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Notes

Novel Organogermanium Compounds via Metalation of 3-Trimethylsilyl-3-ethoxycarbonylcyclopropene Derivatives

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Summary: *Preparation and full spectroscopic characterization of novel trimethylgermyl derivatives of 3-trimethylsilyl-3-ethoxycarbonylcyclopropenes (**4**−**7**) and 1,1-bis(trimethylgermyl)-3-trimethylsilyl-3-ethoxycarbonylallene (**8**) are described.*

Introduction

The syntheses, reactivity, and physical characterization of cyclopropene derivatives substituted with group 14 elements heavier than carbon have intrigued chemists for a long time due to the synthetic challenge, unique physical properties, and remarkable reactivity.[1−11]

Particularly appealing are cyclopropenes bearing trimethylsilyl ($SiMe_3$) and/or ethoxycarbonyl groups at the tetrahedral ring atom, as they serve as the precursors of either cyclopropenyl anions[8,9] (by cleavage of the trimethylsilyl group) or cyclopropenylium cations (via appropriate transformation of the alkoxycarbonyl group).[1a,10,11] Finally, these molecules provide an attractive set of molecules for exploring interaction of the $M(Me)_3$ (M = Si, Ge, Sn) groups with the π-system of the double bond and with high-energy σ-orbitals of the three-membered ring and their impact on the structural and spectroscopic features.[1b,5,6] While synthesis of 1,3-bis(trimethylsilyl)-3-ethoxycarbonylcyclopropene[8a] and 1,2,3-tris(trimethylsilyl)-3-ethoxycarbonylcyclopropene[3c,10] has been described in the literature, synthesis of either 3-ethoxycarbonyl- or 3-trimethylsilylcyclopropenes carrying a germyl- or stannyl-based substituent at the vinylic position(s) has not been, to the best of our knowledge, described in the literature so far. The present study was undertaken with an aim of developing an effective protocol for synthesis of the corresponding trimethylgermyl-substituted cyclopropene derivatives and exploring physicochemical properties of this class of compounds. In the course of this study we also found conditions for the preparation of a novel tetrasubstituted allene with the two trimethylgermyl groups attached to one of the terminal positions. Herein we report details of the synthesis of some of these species, namely, **4**−**8** (Scheme 1).

Results and Discussion

Metalation of olefinic atoms within the cyclopropene ring is commonly achieved by deprotonation followed by quenching with a suitable organometallic reagent.[1a,2a,b] However, an attempt to carry out synthesis of **4** by adding a slight excess of 2 equiv of Me_3GeCl to a freshly prepared solution of deprotonated **1** in THF resulted in exclusive formation of hitherto unknown allene derivative **8** (Scheme 1). A similar procedure has been recently reported by Binger and co-workers for formation of 1,1-bis(trimethylsilyl)-3,3-diphenylallene from 3,3-diphenylcyclopropene, which involves selective rearrangement of incipiently formed 1,2-dilithio-3,3-diphenylcyclopropene to the corresponding 1,1-dilithiopropadiene.[3a] It seems plausible to assume the same mechanism for

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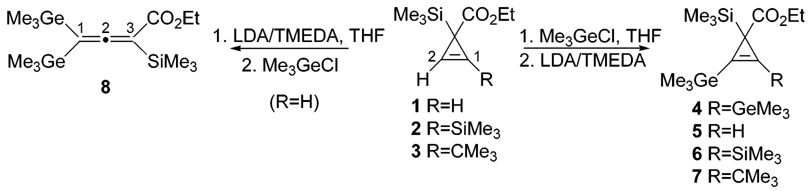
Scheme 1



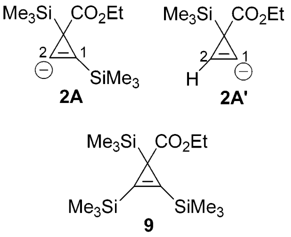
formation of **8** in the present case.[12] It should be, however, stressed that the existence of a 1,1-dilithioallene derivative has not yet been proved unequivocally. For example, dilithiation of allene gives a dilithium derivative, which after trapping with Me_3SiCl yields 1,3-bis(trimethylsilyl)propyne.[14] Similarly, reaction of 3-trimethylsilyl-3-ethoxycarbonylcyclopropene (**1**) with LDA/TMEDA at −60 to −30 °C, followed by addition of Me_3SiCl, affords ethyl 4-trimethylsilyl-3-butynoate.[3c]

To circumvent ring cleavage of the intermediate, we next carried out reaction by adding **1** to the mixture of LDA/TMEDA and Me_3GeCl at −60 °C (molar ratio **1**:LDA/TMEDA:Me_3GeCl = 1:2.2:2.2). After stirring the reaction mixture for an additional 1 h at the same temperature only the starting cyclopropene **1** was isolated, presumably due to reaction of LDA with Me_3GeCl prior to addition of **1**. Ultimately, by adding a freshly prepared solution of LDA/TMEDA to a mixture of **1** and Me_3GeCl at −75 °C and standard workup (molar ratio **1**:LDA/TMEDA:Me_3GeCl = 1:2.2:2.2; see Experimental Section), followed by purification of the crude product at the silica gel column, 1,2-bis(trimethylgermyl)-3-trimethylsilyl-3-ethoxycarbonylcyclopropene (**4**) was obtained in a fair yield (53%). Repeating the reaction with 1.1 molar ratio of LDA/TMEDA and Me_3GeCl under the same conditions provided after ca. 10 min a mixture of mono(trimethylgermyl)cyclopropene derivative **5** and bis(trimethylgermyl)cyclopropene **4**, along with starting compound **1** in a ratio 1:3.6:2.6, respectively (based on GC analysis). Performing the reaction for a longer time (1 h) did not influence the proportion of products, indicating that **5** undergoes instantaneous deprotonation followed by reaction of the so formed anion with the rest of Me_3GeCl. The reaction also proceeded smoothly with cyclopropenes **2** and **3**, giving rise to formation of trisubstituted **6** and **7**, in 53% and 51% isolated yield, respectively.

We have also attempted to prepare **6** and **7** in a sequential mode, i.e., by adding electrophile to a freshly prepared solution of deprotonated **2** and **3**, respectively. Under these conditions **3** gave the desired cyclopropene derivative **7** in a 40% yield. On the other hand, similar treatment of **2** afforded, rather surprisingly, a mixture of **4** and **9**[3c] (Scheme 2) in 5% and 20% yields, respectively, accompanied with the starting cyclopropene **2**.

This, in turn indicates that **2** undergoes deprotonation of the vinylic hydrogen and the cleavage of the C(1)−Si bond of another molecule leading to anions[15] **2A** and **2A′**, respectively, followed by interception of the former with the detached Me_3Si group. This supposition was corroborated by monitoring the progress of the reaction by GC, which unequivocally proved that **9** was formed before the reaction mixture was treated with Me_3GeCl. Additional confirmation of involvement of the anions **2A** and **2A′** in the first step of the reaction is adduced by using MeI instead of Me_3GeCl, which provided again cyclopropene **9** as the main product.

Scheme 2



The structures of all new compounds were fully characterized by their ^1H and ^{13}C NMR, IR, and HRMS spectra (see Experimental Section). For instance, the ^{13}C NMR spectrum of all trimethylgermyl-substituted cyclopropenes contained the expected singlet in the region between 116 and 135 ppm for the vinylic carbon atom(s) connected to the $GeMe_3$ group. In addition, the high-field signals in the region characteristic for the sp^3 carbon atoms of the organometallic substituent were observed. The ^{13}C NMR resonances for the C1, C2, and C3 atoms in allene **8** at 82.48, 204.78, and 78.42 ppm, respectively, also lay in the expected range.[7b] Similarly, the ^{13}C NMR spectrum of **3** showed signals for the terminal olefinic C1 and C2 atoms at 123.97 and 92.57 ppm, respectively. The ^1H NMR and IR spectral features of all new compounds were as expected (see Experimental Section).

Conclusions

We have prepared and fully characterized several hitherto unknown trimethylgermyl derivatives of 3-trimethylsilyl-3-ethoxycarbonylcyclopropene and its derivative, **3**. In addition to providing an excess to the rich chemistry of metalated cyclopropenes,[1a] these compounds may be of interest as precursors of novel cyclopropenyl carbanions and carbocations and in exploring the effect of organometallic substituents on their stability. We have also found conditions for straightforward preparation of novel tetrasubstituted allene compound **8**. To the best of our knowledge, this is the first example of a tetrasubstituted allene with the two trimethylgermyl groups attached at one of the terminal

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[12] This assumption is in accordance with results of B3BYP/6-311+G** calculations, which indicate that in the gas phase the dilithium salt is 49.7 kcal mol^{-1} more stable than the 1,2-dilithio-3-trimethylsilyl-3-ethoxycarbonylcycloropene.[13] Similar computational results are obtained for the parent 1,2-dilithiocyclopropene and the corresponding dilithioallene.[3a]

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[15] We use the “anion” terminology, although we recognize that these and related species discussed in this report are lithium compounds.

positions prepared by low-temperature cyclopropene ring opening. Finally, evidence for competitive cleavage of hydrogen and the $SiMe_3$ group at the olefinic position in **2** in the presence of LDA/TMEDA is reported. We are continuing our investigation of the mechanism of the latter reaction, as well as reactivity studies of the new molecules.

Experimental Section

The starting cyclopropenes **1** and **2** were synthesized according to previously reported procedure.[8a] *n*-Butyllithium 1.6 M solution in hexane, diisopropylamine, TMEDA (*N*,*N*,*N′*,*N′*-tetramethylethylendiamide), Me_3SiCl, Me_3GeCl, and MeI were purchased from Aldrich. Diisopropylamine and TMEDA were dried before use by refluxing over sodium. Column chromatography and filtration were carried out on Aldrich silica gel 60 (63−200 μm) using petroleum ether/Et_2O as eluent. Composition of solvent mixtures is quoted as ratios of volume. Petroleum ether refers to a light petroleum fraction (bp 40−60 °C). Alternatively, the crude product was purified by radial chromatography using a Harrison Research 7924T Chromatotron and Merck silica gel 60 PF_{254} containing $CaSO_4$. GC analyses were carried out on a Varian 3300 gas chromatograph. Infrared spectra (IR) were recorded on a Perkin-Elmer 297 or Perkin-Elmer FT 2000 infrared spectrometer. ^1H and ^{13}C NMR spectra were measured on a Bruker AV-300 or Bruker AV-600 spectrometer. Chemical shifts are reported in parts per million (δ/ppm) downfield from tetramethylsilane using the residual solvent signal as an internal standard. Coupling constants are reported in hertz (Hz). High-resolution mass spectra (HRMS) were measured on an EXTREL FTMS 2001DD spectrometer. Elemental analyses were carried out using an Exeter Analytical CE-440 elemental analyzer at Microanalysis Laboratory, Chemistry Department, University College Dublin, Dublin, Ireland. In reactions requiring anhydrous conditions, solvents were dried by distillation from the appropriate drying agent, and glassware was flame-dried and cooled under a stream of argon.[16] All reactions involving air-sensitive reagents were performed by a syringe/septum technique. Photochemical reactions were carried out in a Rayonet Chamber RPR-100 photochemical reactor with 16 PRP-3500A lamps.

1-(1,1-Dimethylethyl)-3-trimethylsilyl-3-ethoxycarbonylcyclopropene (3). Ethyl diazo(trimethylsilyl)acetate[17] (1.86 g, 0.01 mol) and 3,3-dimethyl-1-butyne (54 mL, 44 mol) were placed in a Pyrex photolysis tube, and the mixture was degassed with argon at 0 °C for 30 min. The mixture was irradiated using 16 lamps ($\lambda_{max} = 350$ nm) for 7 h. The excess of 3,3-dimethyl-1-butyne was recovered by distillation under reduced pressure (10 mmHg/25 °C). Crude reaction product was filtered through a short column of Florisil R using petroleum ether/Et_2O (30:1) as eluent, yielding 1.298 g of **3** (54%). ^1H NMR ($CDCl_3$): 0.03 (s, 9H), 1.16 (s, 9H), 1.23 (t, 3H, $J = 7.2$), 4.04−4.13 (m, 2H), 6.22 (s, 1H). ^{13}C NMR ($CDCl_3$): −1.42 (q), 14.07 (q), 20.79 (s), 28.31 (q), 31.61 (s), 59.78 (t), 92.57 (d), 123.97 (s), 178.27 (s). IR (KBr), ν/cm^{-1}: 1702 (C=O), 1800 (C=C). HRMS (EI): *m*/*z* calcd for $C_{13}H_{24}O_2Si$ (M+) 240.1540, found 240.1467.

1,2-Bis(trimethylgermyl)-3-trimethylsilyl-3-ethoxycarbonylcyclopropene (4). LDA was prepared by adding 1.6 M of BuLi (1.17 mL, 1.9 mmol) to a mixture of dry diisopropylamine (0.26 mL, 1.9 mmol) and dry TMEDA (0.13 mL) in 1.2 mL of dry THF at 0 °C under argon. The freshly prepared LDA solution was added to the mixture of cyclopropene **1** (157 mg, 0.85 mmol) and Me_3GeCl (0.23 mL, 1.9 mmol) in 1 mL of dry THF at −75 °C under argon over 10 min. The reaction mixture was stirred for about 1 h from −75 to −40 °C and then allowed to warm to 0 °C (over ca. 10 min). Cold water was added to the reaction, and organics were extracted with Et_2O. The organic phase was washed with 1 M aqueous HCl, a saturated aqueous solution of NaCl, and aqueous $Na_2S_2O_3$. The extract was dried over $MgSO_4$ and evaporated. The crude reaction products were purified by filtration through a column of Aldrich silica gel 60 (63−200 μm) using petroleum ether/Et_2O (12:1) as eluent, yielding 189 mg of **4** (53%). ^1H NMR ($CDCl_3$, δ/ppm): −0.02 (s, 9H), 0.36 (s, 18H), 1.19 (t, 3H, $J = 7.1$), 4.00 (q, 2H, $J = 7.1$). ^{13}C NMR ($CDCl_3$, δ/ppm): −1.39 (q), −1.08 (q), 14.30 (q), 18.27 (s), 59.31 (t), 126.37 (s), 179.06 (s). IR (KBr), ν/cm^{-1}: 1703/1690 (C=O), 1760 (C=C). HRMS (EI): *m*/*z* calcd for $C_{15}Ge_2H_{32}O_2Si$ 420.0590, found 420.0566. Anal. Calcd for $C_{15}Ge_2H_{32}O_2Si$: C 43.13, H 7.72. Found: C 42.85, H 7.56.

1-Trimethylgermyl-3-trimethylsilyl-3-ethoxycarbonylcyclopropene (5). LDA was prepared by adding 2.5 M of BuLi (1.38 mL, 3.44 mmol) to a mixture of dry diisopropylamine (0.48 mL, 3.44 mmol) and dry TMEDA (0.24 mL) in 4.5 mL of dry THF at 0 °C under argon. The freshly prepared LDA solution was added dropwise to the mixture of cyclopropene **1** (576 mg, 3.13 mmol) and Me_3GeCl (0.43 mL, 3.44 mmol) in 3.5 mL of dry THF at −75 °C under argon over a 10 min interval. The reaction mixture was stirred for about 1 h from −75 to −40 °C, and then it was allowed to warm to 0 °C over ca. 10 min. Then the cold water was added, and organics were extracted with Et_2O. The organic phase was washed with 1 M aqueous HCl, a saturated aqueous NaCl solution, and aqueous $Na_2S_2O_3$. The organic phases were combined and dried over $MgSO_4$. The solvent was evaporated in vacuo, and then products **5** (95 mg, 10%) and **4** (394 mg, 30%), as well as the starting cyclopropene **1**, were isolated by radial chromatography eluting with a mixture of petroleum ether/Et_2O (10:1). Spectroscopic data of **5**: ^1H NMR ($CDCl_3$): −0.01 (s, 9H), 0.38 (s, 9H), 1.23 (t, 3H, $J = 7.2$), 4.05−4.12 (m, 2H), 7.07 (s, 1H). ^{13}C NMR ($CDCl_3$): −1.41 (q), −1.38 (q), 14.25 (q), 17.4 (s), 59.81 (t), 113.85 (d), 116.39 (s), 175.65 (s). IR (KBr), ν/cm^{-1}: 1695 (C=O), 1735 (C=C). HRMS (EI): *m*/*z* calcd for $C_{12}GeH_{24}O_2Si$ (M+) 302.0755, found 302.0750.

1-Trimethylsilyl-2-trimethylgermyl-3-trimethylsilyl-3-ethoxycarbonylcyclopropene (6). Compound **6** was obtained starting from cyclopropene **2** and Me_3GeCl using the same procedure as for preparation of **4**. Yield: 51%. ^1H NMR ($CDCl_3$): −0.01 (s, 9H), 0.19 (s, 9H), 0.36 (s, 9H), 1.19 (t, 3H, $J = 7.0$), 4.02 (q, 2H, $J = 7.1$). ^{13}C NMR ($CDCl_3$): −1.41 (q), −1.22 (q), −1.09 (q), 14.27 (q), 18.48 (s), 59.35 (t), 124.24 (s), 129.06 (s), 178.65 (s). IR (KBr), ν/cm^{-1}: 1705/1692 (C=O), 1759 (C=C). HRMS (EI): *m*/*z* calcd for $C_{15}GeH_{32}O_2Si_2$ (M+) 374.1147, found 374.1275.

1-(1,1-Dimethylethyl)-2-trimethylgermyl-3-trimethylsilyl-3-ethoxycarbonyl cyclopropene (7). Compound **7** was obtained starting from cyclopropene **3** and Me_3GeCl using the same procedure as for preparation of **4**. Yield: 51%. ^1H NMR ($CDCl_3$): 0.03 (s, 9H), 0.36 (s, 9H), 1.16 (s, 9H), 1.21 (t, 3H, $J = 7.1$), 4.05 (m, 2H). ^{13}C NMR ($CDCl_3$): −0.97 (q), −0.92 (q), 14.24 (q), 22.50 (s), 28.74 (q), 32.30 (s), 59.30 (t), 104.01 (s), 134.61 (s), 178.27 (s). IR (KBr), ν/cm^{-1}: 1707/1691 (C=O), 1824 (C=C). HRMS (EI): *m*/*z* calcd for $C_{16}GeH_{32}O_2Si$ (M+) 358.1378, found 358.1452. Anal. Calcd for $C_{16}GeH_{32}O_2Si$: C 53.81, H 9.03. Found: C 53.67, H 9.05.

1,1-Bis(trimethylgermyl)-3-trimethylsilyl-3-ethoxycarbonylallene (8). LDA/TMEDA solution was prepared by adding 2 M n-BuLi in hexane (1.23 mL, 2.5 mmol) to a solution of diisopropylamine (0.35 mL, 2.5 mmol) and 0.16 mL of TMEDA in 1.6 mL of THF at 0 °C. Cyclopropene **1** (206 mg, 1.12 mmol) in 0.5 mL of THF was added to a freshly prepared LDA/TMEDA solution at −60 °C. Stirring was continued for about 3 h, until the reaction mixture reached room tempera-

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ture. The reaction mixture was then cooled to −30 °C, and Me_3GeCl (0.3 mL, 2.5 mmol) was added dropwise. The reaction was allowed to warm to room temperature, the cold water was added at 0 °C, and organics were extracted with Et_2O. The organic phase was washed with 1 M HCl and saturated solutions of NaCl and $Na_2S_2O_3$ and dried over $MgSO_4$. The Et_2O was evaporated in vacuo, and then the crude reaction mixture was purified by column chromatography (silica gel, petroleum ether/Et_2O = 12:1) to afford 318 mg of allene **8** (67%). ^{1}H NMR (C_6D_6): 0.30 (s, 18H), 0.38 (s, 9H), 0.97 (t, 3H, J = 7.1), 4.03 (q, 2H, J = 7.1). ^{13}C NMR (C_6D_6): −0.07 (q), 0.36 (q), 14.77 (q), 60.17 (t), 78.42 (s), 82.48 (s), 170.76 (s), 204.78 (s). IR (KBr), ν/cm^{-1}: 1690 (C═O), 1905 (C═C═C). HRMS (EI): m/z calcd for $C_{15}Ge_2H_{32}O_2Si$ 420.0590, found 420.0625. Anal. Calcd for $C_{15}Ge_2H_{32}O_2Si$: C 43.13, H 7.72. Found: C 43.05, H 7.61.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of cyclopropene derivatives **3**−**7** and allene **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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