BuSi | $Me_2Si$ | Other Signals |
|---|---|---|---|---|---|---|---|---|---|---|
| **35** | 5.98, 5.16, 5.15 (ABX system, $J_{AX}$=17.2, $J_{BX}$=10.6, $J_{AB}$=1.5) | | 3.50, 3.28 (AB system) | 11.5 | 1.65-1.45 (m) | 0.92 0.64 | 5.9 | 0.88 (s) | 0.08 (s) 0.05 (s) | 1.29 (s, Me) |
| **36** | 6.00, 5.18, 5.14 (ABX system, $J_{AX}$=17.1, $J_{BX}$=10.5, $J_{AB}$=1.5) | | 3.55, 3.28 (AB system) | 11.8 | 1.62 (br.s) | 0.94 0.72 | 6.0 | 0.87 (s) | 0.08 (s) 0.07 (s) | [a] |
| **37** | -- | 4.87 (quint, *J*=1.5) 4.83 (s)[c] | 3.38, 3.28 (AB system) | 11.1 | 1.53 (br.s) | 0.95 0.48 | 5.8 | 0.86 (s) | 0.06 (s) 0.05 (s) | 1.80 (s[b], 1'-Me), 1.27 (s, 1-Me) |
| **38** | 6.61, 6.41 (2d, *J*=15.9) | | 3.59, 3.41 (AB system) | 11.5 | 1.70 (br.s) | 1.12 0.81 | 5.9 | 0.98 (s) | 0.17 (s) 0.15 (s) | 7.42-7.27 (m, Ph), 1.40 (s, 1-Me) |

[a] Signals at δ = 5.90 (ddt, *J* = 17.2/10.1/7.1, 1H, 2''-H), 5.12, 5.04 (2 dd, *J* = 17.2/10.1/1.5, 1H each, 3''-H), 2.45, 2.36 (AB system, *J* = 15.0/6.7/7.4, 2H, 1''-H). – [b] Line broadened by long-range and geminal couplings. – [c] Line broadened by long-range coupling.

Table 18. $^{13}$C-NMR data (δ values) of C-1-substituted (hydroxymethyl)cyclopropanes **35–38**

| Compound | C-1' | C-2' | $CH_2OH$ | C-2 | C-1 | C-3 | *t*BuSi | $Me_2Si$ | Other Signals |
|---|---|---|---|---|---|---|---|---|---|
| **35** | 138.9 (d) | 114.6 (t) | 67.6 (t) | 63.6 (s) | 29.5 (s) | 23.1 (t) | 25.8 (q) 18.1 (s) | -3.2 (q) -3.7 (q) | 15.4 (q, 1-Me) |
| **36** | [a] | [b] | 64.7 (t) | 63.7 (s) | 33.0 (s) | 21.9 (t) | 25.7 (q) 18.0 (s) | -3.3 (q) -3.8 (q) | [a] (C-2''), [b] (C-3''), 33.3 (t,C-1'') |
| **37** | 144.8 (s) | 112.8 (t) | 67.1 (t) | 66.6 (s) | 27.5 (s) | 21.0 (t) | 25.6 (q) 18.0 (s) | -3.1 (q) -4.1 (q) | 20.3 (q, 1'-Me), 15.1 (q, 1-Me) |
| **38** | [c] | [c] | 67.7 (t) | 63.3 (s) | 30.3 (s) | 23.9 (t) | 25.8 (q) 18.1 (s) | -3.1 (q) -3.7 (q) | 136.7 (s), [c] (Ph-CH=CH), 15.6 (q, 1-Me) |

[a] Signals at δ = 138.7 (d), 137.0 (d); unambiguous assignment not possible. – [b] Signals at δ = 116.2 (t), 114.8 (t); unambiguous assignment not possible. – [c] Signals at δ = 130.5, 129.9, 128.6, 127.4, 126.7 (5 d); unambiguous assignment not possible.

Table 19. Elemental analyses and IR data ($\tilde{\nu}$ in $cm^{-1}$, film) of C-1-substituted (hydroxymethyl)cyclopropanes **35**–**38**

| Compound | Formular | Molecular weight | | C | H | IR data |
|---|---|---|---|---|---|---|
| **44** | $C_{13}H_{26}O_2Si$ | 242.4 | Calcd. | 64.42 | 10.81 | 3350 (OH), 2950-2820 (=CH,-CH), 1635 |
| | | | Found | 63.86 | 11.08 | (C=C), 1460, 1250, 1190, 830 |
| **45** | $C_{15}H_{28}O_2Si$ | 268.5 | Calcd. | 67.11 | 10.51 | 3340 (OH), 3060-2800 (=CH,-CH), 1250, |
| | | | Found | 67.23 | 10.54 | 910, 830 |
| **46** | $C_{14}H_{28}O_2Si$ | 256.5 | Calcd. | 65.57 | 11.01 | 3340 (OH), 2980-2840 (=CH,-CH), 1640 |
| | | | Found | 65.28 | 11.15 | (C=C), 1250, 1160, 830 |
| **47** | $C_{19}H_{30}O_2Si$ | 318.5 | Calcd. | 71.64 | 9.49 | 3340 (OH), 3100-2680 (=CH,-CH), 1640 |
| | | | Found | 71.32 | 9.54 | (C=C), 1600 ($C=C_{arom}$), 1455, 1250, 850 |

*Reduction of Methyl 2-(tert-Butyldimethylsiloxy)-1-(1-hydroxy-1-methylethyl)-2-vinylcyclopropanecarboxylate* (**19**): According to the general procedure 0.227 g (5.98 mmol) of $LiAlH_4$ in 6 ml of diethyl ether was stirred with 0.946 g (3.01 mmol) of **19** in 6 ml of diethyl ether. After hydrolysis the mixture was extracted with ethyl acetate. After evaporation of the solvent from the extract 0.539 g of a pale yellow oil was obtained which was purified by chromatography (silica gel, hexane/ethyl acetate, 2:1) to furnish 0.266 g (31%) of **39** and 0.100 g (21%) of **40**–**39**: $^1H$ NMR: δ = 6.14, 5.21, 5.14 (ABX system, $J_{AX}$ = 10.5, $J_{BX}$ = 17.3, $J_{AB}$ = 1.4 Hz, 1H each, $H_2C$=CH, X part with fine coupling), 3.64, 3.29 [d with long range coupling ($J \approx 2$ Hz), d, $J$ = 12.6 Hz, 1H each, $CH_2OH$], 1.47, 1.32 (2 s, 3H each, 1′-Me), 1.41, 0.93 (2 d, $J$ = 6.3 Hz, 1H each, 3-H), 0.86 (s, 9H, *t*BuSi), 0.12, 0.10 (2 s, 3H each, $Me_2Si$), signal of OH was not found. – $^{13}C$ NMR: δ = 138.0, 116.2 (d, t, $H_2C$=CH), 72.1 (s, C-1′), 66.5 (s, C-2), 64.3 (t, $CH_2OH$), 39.2 (s, C-1), 29.4, 28.0 (2 q, 1′-Me), 25.7, 17.7, −2.7, −3.8 (q, s, 2 q, *t*$BuMe_2Si$), 16.3 (t, C-3). – **40**: $^1H$ NMR: δ = 5.85 (ddd, $J$ = 17.2, $J$ = 10.4, $J$ = 6.5 Hz, 1H, 2-H), 5.19 (dd, $J$ = 10.4, $J$ = 1.2 Hz, 1H, 1-H), 5.02 (dd, $J$ = 10.4, $J$ = 1.2 Hz, 1H, 1-H), 4.50–4.20 (br. s, 2H, OH), 4.24, 3.86 (2 $m_c$, 1H each, $CH_2OH$), 4.10 ($m_c$, 1H, 3-H), 2.49 (br. d, $J$ = 14.2 Hz, 1H, 4-H), 2.15 (dd, $J$ = 14.2, $J$ = 9.3 Hz, 1H, 4-H), 1.72, 1.66 (2 s, 3H each, 7-H, 6-Me). – $^{13}C$ NMR: δ = 140.9, 114.1, (d, t, C-1,2), 132.5, 128.4 (2 s, C-5,6), 72.4 (d, C-3), 62.6 (t, $CH_2OH$), 39.7, (t, C-4), 20.7, 20.2 (2 q, C-7, 6-Me).

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