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Communication

The reactions of germenes generated thermally from pivaloyl- and adamantoyltris(trimethylsilyl)germane with 1,3-butadienes

Akinobu Naka *, Shinsuke Ueda, Mitsuo Ishikawa *

Department of Life Science, Kurashiki University of Science and the Arts, Nishinoura, Tsurajima-cho, Kurashiki, Okayama 712-8505, Japan

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Abstract

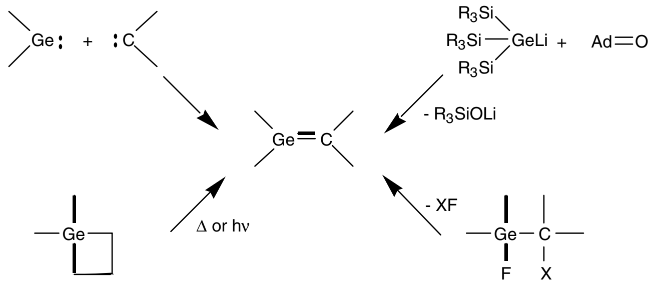
The thermolysis of pivaloyl- and adamantoyltris(trimethylsilyl)germane in the presence of 2,3-dimethyl- and 2,3-diphenyl-1,3-butadiene gave the respective adducts derived from [2+4] cycloaddition of the germenes with butadienes in good yields.

Keywords: Germene; Acylpoly(silyl)germane; Thermolysis; Cycloaddition; Germacyclohexene

1. Introduction

Many papers dealing with the synthesis of both transient and stable germenes have been published to date [1–7]. The methods reported for the synthesis of the germenes mainly involve the following routes: (1) reaction of germylenes with carbenes [8], (2) Peterson-type reactions [9], (3) [2+2] cycloreversion of four-membered rings [10,11], and (4) defluorosilylation [12] or defluorolithiation [13–17]. The range of the synthetic methods for the germenes is rather limited. The photolysis of acylpoly(silyl)silanes offers a convenient route to the silenes, but similar photolysis of acylpoly(silyl)germanes affords no germenes. In fact, Brook et al. have reported that the photolysis of adamantoyltris(trimethylsilyl)germane affords no evidence for the formation of the germene [18]. It is clear that the photolysis of acylpoly(silyl)germanes is quite different from that of their all-silicon analogs, acylpoly(silyl)silanes and that the photolysis of acylpoly(silyl)germanes does not appear to be a promising route to germane–carbon doubly bonded compounds.

We have found that the thermolysis of acylpoly(silyl)germanes readily affords silyl-substituted germenes. In this paper, we report the new route to germenes involving the thermolysis of pivaloyl- and adamantoyltris(trimethylsilyl)germane and the reactions of the germenes thus formed with 2,3-dimethyl- and 2,3-diphenylbutadiene.



2. Results and discussion

We first investigated the thermolysis of pivaloyltris(trimethylsilyl)germane (**1**) and adamantoyltris(trimethylsilyl)germane (**2**) in the absence of a trapping agent, in the hope of obtaining a rather stable germene. Thus, when

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* Corresponding authors.
E-mail address: anaka@chem.kusa.ac.jp (A. Naka).

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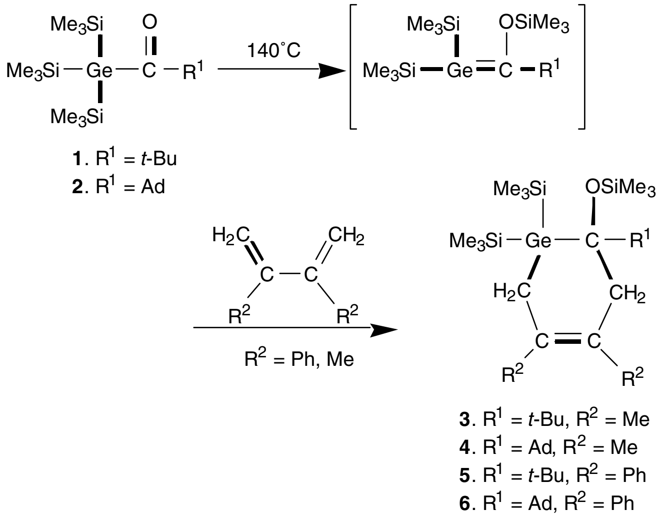
compounds **1** and **2** were heated in a sealed glass tube at 130 °C for 24 h, the starting compounds **1** and **2** were recovered quantitatively. At 140 °C, **1** and **2** reacted, but afforded a large amount of nonvolatile products, together with a small amount of unidentified volatile products. In the thermolysis of the all-silicon analogs, pivaloyl- and adamantoyltris(trimethylsilyl)silane, the starting acylpoly(silyl)silanes were recovered almost quantitatively, due to the reverse reaction of the silenes once formed [19]. Presumably, the present germenes are unstable and decompose to give nonvolatile substances under the conditions used. The thermolysis of **1** and **2** in the presence of a trapping agent, such as butadienes, however, proceeded cleanly to give the respective cycloadducts.

When a mixture of compound **1** and 2,3-dimethyl-1,3-butadiene was heated in a degassed sealed tube at 140 °C for 24 h, [2+4] cycloadduct, 6-*tert*-butyl-3,4-dimethyl-6-trimethylsiloxy-1,1-bis(trimethylsilyl)-1-germacyclohex-3-ene (**3**) was obtained in 62% isolated yield (Scheme 1). The formation of compound **3** may be best understood in terms of formal [2+4] cycloaddition of 2-*tert*-butyl-2-(trimethylsiloxy)bis(trimethylsilyl)germene, generated thermally from acylpoly(silyl)germane, with 2,3-dimethyl-1,3-butadiene. No other isomers such as the ene-type adducts were detected in the resulting reaction mixture. The structure of **3** was confirmed by spectroscopic analysis, as well as by elemental analysis. The mass spectrum of **3** indicates a parent ion at m/z 460, corresponding to the molecular weight of the butadiene adduct. The ^{13}C NMR spectrum for **3** shows three signals at 0.91, 1.23, 3.02 ppm, due to the trimethylsiloxy carbon atoms and two different kinds of the trimethylsilyl carbon atoms, as well as three signals of sp^3-hybridized ring carbons, two signals of methyl carbons, two signals of olefinic carbons, and two signals due to the *tert*-butyl group.

Treatment of **2** with 2,3-dimethyl-1,3-butadiene proceeded to give a product similar to **3**, 6-adamantyl-3,4-dimethyl-6-trimethylsiloxy-1,1-bis(trimethylsilyl)-1-germacyclohex-3-ene (**4**) in 32% isolated yield. Although the formation of nonvolatile substances was observed in the reaction mixture, no volatile products were detected. The ^{1}H NMR spectrum of **4** shows the presence of three different kinds of the trimethylsilyl protons at 0.20, 0.22, and 0.33 ppm, two kinds of the methyl protons at 1.64 and 1.84 ppm, in addition to the adamantyl protons at 1.66–2.02 ppm and the ring methylene protons. The ^{29}Si NMR spectrum of **4** reveals three resonances at −9.5, −7.9, and 4.5 ppm, as expected.



Scheme 1.

Similar thermolysis of compounds **1** and **2** in the presence of 2,3-diphenyl-1,3-butadiene also gave the respective formal [2+4] cycloadducts. Thus, treatment of **1** with 2,3-diphenyl-1,3-butadiene afforded 6-*tert*-butyl-3,4-diphenyl-6-trimethylsiloxy-1,1-bis(trimethylsilyl)-1-germacyclohex-3-ene (**5**) in 65% isolated yield, as a single isomer. The reaction of **2** with 2,3-diphenyl-1,3-butadiene under the same conditions produced 6-adamantyl-3,4-diphenyl-6-trimethylsiloxy-1,1-bis(trimethylsilyl)-1-germacyclohex-3-ene (**6**) in 43% isolated yield. Again, no other isomers were detected in the reaction mixture. The structures of products **5** and **6** were confirmed by mass, and ^{1}H, ^{13}C, ^{29}Si NMR spectroscopic analysis (see Section 3).

It is interesting to us to see if the germacyclohexenes **3**–**6** undergo the retro Diels–Alder reaction to give the germenes and butadienes. Thus, when a mixture of compound **5** and 2,3-dimethyl-1,3-butadiene was heated in a sealed tube at 140 °C for 24 h, no product **3** was detected, but the starting compound **5** was recovered unchanged in almost quantitative yield. Moreover, the thermolysis of **3** with 2,3-diphenyl-1,3-butadiene under the same conditions afforded no products arising from the reaction of the germene with the butadiene. Again, compound **3** was recovered quantitatively. These results clearly indicate that the present germacyclohexenes do not undergo retro Diels–Alder reaction.

In conclusion, the thermolysis of acylpoly(silyl)germanes **1** and **2** proceeded to give the germenes, and the germenes thus formed readily reacted with 2,3-dimethyl- and 2,3-diphenyl-1,3-butadiene to afford the [2+4] cycloadducts, respectively.

3. Experimental

General procedure. The syntheses of germacyclohexenes were carried out in a degassed sealed glass tube (1.0 cm × 15 cm). Yields of the products were calculated on the basis of the isolated products. NMR spectra were recorded on JNM-LA300 spectrometer and JNM-LA500 spectrometer. Low-resolution mass spectra were measured on a JEOL Model JMS-700 instrument. Melting point was measured with a Yanaco-MP-S3 apparatus. Column chromatography was performed by using Wakogel C-300 (WAKO). Gel permeation chromatographic separation was performed with a Model LC-908 Recycling Preparative HPLC.

Materials. Compound **2** was prepared by the method reported by Brook et al. [18].

*Synthesis of **1***. In a 100 mL two-necked flask fitted with a condenser and dropping funnel was placed 0.8829 g (7.32 mmol) of pivaloyl chloride in 20 mL of dry THF. To this was added a solution of tris(trimethylsilyl)germyllithium prepared from 2.1506 g (5.89 mmol) of tetrakis(trimethylsilyl)germane and 7.0 mL (7.90 mmol) of ethereal MeLi at −40 °C. The mixture was allowed to warm up at room temperature, and stirred overnight. The mixture was hydrolyzed with water. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and extracts were combined, washed with water, and dried over magnesium sulfate. The solvent was evaporated and the residue was chromatographed on silica gel eluting with hexane, to give 1.6304 g (73% yield) of **1**. Anal. Calc. for $C_{14}H_{36}OSi_3Ge$ (**1**): C, 44.57; H, 9.62. Found: C, 44.41; H, 9.83%. MS *m*/*z* 378 (M^+); ^1H NMR δ (C_6D_6) 0.31 (s, 27H, Me_3Si), 0.97 (s, 9H, *t*-Bu); ^{13}C NMR δ (C_6D_6) 2.43 (Me_3Si), 25.00 (Me_3C), 49.57 (CMe_3), 243.14 (CO); ^{29}Si NMR δ (C_6D_6) −5.6 (Me_3Si).

*Reaction of **1** with 2,3-dimethyl-1,3-butadiene*. A mixture of compound **1** (0.1587 g, 0.421 mmol) and 0.1036 g (1.26 mmol) of 2,3-dimethyl-1,3-butadiene was heated in a sealed tube at 140 °C for 24 h. Product **3** (0.1210 g, 62% isolated yield) was isolated by column chromatography. Anal. Calc. for $C_{20}H_{46}OSi_3Ge$ (**3**): C, 52.28; H, 10.09. Found: C, 52.30; H, 9.97%. MS *m*/*z* 460 (M^+); ^1H NMR δ (C_6D_6) 0.17 (s, 9H, Me_3Si), 0.19 (s, 9H, Me_3Si), 0.30 (s, 9H, Me_3Si), 1.03 (s, 9H, *t*-Bu), 1.33 (d, 1H, ring proton, $J = 16$ Hz), 1.61 (s, 3H, Me), 1.83 (s, 3H, Me), 2.01 (d, 1H, ring proton, $J = 16$ Hz), 2.22 (d, 1H, ring proton, $J = 19$ Hz), 2.38 (d, 1H, ring proton, $J = 19$ Hz); ^{13}C NMR δ (C_6D_6) 0.91, 1.23, 3.02 (Me_3Si), 16.68 (CH_2Ge), 21.81, 24.14 (Me), 27.83 (Me_3C), 38.91 (CMe_3), 43.62 (CH_2), 89.16 (CO), 125.49, 127.68 (olefinic carbons); ^{29}Si NMR δ (C_6D_6) −9.5, −8.2, 4.4.

*Reaction of **2** with 2,3-dimethyl-1,3-butadiene*. A mixture of compound **2** (0.0924 g, 0.203 mmol) and 0.0212 g (0.258 mmol) of 2,3-dimethyl-1,3-butadiene was heated in a sealed tube at 140 °C for 24 h. Product **4** (0.0353 g, 32% isolated yield) was isolated by column chromatography. Anal. Calc. for $C_{26}H_{52}OSi_3Ge$ (**4**): C, 58.09; H, 9.75. Found: C, 58.09; H, 9.92%. MS *m*/*z* 538 (M^+); ^1H NMR δ (C_6D_6) 0.20 (s, 9H, Me_3Si), 0.22 (s, 9H, Me_3Si), 0.33 (s, 9H, Me_3Si), 1.35 (d, 1H, ring proton, $J = 16$ Hz), 1.64 (s, 3H, Me), 1.66–2.02 (m, 16H, Ad, CH), 1.84 (s, 3H, Me), 2.28 (d, 1H, ring proton, $J = 18$ Hz), 2.41 (d, 1H, ring proton, $J = 18$ Hz); ^{13}C NMR δ (C_6D_6) 1.04, 1.31, 3.13 (Me_3Si), 16.49 (CH_2Ge), 21.86, 24.16 (Me), 29.35, 37.73, 39.74, 40.47 (Ad), 42.12 (CH_2), 89.78 (CO), 125.37, 127.44 (olefinic carbons); ^{29}Si NMR δ (C_6D_6) −9.5, −7.9, 4.5.

*Reaction of **1** with 2,3-diphenyl-1,3-butadiene*. A mixture of compound **1** (0.1068 g, 0.283 mmol) and 0.1762 g (0.854 mmol) of 2,3-diphenyl-1,3-butadiene was heated in a sealed tube at 140 °C for 24 h. Product **5** (0.1073 g, 65% isolated yield) was isolated by recycling HPLC. Anal. Calc. for $C_{30}H_{50}OSi_3Ge$ (**5**): C, 61.74; H, 8.63. Found: C, 62.05; H, 8.76%. Mp. 168.0–170.0 °C; MS *m*/*z* 584 (M^+); ^1H NMR δ (C_6D_6) 0.30 (s, 9H, Me_3Si), 0.31 (s, 9H, Me_3Si), 0.32 (s, 9H, Me_3Si), 1.05 (s, 9H, *t*-Bu), 1.88 (d, 1H, ring proton, $J = 18$ Hz), 2.74 (d, 1H, ring proton, $J = 18$ Hz), 2.78 (d, 1H, ring proton, $J = 18$ Hz), 3.13 (d, 1H, ring proton, $J = 18$ Hz), 6.86–7.22 (m, 10H, phenyl ring protons); ^{13}C NMR δ (C_6D_6) 0.92, 1.51, 3.42 (Me_3Si), 17.52 (CH_2Ge), 27.87 (Me_3C), 39.14 (CMe_3), 43.92 (CH_2), 88.01 (CO), 125.71, 126.03, 128.53, 129.11, 129.74, 135.39, 137.31 (phenyl ring carbons) [20], 146.08, 148.17 (olefinic carbons); ^{29}Si NMR δ (C_6D_6) −9.0, −7.7, 5.2.

*Reaction of **2** with 2,3-diphenyl-1,3-butadiene*. A mixture of compound **2** (0.0991 g, 0.218 mmol) and 0.1310 g (0.635 mmol) of 2,3-diphenyl-1,3-butadiene was heated in a sealed tube at 140 °C for 24 h. Product **6** (0.0631 g, 43% isolated yield) was isolated by column chromatography. Anal. Calc. for $C_{36}H_{56}OSi_3Ge$ (**6**): C, 65.35; H, 8.53. Found: C, 65.35; H, 8.58%. Mp. 227.0–229.0 °C; MS *m*/*z* 662 (M^+); ^1H NMR δ (C_6D_6) 0.33 (br s, 27H, Me_3Si), 1.63–2.00 (m, 15H, Ad), 1.88 (d, 1H, ring proton, $J = 16$ Hz), 2.76 (d, 1H, ring proton, $J = 16$ Hz), 2.81 (d, 1H, ring proton, $J = 18$ Hz), 3.16 (d, 1H, ring proton, $J = 18$ Hz), 6.85–7.22 (m, 10H, phenyl ring protons); ^{13}C NMR δ (C_6D_6) 1.06, 1.61, 3.56 (Me_3Si), 17.28 (CH_2Ge), 29.28, 37.60, 39.74, 40.73 (Ad), 42.44 (CH_2), 89.69 (CO), 125.70, 126.01, 128.08, 128.30, 129.12, 129.78, 135.35, 137.31 (phenyl ring carbons), 146.26, 148.25 (olefinic carbons); ^{29}Si NMR δ (C_6D_6) −9.0, −7.3, 5.3.

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References

[1] J. Satgé, Adv. Organomet. Chem. 21 (1982) 241.
[2] N. Wiberg, J. Organomet. Chem. 273 (1984) 141.
[3] J. Satgé, Pure Appl. Chem. 56 (1984) 137.
[4] J. Barrau, J. Escudié, J. Satgé, Chem. Rev. 90 (1990) 283.
[5] J. Escudié, H. Ranaivonjatovo, Adv. Organomet. Chem. 44 (1999) 113.
[6] W.J. Leigh, Pure Appl. Chem. 71 (1999) 453.
[7] N. Tokitoh, K. Kishikawa, R. Okazaki, J. Chem. Soc., Chem. Commun. (1995) 1425.
[8] (a) H. Meyer, G. Baum, W. Massa, A. Berndt, Angew. Chem., Int. Ed. Engl. 26 (1987) 798;
(b) H. Schumann, M. Glanz, F. Girgsdies, F.E. Hahn, M. Tamm, A. Grzegorzewski, Angew. Chem., Int. Ed. Engl. 36 (1997) 2232.
[9] D. Bravo-Zhivotovskii, I. Zharov, M. Kapon, Y. Apeloig, J. Chem. Soc., Chem. Commun. (1995) 1625.
[10] N.P. Toltl, W.J. Leigh, J. Am. Chem. Soc. 120 (1998) 1172.
[11] V.N. Khabashesku, K.N. Kudin, J. Tamás, S.E. Boganov, J.L. Margrave, O.M. Nefedov, J. Am. Chem. Soc. 120 (1998) 5005.
[12] M.A. Chaubon, J. Escudié, H. Ranaivonjatovo, J. Satgé, J. Chem. Soc., Dalton Trans. (1996) 893.
[13] C. Couret, J. Escudié, J. Satgé, M. Lazraq, J. Am. Chem. Soc. 109 (1987) 4411.

[14] G. Anselme, J. Escudié, C. Couret, J. Satgé, J. Organomet. Chem. 403 (1991) 93.

[15] C. Couret, J. Escudié, G. Delpon-Lacaze, J. Satgé, Organometallics 11 (1992) 3176.

[16] N. Wiberg, H.-S. Hwang-Park, P. Mikulcik, G. Müller, J. Organomet. Chem. 511 (1996) 239.

[17] N. Wiberg, H.-S. Hwang-Park, J. Organomet. Chem. 519 (1996) 107.

[18] A.G. Brook, F. Abdesaken, H. Söllradl, J. Organomet. Chem. 299 (1986) 9.

[19] M. Ishikawa, S. Matsui, A. Naka, J. Ohshita, Main Group Chem. 1 (1996) 219.

[20] The signal of one phenyl carbon may overlap with that of C_6D_6.