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Trimethylsilylketene dialkylacetals in organic synthesis: reactions with alkyldiazoacetates

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Abstract

The reaction of trimethylsilylketene dialkylacetals with alkyldiazoacetates in the presence of $Cu(acac)_2$ or $Rh_2(OAc)_4$ results in the formation of alkyl-2,2-dialkoxy-3-trimethylsilylcyclopropane-1-carboxylates **3–8**. The cycloaddition proceeds stereoselectively, giving exclusively one of two possible diastereomers. Compounds **4** and **6** are transformed by reaction with $LiAlH_4$ to cyclopropylmethanols **9** and **10** in high yields. All compounds have been characterized by elemental analyses, ^1H, ^{13}C NMR and IR spectroscopy.

Keywords: Silicon; Ketene dialkylacetals; Cyclopropanation

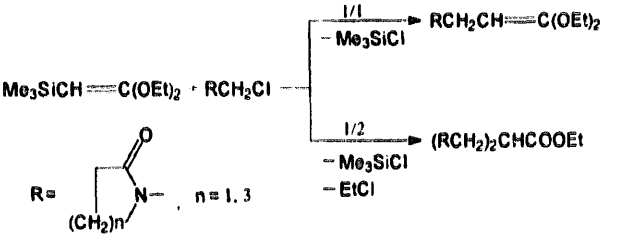
1. Introduction

Trimethylsilylketene dialkylacetals **1**, little investigated so far, can be obtained by direct silylation of ketene dialkylacetals **2** with active silylating reagents such as trimethylsilyltrifluoromethanesulfonate [1] and trimethyliodosilane [2,3].

$$Me_3SiX + \underset{2}{CH_2{=}C(OR)_2} \xrightarrow[-X^-]{Et_3N} \underset{1}{Me_3SiCH{=}C(OR)_2}$$

$X = OSO_2CF_3$, I; R = Me (a), Et (b), ^iPr (c)

Our recent studies revealed that the interaction of trimethylsilylketene dialkylacetals with electrophilic reagents proceeds under mild conditions and more selectively than yet observed for non-silylated ketene dialkylacetals, $CH_2{=}C(OR)_2$ **2**. Thus the alkylation of ketene acetals **2** requires heating to high temperatures, even when reactive alkylhalides (e.g. $PhCH_2Br$/125 °C/5 h) are used, and usually gives a mixture of products [4]. A complex mixture of products has also been obtained in reactions of N-chloromethyllactams with ketene acetal **2b**. By contrast, amidoalkylation of ketene acetal **1b** proceeds smoothly and affords, depending on the reagent ratio, either diethylacetals of the corresponding ketenes or esters of bis(amidomethyl)acetic acid [2].



The reaction of polyhalogenated carbonyl compounds with ketene acetals **1** takes place even at −78 °C and leads almost quantitatively to 1:1 adducts – silylethers of β,β-dialkoxyvinyl carbinols. ^1H and ^{19}F

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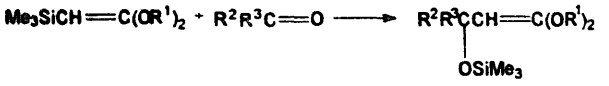
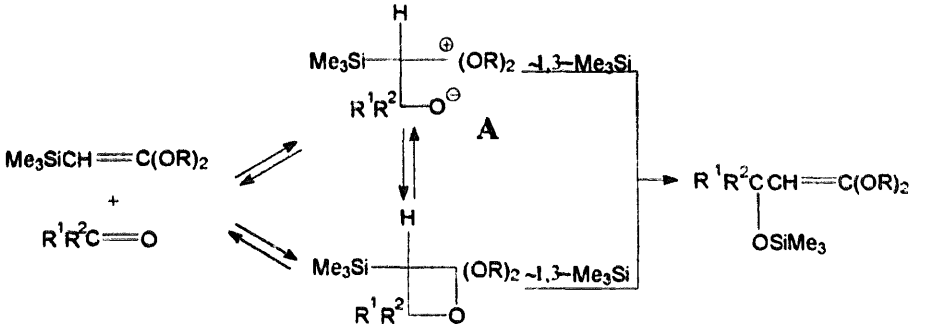
NMR monitoring indicates the intermediate formation of [2 + 2]-cycloadducts – 2,2-dialkoxyoxetanes [5].



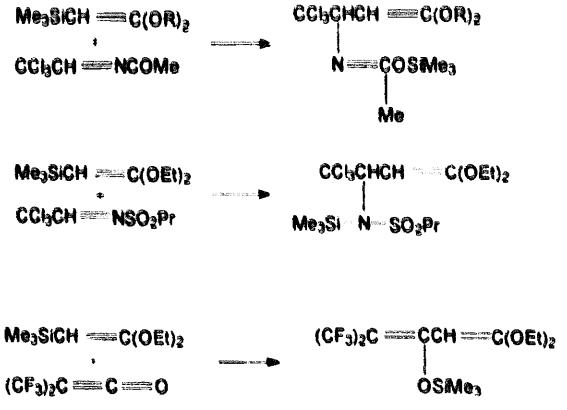
$R^1R^2C{=}O$: CCl_3CHO, CF_3COCF_3, $CF_2ClCOCF_2Cl$, $CF_2ClCOCFCl_2$

These results can be rationalized on the basis of an intermediate formation of the bipolar ion **A**.



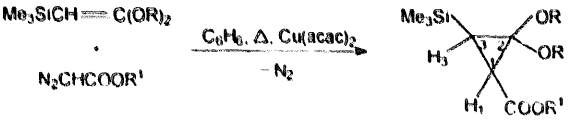
The reaction resulting in the formation of only one product contrasts with reactions of carbonyl compounds with ketene acetals **2**, where a mixture of products is usually obtained [5].

The products resulting from a formal Si=C bond cleavage and containing ketene dialkylacetal fragments are also found during the reaction of ketene acetals **1** with chloralimines [3,6] and bis(trifluoromethyl)ketene [7]:



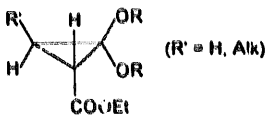
2. Results and discussion

This work deals with reactions of trimethylsilylketene acetals **1** with alkyldiazoacetates. According to the well-known nucleophilic behaviour of ketene acetals we expected the formation of carbene intermediates in spite of a definite steric hindrance imposed by the trimethylsilyl group. According to the literature [8,9], the synthesis of *gem*-dialkoxycyclopropanes by [2 + 1]-cycloaddition of common ketene dialkylacetals is difficult mainly due to a relative instability of cyclopropanes of this type. The tendency of starting ketene dialkylacetals to polymerize may also prevent a cycloaddition reaction. We expected that the presence of a trimethylsilyl substituent in our starting materials and final products would be favourable because of the known potential of trialkylsilyl groups to stabilize 'labile' molecules such as aldoketenes, diazoalkanes, cyclopropanones, etc. [10]. The reaction of alkyldiazoacetates with a three-fold excess of ketene acetals **1a–c** in the presence of equimolar amounts of $Cu(acac)_2$ in boiling benzene leads to trimethylsilylcyclopropanone dialkylacetals – alkyl-2,2-dialkoxy-3-trimethylsilylcyclopropane-1-carboxylates **3–8** – in high yield.



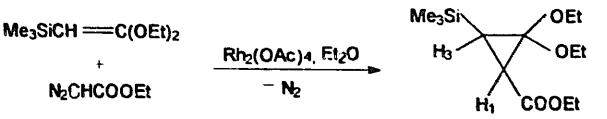
3, R = R' = Me; **4**, R = Me, R' = Et; **5**, R = Et, R' = Me; **6**, R = R' = Et; **7**, R = ^{i}Pr, R' = Me; **8**, R = ^{i}Pr, R' = Et

The reaction results in the formation of only one of two possible diastereomers, as has been established by spectroscopic data. Thus, the ^{1}H NMR spectrum of compound **5** in $CDCl_3$ consists of singlets of $SiMe_3$ (0.00 ppm) and MeO groups (3.64 ppm) and two triplets corresponding to the methyl groups of ethyl substituents (1.13 and 1.15 ppm), two multiplets at 3.5–4.2 ppm corresponding to different CH_2O fragments (AB parts of two ABX_3 spin systems) and two doublets at 1.07 and 1.88 ppm with $^3J(H_1H_3) = 8.44$ Hz corresponding to the protons H_1 and H_3 respectively. The latter signals are shifted downfield in C_6H_6: $\delta(H_1) = 1.42$ and $\delta(H_3) = 2.17$ ppm, $^3J(H_1H_3) = 8.24$ Hz. Cyclopropanes **3**, **4** and **6–8** have similar $^3J(H_1H_3)$ coupling constants (see Experimental section). Unfortunately, the configuration of cyclopropanes **3–8** cannot be determined on the basis of NMR parameters of the diastereomers due to the complete absence of the second isomer in the reaction mixture. A comparison of the observed $^3J(H_1H_3)$ values of 8.3–8.5 Hz with corresponding values for $^3J(H_1H_3)$ ($^3J_{trans} = 7.0$ Hz, $^3J_{cis} = 9.6$ Hz) [8] in the non-silylated analogues of compounds **3–8** does not allow a reliable determination of the configuration of our products. It is noteworthy that [2 + 1]-cycloadducts, prepared from alkyldiazoacetates and alkylketene dialkylacetals, possess a *trans*-configuration ($^3J_{trans} = 6.6$ Hz) [8]. Assuming that the stereochemistry of the cycloaddition reaction remains independent of whether R′ (see below) is an alkyl or silyl group, we would prefer an analogous *trans*-configuration:



The structures of cyclopropanes **3–8** are also confirmed by IR and ^{13}C NMR spectroscopy. The dominant signals in the ^{13}C NMR spectrum are: Me_3Si (−1.95 to −1.6 ppm), cyclopropane C-1 (30.5–31.3 ppm), C-2 (94–96 ppm) and C-3 (20.6–20.8 ppm) and carbonyl (168–170 ppm). An absorption in the region 1740–1750 cm^{-1} in the IR spectrum corresponds to the alkoxycarbonyl group.

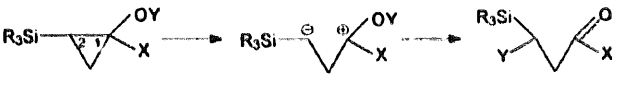
A cyclopropanation reaction of ketene acetal **1b** with ethyldiazoacetate, carried out under ambient conditions (Et_2O, $Rh_2(OAc)_4$), is stereochemically identical to that with $Cu(acac)_2$ as coreagent. The ^{1}H NMR spectra of the reaction mixture indicate the absence of a second diastereomer.



6

Although compound **6** has been reported earlier [11], a full characterization and some new properties of 2,2-dialkoxy-3-trimethylsilylcyclopropane carboxylic esters **3–8** are reported in this paper for the first time.

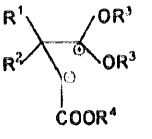
The zwitterionic intermediate **B** or similar transition states, stabilized by a trialkylsilyl group at the carbanionic centre [11], are proposed according to our qualitative study of the relative thermal stabilities of products obtained by addition to the carbonyl group of trialkylsilylcyclopropanones and their readiness to undergo a thermal rearrangement with scission of the three-membered ring to linear isomers. This suggestion is confirmed by a smooth ring opening in cyclopropanes with donating X-substituents, being observed exclusively at the C(1)–C(2) bond of the cyclopropane ring.



B

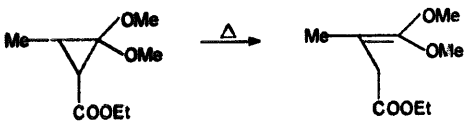
Y = H, X = H, OH, OMe, NMe_2, $OSiEt_3$, Alk; Y = R_3M (M = Si, Ge, Sn), X = NR_2; Y = Et_3Sn, X = OMe; Y = Me_3Si, X = $P(O)(OR)_2$, $-(CH_2)_nCH_2NCOCH_2-$ (n = 1, 3).

In contrast to this observation, a ring scission in *gem*-dialkoxycyclopropylcarboxylic esters results in the opening of the bond between the carbon atoms bearing acetal and carboxylic functionalities. Many products of [3 + 2]-cycloadditions have been obtained by reactions of *gem*-dialkoxycyclopropylcarboxylic esters with aldehydes and ketones, their imino derivatives and activated alkenes and alkynes. The zwitterionic intermediate **C** has been proposed for these reactions [12].



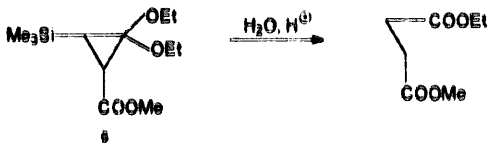
C

Additionally, the [2 + 1]-cycloaddition product of ethyldiazoacetate and methylketene dimethylacetal can be readily converted into the corresponding linear isomer at 130°C in the absence of moisture; a slow rearrangement also occurs at room temperature [8].

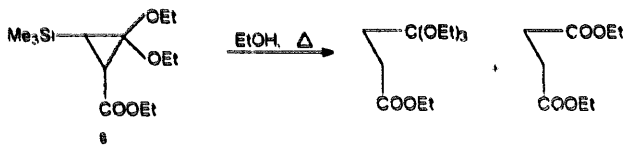


However, silylated cyclopropanes **3–8** appear to be stable up to 130°C, while heating at more elevated temperatures leads to the formation of a mixture of products difficult to identify, indicating the occurrence of a number of alternative routes for the ring scission.

In the case of cyclopropane **5**, a smooth ring opening proceeds only under conditions of acidic hydrolysis; the process involves a desilylation reaction.

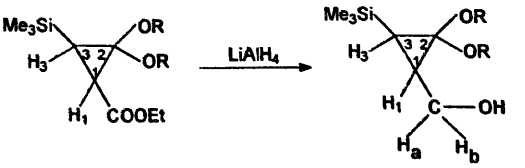


A mixture of linear products, with a predominance of the *ortho* ester, is obtained by refluxing ethyl-2,2-diethoxy-3-trimethylsilylcyclopropylcarboxylate for several hours with an excess of EtOH:



An analogous reaction including non-silylated cyclopropanes has been proposed as a method for the preparation of synthetically useful *ortho* esters [9].

The cyclopropane ring is stable towards reduction by $LiAlH_4$, which results in the formation of the corresponding cyclopropylcarbinols **9** and **10** in high yields:



R = Me (9), Et (10)

The ^1H NMR spectrum of **10** shows a doublet at 0.08 ppm corresponding to proton H_3 with $^3J(H_3H_1)$ = 8.0 Hz. The resonance of H_1 at 1.37 ppm is split into four doublets by coupling with H_3 and two diastereotopic hydrogen atoms in the CH_2OH fragment, the coupling constants of these spin–spin interactions are: $^3J(H_1H_3) = {}^3J(H_1H_a)$ = 8.0 Hz; $^3J(H_1H_b)$ = 5.2 Hz. Since the two coupling constants are equal, the multiplet is reduced to a doublet of triplets. An additional two doublets of doublets at 3.43 ppm [$^2J(H_aH_b)$ = 11.6 Hz and $^3J(H_aH_1)$ = 8.0 Hz] and 3.79 ppm [$^2J(H_bH_a)$ = 11.6 Hz] and $^3J(H_bH_1)$ = 5.2 Hz] correspond to the diastereotopic methylene protons H_a and H_b in the CH_2OH fragment. These signals are partially obscured by the signals of methylene protons of the ethoxy groups. Their assignment can be made on the basis of homonuclear double resonance experiments: the signals at 3.43 and 3.79 ppm collapse into two doublets with J = 11.6 Hz upon irradiation of the H_1 signal at 1.37 ppm. Methylene protons of ethoxy groups are diastereotopic and their signals in the ^1H NMR spectrum consist of four, in part overlapping, quartets at 3.41–3.51 ppm and 3.65–3.80 ppm (AB parts of two ABX_3 spin systems). The correlation of methyl protons of the ethoxy groups with CH_2O protons in both regions is demonstrated in a 2D COSY experiment. A full assignment of the signals of the 'ethoxy protons' is difficult because of the overlap of their resonance positions. A spin–spin coupling with the hydroxylic proton is not detectable due to a rapid exchange process via hydrogen bonds. ^{13}C NMR signals have been assigned by means of 2D ^1H–^{13}C heteronuclear correlation spectroscopy. Thus, peaks at 18.39, 29.75 and 93.95 ppm correspond to carbon atoms in the ring: C_3, C_1 and C_2 respectively, whereas the resonance at 63.60 ppm belongs to the CH_2OH carbon atom.

In summary, we have shown that the silylated ketene

dialkylacetals can undergo smooth cyclopropanation reactions under catalysis by $Rh_2(OAc)_4$ or under initiation by $Cu(acac)_2$, both resulting in the formation of only one diastereomer. A full assignment of the configuration of the products of cyclopropanation on the basis of NMR data has been found difficult, but some conclusions could be drawn according to analogous reactions carried out with non-silylated ketenes. A study of the thermal stability of silylated alkylcyclopropylcarboxylates shows the possibility of performing some ring opening reactions, resulting in the formation of linear desilylated products. Reducing alkylcyclopropylcarboxylic derivatives by action of $LiAlH_4$, appropriate dialkoxycyclopropylcarbinols can be synthesized in high yields.

3. Experimental section

3.1. General

Solvents were dried by standard methods and distilled prior to use. Elemental analyses were carried out by the Microanalytical Laboratory of the Chemistry Department of the Moscow State University. IR spectra of thin liquid films were recorded on a UR-20 spectrometer. Unless otherwise noted, ^1H and ^{13}C NMR spectra were recorded on Varian VXR-400 and Bruker AM-360 spectrometers using $CDCl_3$ as solvent and for the internal deuterium lock. Chemical shifts are given in δ (ppm) downfield from TMS. Mass spectra (EI-MS) were recorded on a Varian CH-7a spectrometer using electron impact with an ionization energy of 70 eV.

3.2. Reaction of trimethylsilylketene dialkyl acetals with alkyldiazo acetates in the presence of $Cu(acac)_2$

A mixture of trimethylsilylketene dialkylacetal **1** (13 mmol) and 0.025 g of $Cu(acac)_2$ in 10 ml of benzene was heated to reflux under an argon atmosphere. Then a solution of alkyldiazoacetate (13 mmol) and an additional 26 mmol of **1** in 40 ml of benzene were added within 1.5 h under stirring. The reaction mixture was refluxed for another 0.5 h. The mixture was filtered and benzene was removed under reduced pressure at room temperature. The ^1H NMR spectra of the residue show the presence of unreacted **1**, cyclopropane **3–8** and very small quantities of dialkyl fumarate and maleate; distillation affords pure **3–8**.

3.2.1. Methyl-2,2-dimethoxy-3-trimethylsilylcyclopropane-1-carboxylate (3)

Yield 72%; b.p. 79–80 °C/2 Torr. ^1H NMR ($CDCl_3$): 0.05 (s, 9H, Me_3Si), 1.08 (d, 1H, H_3, $^3J(H_3H_1)$ = 8.5 Hz); 1.87 (d, 1H, H_1, $^3J(H_1H_3)$ = 8.5 Hz), 3.34 (s, 6H, 2 × OMe), 3.64 (s, 3H, COOMe). ^{13}C NMR: −1.95 (Me_3Si), 20.76 (C_3), 30.51 (C_1), 51.57 (OMe), 53.39 (OMe), 54.11 (OMe), 96.01 (C_2), 169.87 (C=O). IR: 1750 (ν(C=O)) cm^{-1}. Anal. Found: C, 51.62; H, 8.85; Si, 11.60. $C_{10}H_{20}O_4Si$ (232.11) Calc.: C, 51.69; H, 8.67; Si, 12.05%.

3.2.2. Ethyl-2,2-dimethoxy-3-trimethylsilylcyclopropane-1-carboxylate (4)

Yield 74%; b.p. 102–103 °C/4 Torr. ^1H NMR ($CDCl_3$): 0.02 (s, 9H, Me_3Si), 1.07 (d, 1H, H_3, $^3J(H_3H_1)$ = 8.45 Hz); 1.87 (d, 1H, H_1, $^3J(H_1H_3)$ = 8.45 Hz), 1.27 (t, 3H, $OCCH_3$), 3.30 (s, 6H, 2 × OMe), 3.92 (q, 2H, (OCH_2)). ^{13}C NMR: −1.92 (Me_3Si), 13.96 (OCH_2CH_3), 20.60 (C_3), 30.72 (C_1), 53.43 (OMe), 54.13 (OMe), 60.38 (OCH_2), 96.05 (C_2), 169.12 (C=O). IR: 1735 (ν(C=O)) cm^{-1}. Anal. Found: C, 53.88; H, 8.71. $C_{11}H_{22}O_4Si$ (246.38) Calc.: C, 53.63; H, 9.00%.

3.2.3. Methyl-2,2-diethoxy-3-trimethylsilylcyclopropane-1-carboxylate (5)

Yield 71%; b.p. 80–81 °C/1 Torr. ^1H NMR ($CDCl_3$): 0.0 (s, 9H, Me_3Si), 1.07 (d, 1H, H_3, $^3J(H_3H_1)$ = 8.44 Hz); 1.88 (d, 1H, H_1, $^3J(H_1H_3)$ = 8.44 Hz), 1.13 (t, 3H, $OCCH_3$, ^3J = 7.2 Hz), 1.15 (t, 3H, $OCCH_3$, ^3J = 7.2 Hz), 3.64 (s, 3H, OMe). ^1H NMR (C_6D_6): 0.12 (s, 9H, Me_3Si), 1.42 (d, 1H, H_3, $^3J(H_3H_1)$ = 8.29 Hz); 2.17 (d, 1H, H_1, $^3J(H_1H_3)$ = 8.29 Hz), 1.09 (t, 3H, $OCCH_3$), 1.18 (t, 3H, $OCCH_3$), 3.51 (s, 3H, OMe). ^{13}C NMR: −1.76 (Me_3Si), 14.93 (OCH_2CH_3), 20.64 (C_3), 30.92 (C_1), 62.00 (OCH_2), 63.02 (OCH_2), 51.52 (OMe), 94.59 (C_2), 168.41 (C=O). IR: 1745 (ν(C=O)) cm^{-1}. Anal. Found: C, 56.05; H, 9.62%. $C_{12}H_{24}O_4Si$ (260.41) Calc.: C, 55.35; H, 9.29%.

3.2.4. Ethyl-2,2-diethoxy-3-trimethylsilylcyclopropane-1-carboxylate (6)

Yield 72%; b.p. 88–89 °C/1 Torr. ^1H NMR ($CDCl_3$): 0.01 (s, 9H, Me_3Si), 1.11 (d, 1H, H_3, $^3J(H_3H_1)$ = 8.5 Hz); 1.97 (d, 1H, H_1, $^3J(H_1H_3)$ = 8.5 Hz), 1.16 (t, 3H, $OCCH_3$), 1.20 (t, 3H, $OCCH_3$), 1.23 (t, 3H, $OCCH_3$). ^1H NMR (C_6D_6): 0.11 (s, 9H, Me_3Si), 1.49 (d, 1H, H_3, $^3J(H_3H_1)$ = 8.39 Hz); 2.22 (d, 1H, H_1, $^3J(H_1H_3)$ = 8.39 Hz), 1.08 (t, 3H, $OCCH_3$), 1.10 (t, 3H, $OCCH_3$), 1.21 (t, 3H, $OCCH_3$). ^{13}C NMR: −1.61 (Me_3Si), 14.17 (OCH_2CH_3), 15.04 (OCH_2CH_3), 15.11 (OCH_2CH_3), 20.63 (C_3), 31.25 (C_1), 60.43 (OCH_2), 62.12 (OCH_2), 63.11 (OCH_2), 94.73 (C_2), 169.73 (C=O). IR: 1745 (ν(C=O)) cm^{-1}. EI-MS, m/z (rel. int.%, assign.): 274 (4, M^+), 201 (21, M^+-Me_3Si), 73 (100%, Me_3Si). Anal. Found: C, 56.89; H, 9.32; Si, 10.16. $C_{13}H_{26}O_4Si$ (274.43) Calc.: C, 56.90; H, 9.55; Si, 10.23%.

3.2.5. Methyl-2,2-diisopropoxy-3-trimethylsilylcyclopropane-1-carboxylate (7)

Yield 71%; b.p. 74–75 °C/0.5 Torr. ^{1}H NMR ($CDCl_3$): 0.0 (s, 9H, Me_3Si), 1.74 (d, 1H, H_1, $^3J(H_1H_3) = 8.5$ Hz), 3.54 (s, 3H, OMe). IR: 1740 (υ(C=O)) cm^{-1}. Anal. Found: C, 58.90; H, 10.30. $C_{14}H_{28}O_4Si$ (288.46) Calc.: C, 58.29; H, 9.78%.

3.2.6. Ethyl-2,2-diisopropoxy-3-trimethylsilylcyclopropane-1-carboxylate (8)

Yield 76%; b.p. 80–81 °C/0.5 Torr. ^{1}H NMR ($CDCl_3$): 0.0 (s, 9H, Me_3Si), 1.73 (d, 1H, H_1, $^3J(H_1H_3) = 8.5$ Hz). IR: 1745 (υ(C=O)) cm^{-1}. Anal. Found: C, 59.37; H, 9.78. $C_{15}H_{30}O_4Si$ (302.19) Calc.: C, 59.56; H, 10.01%.

3.3. Reaction of 1b with ethyldiazoacetate in the presence of $Rh_2(OAc)_4$

A solution of ethyldiazoacetate (2.0 g, 17 mmol) in 5 ml of Et_2O was added dropwise to a mixture of **1b** (5.1 g, 27 mmol) and 75 mg $Rh_2(OAc)_4 \cdot 2H_2O$ in 20 ml Et_2O within 3 h at room temperature under argon. The mixture was passed through a column charged with neutral Al_2O_3. Distillation gave 3.6 g (76% relative to ethyldiazoacetate) of **6**, b.p. 100–101 °C/3 Torr.

3.4. Ring scission of 5

A mixture of **5** (0.16 g, 0.6 mmol) and 0.5 ml of $CDCl_3$ was stored at room temperature for a period of 30 days. The reaction was monitored by ^{1}H NMR spectroscopy. When the signals of the cyclopropane protons disappeared, the mixture was distilled and 0.1 g (97%) of methylethylsuccinate was obtained, b.p. 92–93 °C/12 Torr (lit. [13] b.p. 208.2 °C). IR: 1740 (υ(C=O)) cm^{-1}. ^{1}H NMR (CCl_4): 1.25 (t, 3H, $OCCH_3$), 2.52 (s, 4H, $(CH_2)_2$), 3.57 (s, 3H, OMe), 4.07 (q, 2H, OCH_2). IR: 1740 (υ(C=O)) cm^{-1}.

3.5. Interaction of 6 with EtOH

A mixture of **6** (2.8 g, 10 mmol) and 10 ml EtOH was refluxed for 4 h; the resulting mixture (2 g, b.p. 102–103 °C/11 Torr) of two products was obtained by distillation. ^{1}H NMR (60 MHz, Tesla BS-467 spectrometer, CCl_4): 1.22 (t, 3H, $OCCH_3$), 2.56 (s, 4H, $(CH_2)_2$), 4.08 (q, 2H, OCH_2) – diethylsuccinate and 1.19 (t, 9H, 3 × $OCCH_3$), 1.23 (t, H, $COOCCH_3$), 2.10–2.50 (m, 4H, $(CH_2)_2$), 3.53 (q, 6H, 3 × OCH_2), 4.10 (q, 2H, $COOCH_2$) – ethyl-4,4,4-triethoxybutanoate [9]. IR: 1730–1740 (υ(C=O)) cm^{-1}.

3.6. (2,2-Diethoxy-3-trimethylsilylcyclopropyl)methanol (10)

A suspension of $LiAlH_4$ (0.6 g, 16 mmol) in Et_2O was refluxed for 0.5 h, then cooled to room temperature. **6** (3.3 g, 12 mmol) was added dropwise under stirring. The resulting mixture was stirred at room temperature for 1 h. After addition of wet Et_2O and then water, the ether layer was separated and dried over anhydrous $MgSO_4$. Distillation gave 1.9 g (68%) of **10**, b.p. 96–97 °C/0.5 Torr. ^{1}H NMR ($CDCl_3$): −0.02 (s, 9H, Me_3Si), 0.08 (d, 1H, H_3, $^3J(H_3H_1) = 8.00$ Hz), 1.13 (t, 3H, $OCCH_3$), 1.17 (t, 3H, $OCCH_3$), 1.37 (ddd, 1H, H_1, $^3J(H_1H_3) = {}^3J(H_1H_a) = 8.00$ Hz, $^3J(H_1H_b) = 5.20$ Hz), 3.43 (dd, 1H, H_a, $^2J(H_aH_b) = 11.6$ Hz, $^3J(H_aH_1) = 8.0$ Hz), 3.41–3.51 (m, 2H, OCH_2), 3.65–3.80 (m, 2H, OCH_2), 3.79 (dd, 1H, H_b, $^2J(H_bH_a) = 11.6$ Hz, $^3J(H_bH_1) = 5.2$ Hz). ^{13}C NMR: −1.34 (Me_3Si), 15.25 (OCH_2CH_3), 15.35 (OCH_2CH_3), 18.39 (C_3), 29.75 (C_1), 61.97 (OCH_2), 62.15 (OCH_2), 63.60 (CH_2OH), 94.95 (C_2). IR: 3455 (υ(OH)) cm^{-1}. Anal. Found: C, 56.07; H, 10.90; Si, 12.35. $C_{11}H_{24}O_3Si$ Calc.: C, 56.85; H, 10.41; Si, 12.09%.

3.7. (2,2-Dimethoxy-3-trimethylsilylcyclopropyl)methanol (9)

The title compound was prepared from **4** in 82% yield following a procedure similar to that for the synthesis of **10**, b.p. 68–69 °C/0.5 Torr. ^{1}H NMR ($CDCl_3$): −0.01 (s, 9H, Me_3Si), 0.08 (d, 1H, H_3, $^3J(H_3H_1) = 8.20$ Hz), 1.37 (ddd, 1H, H_1, $^3J(H_1H_3) = 8.2$ Hz, $^3J(H_1H_a) = 8.4$ Hz, $^3J(H_1H_b) = 5.4$ Hz), 3.30 (s, 3H, OMe), 3.34 (s, 3H, OMe), 3.41 (dd, 1H, H_a, $^2J(H_aH_b) = 11.5$ Hz, $^3J(H_aH_1) = 8.4$), 3.79 (dd, 1H, H_b, $^2J(H_bH_a) = 11.5$ Hz, $^3J(H_bH_1) = 5.4$ Hz). ^{13}C NMR: −1.37 (Me_3Si), 18.52 (C_3), 29.95 (C_1), 53.52 (OMe), 53.62 (OMe), 63.46 (CH_2OH), 96.61 (C_2). IR: 3390 (υ(OH)) cm^{-1}. Anal. Found: C, 52.88; H, 9.94; Si, 13.45. $C_9H_{20}O_3Si$ Calc.: C, 52.91; H, 9.87; Si, 13.71%.

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