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ScienceDirect
Tetrahedron 63 (2007) 4271–4277
Tetrahedron

Hyperconjugative effect of C–Ge bonds: synthesis of multisubstituted alkenylgermanes via torquoselective olefination of acylgermanes with ynolates

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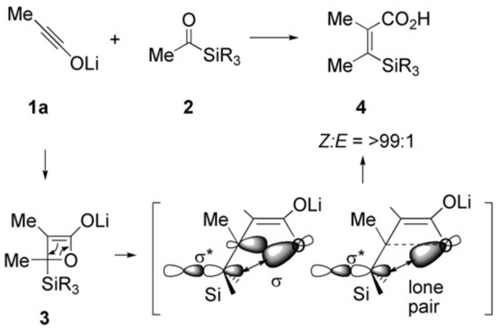
Received 19 February 2007; revised 7 March 2007; accepted 8 March 2007
Available online 12 March 2007

Abstract—The first highly *Z*-selective olefination of acylgermanes with ynolates affording multisubstituted alkenylgermanes was achieved. The torquoselectivity was ascribed to the hyperconjugative effect of C–Ge bonds in the transition state. The resulting (*Z*)-β-trialkylgermylacrylic acid has a hypervalent structure, which was converted into novel germalactones. A stereochemical complementary olefination via protonation of the β-lactone enolate, followed by decarboxylation, was also achieved.

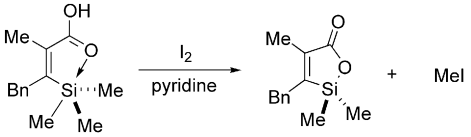
1. Introduction

Alkenylsilanes and alkenylstannanes are widely used in synthetic organic chemistry notably in palladium-catalyzed coupling reactions.[1] Although germanium is positioned between silicon and tin in the group 14 elements, the chemistry of alkenylgermanes,[2–4] especially highly substituted alkenes, has been less well studied, in part due to the lack of efficient general synthetic methods. Alkenylgermanes, however, should be more reactive than silylalkenes, and more stable and less toxic than stannylalkenes. Consequently, we believe that alkenylgermanes should have great potential in synthetic organic chemistry. Although stereoselective olefination of acylgermanes is expected to become an efficient synthetic method, only a few reports have appeared on this process, including the Wittig reaction and the Peterson olefination.[5]

In the course of our studies on the torquoselective olefination of carbonyl compounds via ynolates **1**,[6] we discovered the highly *Z*-selective olefination of acylsilanes **2** leading to silylalkenes **4** (Scheme 1),[7] in which the stereochemistry is controlled in the electrocyclic ring-opening step of the β-lactone enolate intermediate **3**. The high torquoselectivity[8] is achieved by the hyperconjugative interactions between the breaking C–O σ orbital and the Si–C σ* orbital as well as the interaction between the non-bonding orbital of the oxygen atom in the oxetene and the Si–C σ* orbital in the transition state.[9] The (*Z*)-β-trialkylsilylacrylic acids show unusual reactivity, including the generation of silalactones by treatment with iodine, because the acids form a pentacoordinate hypervalent silane by intramolecular coordination of the carbonyl group (Scheme 2).[10] The stereochemical complementary olefination of acylsilanes with ynolates was also achieved by a stereoselective formation of β-silyl-β-lactones, followed by decarboxylation as shown in



Scheme 1. Olefination of acylsilanes with ynolates.



Scheme 2. Electrophilic cleavage of hypervalent C–Si bond forming silalactone.

Keywords: Hypervalency; Germanium; Olefination; Torquoselectivity; Ynolates.

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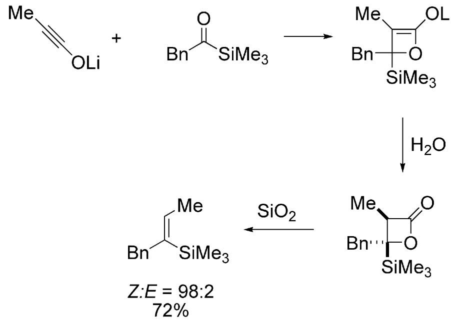
0040–4020/$ - see front matter
doi:10.1016/j.tet.2007.03.048



Scheme 3. Stereochemical complementary olefination of acylsilanes.

Scheme 3.[11] We envisaged a torquoselective olefination for the olefination of acylgermanes, since the Ge–C bond also has an energetically low-lying σ* orbital,[12] which should induce high torquoselectivity, leading to high *Z*-selectivity in the olefination. Furthermore, formation of the hypervalent germanium compounds and the stereochemical complementary olefination would be possible. Herein, we describe the highly stereoselective olefination of acylgermanes with ynolates to provide multisubstituted alkenylgermanes, and their hypervalent character.

2. Results and discussion

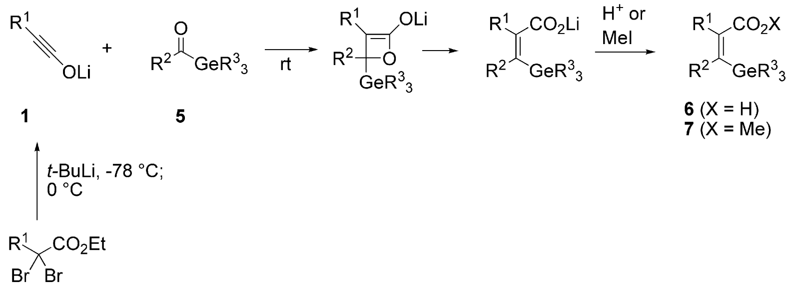
2.1. Torquoselective olefination of acylgermanes with ynolates

The ynolate **1a**, prepared from ethyl 2,2-dibromopropionate and *tert*-butyllithium,[7b,13] reacted with benzoyltriphenylgermane (**5a**) at room temperature for 30 min to afford methyl 2-methyl-3-phenyl-3-triphenylgermylpropenoate (**7aa**) after esterification in 85% yield with excellent *Z*-selectivity (Table 1, entry 1). In order to show its generality, several combinations of acylgermanes **5** and ynolates **1** were subjected to this olefination (Table 1). In most cases, the products were isolated as methyl esters (**7**) after treatment with iodomethane and HMPA in one-pot for convenience of purification. The olefination of benzoyl and *para*-substituted benzoylgermanes with various kinds of ynolates afforded the alkenylgermanes in good yields with excellent *Z*-selectivities (entries 1–9). The substituents (R^3: phenyl or ethyl) on the germanium did not affect the selectivity (entry 1 vs 7). The olefination of the acylgermanes having aliphatic substituents in R^2 provided the alkenylgermanes with good selectivities (entries 10 and 11), which were slightly lower than those of the benzoylgermanes. Since an aromatic group is more electron donating than an aliphatic group, the aromatic group prefers outward rotation,[14] and hence the torquoselectivity of the aromatic acylgermanes is higher than that of the aliphatic ones. By comparison with acylsilanes, which gave excellent selectivity in all cases, the torquoselectivity was lower. This would be ascribed to the longer C–Ge bond length (1.95 Å) compared with that of the C–Si (1.88 Å) leading to the less orbital overlap as described in Scheme 1.[15] This is the first general stereoselective olefination of acylgermanes giving multisubstituted alkenylgermanes.

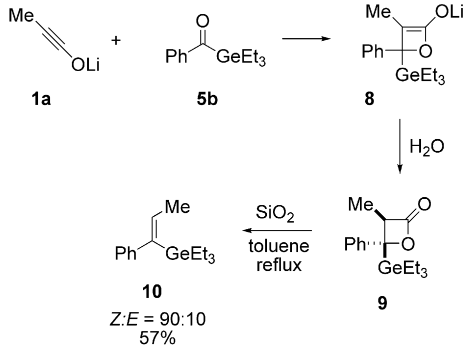
2.2. Complementary olefination of acylgermanes via decarboxylation of β-lactones

The addition of the ynolate **1a** to the acylgermane **5b** was carried out at −78 °C to afford the β-triethylgermyl-β-lactone **9** by quenching with aqueous NH_4Cl solution. Without purification, **9** underwent thermal decarboxylation[16] under reflux in toluene in the presence of silica gel to furnish the alkenylgermane **10** in 57% yield with a *Z*/*E* ratio of 90:10 (Scheme 4). The stereochemistry is determined in the protonation of **8**, since the thermal decarboxylation is a *syn*-elimination. As in the case of the trialkylsilyl group,[11] the trialkylgermyl substituent also exerts steric and stereoelectronic effects on the protonation *anti* to the germyl group.[17] This process is regarded as a complementary method to the torquoselective olefination described above,

Table 1. Torquoselectieve olefination of acylgermanes with ynolates



Entry	**1**	R^1	**5**	R^2	R^3	Product (**6**/**7**)	Yield (%)	*Z*:*E*
1	**1a**	Me	**5a**	Ph	Ph	**7aa**	85	>99:1
2	**1b**	Bu	**5a**	Ph	Ph	**7ba**	80	97:3
3	**1c**	*i*-Pr	**5a**	Ph	Ph	**7ca**	88	96:4
4	**1d**	Ph	**5a**	Ph	Ph	**7da**	36	96:4
5	**1e**	Me_3Si	**5a**	Ph	Ph	**7ea**	51	>99:1
6	**1a**	Me	**5b**	Ph	Et	**6ab**	96	>99:1
7	**1c**	*i*-Pr	**5b**	Ph	Et	**6cb**	98	>99:1
8	**1a**	Me	**5c**	4-MeO–C_6H_4	Ph	**7ac**	52	>99:1
9	**1a**	Me	**5d**	4-Cl–C_6H_4	Ph	**7ad**	82	99:1
10	**1a**	Me	**5e**	$PhCH_2$	Me	**7ae**	74	90:10
11	**1a**	Me	**5f**	Et	Ph	**7af**	97	90:10



Scheme 4. Stereoselective protonation of the β-lactone enolate, followed by decarboxylation.

since the methyl group has a cis-relationship with the germyl group here and a trans-relationship in the above case.

2.3. Hypervalency of (*Z*)-β-trialkylgermyl-α,β-unsaturated carboxylic acid

The X-ray crystal structure analysis of the (*Z*)-2-methyl-4-phenyl-3-trimethylgermyl-2-butenoic acid **6ae**, derived from the same reaction conditions as for entry 10 in Table 1, revealed a hypervalent pentacoordinate tetraorganogermane structure, where the carbonyl oxygen intramolecularly coordinates to the germane (Fig. 1, Table 2). The distances between the germanium atom and the carbonyl oxygen are 2.89 (Ge1–O1) and 2.93 Å (Ge2–O3), which are shorter than the sum of the van der Waals radii (3.62 Å). The bond lengths of C14–Ge1 and C28–Ge2 are longer than those of the other C–Ge bonds. Given these results, these structures were found to be distorted trigonal–bipyramidal pentacoordinate structures. The pentacoordination character TBPa, according to the Tamao equation,[18] is in the range of 17.3–19.6%, which is slightly smaller than for the corresponding hypervalent silicons (TBPa=20%).[10] From these values, the rigid (*Z*)-geometry renders a weak intramolecular coordination of the neutral carbonyl oxygen to the tetraorganogermanes, resulting in the hypervalent germane structures.

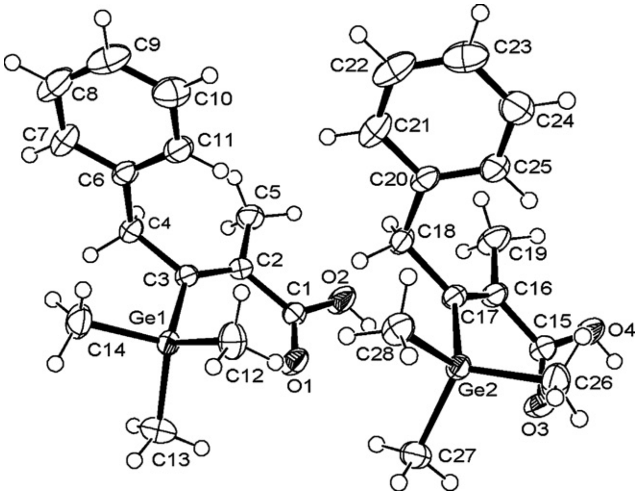


Figure 1. ORTEP drawing of the X-ray crystal structures of **6ae** (thermal ellipsoid set at the 50% probability level).

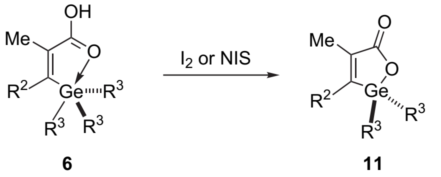
Table 2. Selected bond lengths (Å) and angles (deg) for **6ae**

Left	Distances	Right	Distances
Ge1–O1	2.8953(16)	Ge2–O3	2.9309(16)
Ge1–C3	1.9866(19)	Ge2–C17	1.9853(19)
Ge1–C12	1.938(2)	Ge2–C26	1.952(2)
Ge1–C13	1.941(2)	Ge2–C27	1.9430(18)
Ge1–C14	1.960(2)	Ge2–C28	1.962(2)

Left	Angles	Right	Angles
C3–Ge1–C14	106.46(9)	C17–Ge2–C28	106.06(8)
C12–Ge1–C14	105.59(10)	C26–Ge2–C28	106.61(9)
C13–Ge1–C14	104.81(10)	C27–Ge2–C28	105.62(9)

The carbon–germanium bond length on the apical position of the hypervalent germanes was longer than that of the equatorial carbon–germane bonds, and hence these organogermanes should be more reactive. The (*Z*)-β-trialkylgermyl α,β-unsaturated acids **6** were treated with iodine under reflux in CCl_4 to afford a novel germalactone **11** in excellent yield (Table 3, entries 1–3). When *N*-iodosuccinimide was used instead of iodine, the germalactone **11** was also generated under milder conditions (entry 4). As was seen in the generation of the silalactones,[10] the activated carbon–germanium bond at the apical position was electrophilically cleaved by iodine, namely, the cooperative push–pull mechanism involving the nucleophilic carbonyl oxygen and electrophilic iodine (Fig. 2). The germalactone **11b** reacted with the Grignard reagent to afford the (*Z*)-β-germylacrylic acid **12** in good yield (Scheme 5). Repetition of this sequence would provide various kinds of hypervalent organogermane species.

Table 3. Electrophilic cleavage of the C–Ge bond forming germalactone



Entry	6	R^2	R^3	Method[a]	Time (h)	11	Yield (%)
1	**6aa**	Ph	Ph	A	27	**11a**	81
2	**6ab**	Ph	Et	A	24	**11b**	95
3	**6ae**	$PhCH_2$	Me	A	23	**11c**	91
4	**6ae**	$PhCH_2$	Me	B	1	**11c**	57

[a] Method A: I_2 and pyridine in CCl_4 under reflux. Method B: NIS in CH_2Cl_2.

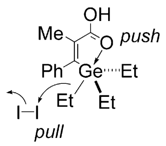
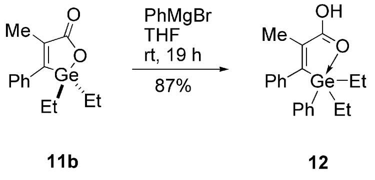


Figure 2. Proposed push–pull mechanism.



Scheme 5. Reconversion to the β-germylacrylic acid.

3. Conclusion

We have developed the first general highly *Z*-selective olefination of acylgermanes affording trisubstituted alkenylgermanes. This is the first example of the hyperconjugate effect of germanium in the electrocyclic reactions. The resulting (*Z*)-β-trialkylgermylacrylic acids were found to have hypervalent structures, which were converted into novel germalactones. Since organogermanes are expected to be more reactive than the corresponding organosilanes, these new transformations should contribute to the development of as yet unexplored germanium chemistry.

4. Experimental

4.1. Preparation of acylgermanes

Acylgermanes **5a**,[19] **5b**,[20] **5c**, and **5d** were prepared according to the literature.[21]

4.1.1. Benzoyltriphenylgermane (5a).[19] Yellow needles (mp 98.1–99.1 °C). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.32–7.44 (11H, m), 7.46–7.52 (1H, m), 7.54–7.60 (6H, m), 7.82–7.87 (2H, m). IR ($CHCl_3$): 1628 cm^{-1}.

4.1.2. Benzoyltriethylgermane (5b).[20] Yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.05–1.17 (15H, m), 7.45–7.57 (3H, m), 7.75–7.80 (2H, m). IR (neat): 1624 cm^{-1}.

4.1.3. 4-Methoxybenzoyltriphenylgermane (5c). Yellow prisms (ethyl acetate–hexane, mp 142–143 °C). ^1H NMR (400 MHz, $CDCl_3$) δ: 3.81 (3H, s), 6.81–6.86 (2H, m), 7.35–7.45 (9H, m), 7.54–7.60 (6H, m), 7.82–7.87 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.5 (q), 113.8 (d), 128.4 (d), 129.3 (d), 131.3 (d), 135.3 (d), 135.4 (s), 135.6 (s), 163.6 (s), 224.1 (s). IR ($CHCl_3$): 1621, 1592, 1572 cm^{-1}. MS (EI) *m/z* 440 (M^+), 305 ($GePh_3$, 100%). Anal. Calcd for $C_{26}H_{22}GeO_2$: C, 71.12; H, 5.05. Found: C, 70.95; H, 5.10.

4.1.4. 4-Chlorobenzoyltriphenylgermane (5d). Yellow prisms (ethanol, mp 106.6–107.4 °C). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.30–7.35 (2H, m), 7.35–7.46 (9H, m), 7.52–7.58 (6H, m), 7.75–7.80 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 128.5 (d), 128.9 (d), 129.5 (d), 129.8 (d), 134.8 (s), 135.1 (d), 139.5 (s), 139.6 (s), 226.0 (s). IR ($CHCl_3$): 1634, 1090 cm^{-1}. MS (EI) *m/z* 444 (M^+), 151 (100%). Anal. Calcd for $C_{25}H_{19}ClOGe$: C, 67.71; H, 4.32. Found: C, 67.68; H, 4.35.

4.1.5. Trimethyl(phenylacetyl)germane (5e). To a solution of 2-benzyl-1,3-dithiane (421 mg, 2.0 mmol) in THF (10 mL) was added dropwise a solution of *n*-butyllithium (1.0 mL, 2.2 mmol, 2.20 M in hexane) at −40 °C under argon. The solution was stirred for 2 h at −20 °C. After chlorotrimethylgermane (368 mg, 2.4 mmol) was added, the reaction mixture was allowed to warm to 0 °C. After 2 h, water (20 mL) was added and the resulting mixture was extracted with ethyl acetate. The organic phase was washed with a saturated $NaHCO_3$ solution and brine, dried over $MgSO_4$, filtered, and concentrated to afford a colorless solid, which was chromatographed over silica gel (3% ethyl acetate in hexane) to yield 629 mg (96%) of 2-benzyl-2-trimethylgermyl-1,3-dithiane. Colorless prisms (hexane, mp 104.4–105.6 °C). ^1H NMR (400 MHz, $CDCl_3$) δ: 0.17 (9H, s), 1.99 (3H, s), 3.76 (2H, br s), 3.77 (3H, s), 7.05–7.10 (2H, m), 7.14–7.21 (1H, m), 7.23–7.29 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: −3.1 (q), 24.3 (t), 24.7 (t), 39.4 (s), 45.1 (t), 126.6 (d), 127.8 (d), 130.9 (d), 138.7 (s). IR ($CHCl_3$): 1602, 1494, 1237, 828 cm^{-1}. MS (FAB) *m/z* 329 (M^++H). Anal. Calcd for $C_{14}H_{22}GeS_2$: C, 51.41; H, 6.78. Found: C, 51.18; H, 6.71.

To a solution of 2-benzyl-2-trimethylgermyl-1,3-dithiane (250 mg, 0.764 mmol) and $NaHCO_3$ (321 mg, 3.82 mmol) in MeCN–H_2O (4:1, 10 mL) was added iodomethane (1.43 mL, 22.9 mmol). After stirred for 21 h at 55 °C, water was added and the resulting mixture was extracted with ethyl acetate. The organic phase was washed with brine, dried over $MgSO_4$, filtered, and concentrated to afford a yellow oil, which was chromatographed over silica gel (3% ethyl acetate in hexane) to yield 123 mg (68%) of trimethyl(phenylacetyl)germane (**5e**) as a pale yellow oil (Kügelrohr distillation, 120–140 °C/2.8 mmHg). ^1H NMR (400 MHz, $CDCl_3$) δ: 0.12 (9H, s), 3.75 (2H, s), 7.01–7.25 (5H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: −2.2 (q), 56.6 (t), 126.8 (d), 128.5 (d), 129.8 (d), 132.6 (s), 241.2 (s). IR (neat): 1654, 830 cm^{-1}. MS (EI) *m/z* 329 (M^+), 119 ($GeMe_3$, 100%). HRMS (EI) Calcd for $C_{11}H_{16}GeO$ (M^+): 238.0413, found: 238.0384.

4.1.6. Propanoyltriphenylgermane (5f).[20] To a solution of triphenylgermanium hydride (306 mg, 1.0 mmol) in THF (10 mL) was added a solution of butyllithium (0.75 mL, 1.1 mmol, 1.46 M in hexane) at 0 °C under argon. After being stirred at 0 °C for 0.5 h, the resulting solution was allowed to warm to room temperature and then a solution of ethyl propanoate (306 mg, 3.0 mmol) in THF (2 mL) was added. After being stirred at room temperature for 5 h, a saturated NH_4Cl solution (10 mL) was added and the resulting mixture was extracted with hexane. The organic phase was washed with a saturated $NaHCO_3$ solution and brine, dried over $MgSO_4$, filtered, and concentrated to afford a pale yellow oil, which was chromatographed over silica gel (ethyl acetate/hexane, 2%) and then recrystallized from ethanol to yield 144 mg (40%) of propanoyltriphenylgermane as colorless needles (ethanol, mp 112.9–114.2 °C). ^1H NMR (400 MHz, $CDCl_3$) δ: 0.99 (3H, t, J=7.1 Hz), 2.91 (2H, q, J=7.1 Hz), 7.36–7.45 (9H, m), 7.52–7.56 (6H, m). IR ($CHCl_3$): 1661 cm^{-1}.

4.2. General procedure for the olefination of acylgermanes via ynolates to produce olefins (methyl esterification in one-pot)

To a solution of ethyl 2,2-dibromopropanoate (260 mg, 1.0 mmol) in THF (6 mL) was added dropwise a solution of *tert*-butyllithium (3.01 mL, 4.0 mmol, 1.33 M in pentane) at −78 °C under argon. The yellow solution was stirred for 3 h at −78 °C and allowed to warm to 0 °C. After 30 min, the resulting colorless reaction mixture was warmed to room temperature and a solution of acylgermane (0.80 mmol) in THF (2 mL) was added. After 1 h, iodomethane (0.62 mL, 10 mmol) and HMPA (1.74 mL, 10 mmol) were added. After 19 h, a saturated NH_4Cl solution (5 mL) was added and the resulting mixture was extracted with ethyl acetate. The organic phase was washed with H_2O, a saturated

$NaHCO_3$ solution, and brine, dried over $MgSO_4$, filtered, and concentrated. The residue was chromatographed over silica gel to yield the corresponding ester. The ratio of *Z*/*E* was determined by ^1H NMR of the crude mixture. Some of the stereochemistries were determined by NOE experiments,[22] unless otherwise noted. When the carboxylic acids were isolated without esterification, a saturated NH_4Cl solution was added instead of iodomethane.

4.2.1. (*Z*)-2-Methyl-3-phenyl-3-(triphenylgermyl)propenoic acid (6aa). Colorless prisms (methanol, mp 210–213 °C). ^1H NMR (400 MHz, $CDCl_3$) δ: 2.00 (3H, s), 6.70–6.74 (2H, m), 6.96–7.07 (3H, m), 7.18–7.35 (15H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 17.9 (q), 125.6 (d), 126.7 (d), 127.5 (d), 127.8 (d), 128.1 (d), 134.8 (d), 137.0 (s), 139.0 (s), 142.1 (s), 154.5 (s), 172.5 (s). IR ($CHCl_3$): 3010, 1695, 1585, 700 cm^{-1}. MS (FAB) *m*/*z* 489 (M^++Na). HRMS (FAB) Calcd for $C_{28}H_{24}GeO_2Na$ (M^++Na): 489.0886, found: 489.0861. Anal. Calcd for $C_{28}H_{24}GeO_2$: C, 72.31; H, 5.20. Found: C, 72.26; H, 5.33.

4.2.2. (*Z*)-Methyl-2-methyl-3-phenyl-3-(triphenylgermyl)propenoate (7aa). Colorless needles (ethanol, mp 113.0–113.4 °C). ^1H NMR (400 MHz, $CDCl_3$) δ: 1.92 (3H, s), 2.90 (3H, s), 6.68–6.74 (2H, m), 6.95–7.06 (3H, m), 7.20–7.36 (15H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 18.4 (q), 50.9 (q), 125.6 (d), 126.9 (d), 127.7 (d), 127.8 (d), 128.4 (d), 134.8 (d), 136.9 (s), 140.4 (s), 142.1 (s), 150.2 (s), 168.9 (s). IR ($CHCl_3$): 1714 cm^{-1}. MS (EI) *m*/*z* 480 (M^+), 403 (M^+-Ph), 205 (100%). Anal. Calcd for $C_{29}H_{26}GeO_2$: C, 72.69; H, 5.47. Found: C, 72.80; H, 5.61.

4.2.3. (*Z*)-Methyl-2-butyl-3-phenyl-3-(triphenylgermyl)-propenoate (7ba). Colorless needles (ethanol, mp 114.5–116.5 °C). ^1H NMR (400 MHz, $CDCl_3$) δ: 0.77 (3H, t, *J*=7.2 Hz), 1.19 (2H, sext, *J*=7.2 Hz), 1.32–1.42 (2H, m), 2.27–2.34 (2H, m), 2.84 (3H, s), 6.69–6.74 (2H, m), 6.95–7.05 (3H, m), 7.20–7.35 (15H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.8 (q), 22.5 (t), 31.5 (t), 31.9 (t), 50.8 (q), 125.5 (d), 127.1 (d), 127.6 (d), 127.7 (d), 128.4 (d), 134.9 (d), 136.6 (s), 141.6 (s), 145.9 (s), 148.2 (s), 168.8 (s). IR ($CHCl_3$): 1715 cm^{-1}. MS (EI) *m*/*z* 522 (M^+), 445 (M^+-Ph, 100%). Anal. Calcd for $C_{32}H_{32}GeO_2$: C, 73.74; H, 6.19. Found: C, 73.74; H, 6.39.

4.2.4. (*Z*)-Methyl-2-isopropyl-3-phenyl-3-(triphenylgermyl)propenoate (7ca). Colorless needles (ethanol, mp 140–141 °C). ^1H NMR (400 MHz, $CDCl_3$) δ: 1.09 (6H, d, *J*=7.1 Hz), 2.73 (1H, quin, *J*=7.1 Hz), 2.78 (3H, s), 6.73–6.77 (2H, m), 6.99–7.07 (3H, m), 7.22–7.35 (15H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.5 (q), 31.8 (d), 50.4 (q), 125.5 (d), 127.1 (d), 127.6 (d), 127.7 (d), 128.4 (d), 135.1 (d), 135.9 (s), 141.3 (s), 143.8 (s), 151.2 (s), 168.3 (s). IR ($CHCl_3$): 1717 cm^{-1}. MS (EI) *m*/*z* 508 (M^+), 431 (M^+-Ph, 100%). Anal. Calcd for $C_{31}H_{30}GeO_2$: C, 73.41; H, 5.96. Found: C, 73.22; H, 6.09.

4.2.5. (*Z*)-Methyl-2,3-diphenyl-3-(triphenylgermyl)propenoate (7da). Colorless prisms (CCl_4–hexane, mp 156–157 °C). ^1H NMR (400 MHz, $CDCl_3$) δ: 2.89 (3H, s), 6.62–6.65 (2H, m), 6.82–6.85 (3H, m), 7.05–7.15 (5H, m), 7.24–7.36 (9H, m), 7.42–7.46 (6H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 51.5 (q), 125.3 (d), 126.9 (d), 127.1 (d), 127.4 (d), 127.7 (d), 128.2 (d), 128.5 (d), 129.4 (d), 135.0 (d), 136.2 (s), 137.1 (s), 140.7 (s), 145.4 (s), 150.5 (s), 168.2 (s). IR ($CHCl_3$): 1716 cm^{-1}. MS (EI) *m*/*z* 542 (M^+), 178 (100%). Anal. Calcd for $C_{34}H_{28}GeO_2$: C, 75.45; H, 5.21. Found: C, 75.50; H, 5.16.

4.2.6. (*Z*)-Methyl-2-trimethylsilyl-3-phenyl-3-(triphenylgermyl)propenoate (7ea). Colorless prisms (acetone, mp 175–177 °C). ^1H NMR (400 MHz, $CDCl_3$) δ: -0.14 (9H, s), 2.78 (3H, s), 6.78–6.83 (2H, m), 7.02–7.06 (3H, m), 7.22–7.36 (15H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 0.3 (q), 50.6 (q), 126.1 (d), 127.36 (d), 127.44 (d), 127.6 (d), 128.5 (d), 135.3 (d), 135.7 (s), 143.0 (s), 151.2 (s), 160.2 (s), 171.0 (s). IR ($CHCl_3$): 1685 cm^{-1}. MS (EI) *m*/*z* 538 (M^+), 279 (100%). Anal. Calcd for $C_{31}H_{32}GeO_2Si$: C, 69.30; H, 6.00. Found: C, 69.36; H, 5.97.

4.2.7. (*Z*)-2-Methyl-3-phenyl-3-(triethylgermyl)propenoic acid (6ab). Colorless needles (acetonitrile, mp 85–86 °C). ^1H NMR (400 MHz, $CDCl_3$) δ: 0.79 (6H, q, *J*=8.0 Hz), 0.95 (9H, t, *J*=8.0 Hz), 1.78 (3H, s), 6.80–6.85 (2H, m), 7.15–7.21 (1H, m), 7.30–7.35 (2H, m). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 6.3 (t), 9.3 (q), 17.3 (q), 125.5 (d), 125.6 (d), 128.2 (d), 136.1 (s), 144.7 (s), 162.7 (s), 174.7 (s). IR ($CHCl_3$): 3018, 1690 cm^{-1}. MS (EI) *m*/*z* 293 ($M^+-C_2H_5$). Anal. Calcd for $C_{16}H_{24}GeO_2$: C, 59.87; H, 7.50. Found: C, 59.83; H, 7.50.

4.2.8. (*Z*)-2-Ethyl-3-phenyl-3-(triethylgermyl)propenoic acid (6cb). Colorless prisms (acetonitrile, mp 106–107 °C). ^1H NMR (400 MHz, $CDCl_3$) δ: 0.77 (6H, q, *J*=7.6 Hz), 0.948 (12H, t, *J*=7.6 Hz), 2.19 (2H, q, *J*=7.6 Hz), 6.83–6.88 (2H, m), 7.15–7.21 (1H, m), 7.28–7.34 (2H, m). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 6.2 (t), 9.2 (q), 14.3 (q), 24.4 (t), 125.4 (d), 125.8 (d), 128.0 (d), 142.7 (s), 144.2 (s), 160.7 (s), 174.5 (s). IR ($CHCl_3$): 2952, 1686 cm^{-1}. MS (EI) *m*/*z* 307 ($M^+-C_2H_5$). Anal. Calcd for $C_{17}H_{26}GeO_2$: C, 60.95; H, 7.82. Found: C, 60.91; H, 7.78.

4.2.9. (*Z*)-Methyl-3-(4-methoxyphenyl)-2-methyl-3-(triphenylgermyl)propenoate (7ac). Colorless needles (acetonitrile, mp 126.5–127.4 °C). ^1H NMR (400 MHz, $CDCl_3$) δ: 1.93 (3H, s), 2.88 (3H, s), 3.67 (3H, s), 6.56–6.65 (4H, m), 7.21–7.38 (15H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 18.5 (q), 50.9 (q), 55.3 (q), 113.3 (d), 127.6 (d), 128.1 (d), 128.3 (d), 134.3 (s), 134.8 (d), 136.9 (s), 140.7 (s), 149.8 (s), 157.5 (s), 168.9 (s). IR ($CHCl_3$): 1715, 1607, 1507 cm^{-1}. MS (EI) *m*/*z* 510 (M^+), 432 (M^+-Ph, 100%). Anal. Calcd for $C_{30}H_{28}GeO_3$: C, 70.76; H, 5.54. Found: C, 70.66; H, 5.60.

4.2.10. (*Z*)-Methyl-3-(4-chlorophenyl)-2-methyl-3-(triphenylgermyl)propenoate (7ad). Colorless prisms (hexane, mp 122.5–123.9 °C). ^1H NMR (400 MHz, $CDCl_3$) δ: 1.91 (3H, s), 2.89 (3H, s), 6.61–6.65 (2H, m), 6.98–7.02 (2H, m), 7.23–7.36 (15H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 18.5 (q), 51.0 (q), 127.7 (d), 127.9 (d), 128.3 (d), 128.5 (d), 131.4 (s), 134.7 (d), 136.3 (s), 140.5 (s), 140.9 (s), 149.0 (s), 168.5 (s). IR ($CHCl_3$): 1716 cm^{-1}. MS (EI) *m*/*z* 514 (M^+), 150 (100%). Anal. Calcd for $C_{29}H_{25}ClGeO_2$: C, 67.82; H, 4.91. Found: C, 67.57; H, 5.07.

4.2.11. (*Z*)-2-Methyl-3-trimethylgermyl-4-phenyl-2-butenoate (6ae). Colorless prisms (acetonitrile, mp 111.5–

112.5 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.21 (9H, s), 2.03 (3H, s), 3.81 (2H, s), 7.04–7.08 (2H, m), 7.15–7.21 (1H, m), 7.24–7.30 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 1.0 (q), 15.6 (q), 39.3 (t), 126.0 (d), 128.0 (d), 128.3 (d), 135.9 (s), 138.1 (s), 160.4 (s), 173.7 (s). IR (neat): 2979, 1685, 1284, 832 cm^{-1}. MS (FAB) *m/z* 293 ($M^{+}-Me$). Anal. Calcd for $C_{14}H_{20}GeO_2$: C, 57.41; H, 6.88. Found: C, 57.17; H, 6.88.

4.2.12. (*Z*)-Methyl-2-methyl-3-trimethylgermyl-4-phenyl-2-butenoate (7ae). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.17 (9H, s), 1.99 (3H, s), 3.76 (2H, br s), 3.77 (3H, s), 7.05–7.10 (2H, m), 7.14–7.21 (1H, m), 7.23–7.29 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 0.6 (q), 15.9 (q), 38.8 (t), 51.6 (q), 125.9 (d), 128.1 (d), 128.3 (d), 136.9 (s), 138.5 (s), 155.1 (s), 169.5 (s). IR (neat): 1715 cm^{-1}. MS (FAB) *m/z* 293 ($M^{+}-Me$). HRMS (FAB) Calcd for $C_{14}H_{19}GeO_2$ ($M^{+}-Me$): 293.0597, found: 293.0612.

4.2.13. (*Z*)-2-Methyl-3-trimethylgermyl-4-phenyl-2-butenoic acid (6ae). Colorless prisms (acetonitrile, mp 111.5–112.5 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.21 (9H, s), 2.03 (3H, s), 3.81 (2H, s), 7.04–7.08 (2H, m), 7.15–7.21 (1H, m), 7.24–7.30 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 1.0 (q), 15.6 (q), 39.3 (t), 126.0 (d), 128.0 (d), 128.3 (d), 135.9 (s), 138.1 (s), 160.4 (s), 173.7 (s). IR (neat): 2979, 1685, 1284, 832 cm^{-1}. MS (FAB) *m/z* 293 ($M^{+}-Me$). Anal. Calcd for $C_{14}H_{20}GeO_2$: C, 57.41; H, 6.88. Found: C, 57.17; H, 6.88. The stereochemistry was determined by X-ray crystal structure analysis: CCDC 630268 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4.2.14. (*Z*)-Methyl-2-methyl-3-triphenylgermyl-2-pentenoate (7af). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.77 (3H, t, J=7.6 Hz), 2.14 (3H, s), 2.29 (2H, q, J=7.6 Hz), 2.81 (3H, s), 7.28–7.35 (9H, m), 7.45–7.50 (6H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 12.7 (q), 15.7 (q), 27.0 (t), 50.6 (q), 127.8 (d), 128.4 (d), 134.8 (d), 138.1 (s), 138.6 (s), 151.3 (s), 168.8 (s). IR (neat): 1716 cm^{-1}. MS (FAB) *m/z* 455 (M^{+}+Na). HRMS (FAB) Calcd for $C_{25}H_{26}GeO_2Na$ (M^{+}+Na): 455.1042, found: 455.1010.

4.3. (*Z*)-1-(Triethylgermyl)-1-phenyl-1-propene (10)

To a solution of ethyl 2,2-dibromopropionate (156 mg, 0.6 mmol) in THF (12 mL) at −78 °C under argon, was added dropwise a solution of *tert*-butyllithium (1.67 mL, 2.4 mmol in pentane). The yellow solution was stirred for 3 h at −78 °C and allowed to warm to 0 °C. After 30 min, the resulting colorless reaction mixture was cooled to −78 °C and a solution of benzoyltriethylgermane (**5b**, 132 mg, 1.6 mmol) in THF (2 mL) was added. After 2.5 h at −78 °C, a saturated aqueous NH_4Cl solution (10 mL) was added and the resulting mixture was extracted with ethyl acetate. The organic phase was washed with brine, dried over $MgSO_4$, filtered, and concentrated to afford a pale yellow solid (187 mg) of **9**. It was decarboxylated with 55 mg of silica gel under reflux in toluene for 16 h to afford 79 mg (57%) of **10** as a mixture of stereoisomers (90:10). Major isomer: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.85 (6H, q, J=7.6 Hz), 0.99 (9H, t, J=7.6 Hz), 1.87 (3H, d, J=7.2 Hz), 6.18 (1H, q, J=7.2 Hz), 6.96–7.02 (2H, m), 7.10–7.16 (1H, m), 7.20–7.26 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 5.9 (t), 9.1 (q), 18.2 (q), 125.1 (d), 127.1 (d), 127.6 (d), 138.0 (d), 143.2 (s), 147.2 (s). IR (neat): 1597, 1487, 1013 cm^{-1}. MS (EI) *m/z* 278 (M^{+}), 249 ($M^{+}-Et$, 100%). HRMS (EI) Calcd for $C_{15}H_{24}Ge$ (M^{+}): 278.1093, found: 278.1092. The stereochemistry was determined by NOE experiments.[22]

4.4. Synthesis of germalactones

4.4.1. 2,2-Diethyl-4-methyl-3-phenyl-2*H*-[1,2]oxagermal-5-one (11b) (method A). To a solution of (*Z*)-2-methyl-4-phenyl-3-triethylgermyl-2-butenoic acid (**6ab**, 400 mg, 1.25 mmol) in CCl_4 (15 mL) were added iodine (474 mg, 1.87 mmol) and pyridine (0.20 mL, 2.49 mmol). The reaction mixture was heated under reflux for 23 h. After cooling to room temperature, a saturated $Na_2S_2O_3$ solution was added and the resulting mixture was extracted with CH_2Cl_2. The organic phase was washed with brine, dried over $MgSO_4$, filtered, and concentrated to afford a yellow oil, which was chromatographed over silica gel (15% ethyl acetate in hexane) to yield 345 mg (95%) of **11b** as colorless needles (ethyl acetate–hexane, mp 66–67 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.13 (6H, t, J=7.6 Hz), 1.32 (2H, dq, J=7.6, 15.6 Hz), 1.44 (2H, dq, J=7.6, 15.6 Hz), 2.14 (3H, s), 7.16–7.21 (2H, m), 7.32–7.38 (1H, m), 7.40–7.48 (2H, m). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 7.5 (q), 9.1 (t), 14.2 (q), 127.7 (d), 128.2 (d), 129.0 (d), 137.1 (s), 139.9 (s), 152.0 (s), 173.4 (s). IR ($CHCl_3$): 1693, 1130 cm^{-1}. MS (EI) *m/z* 292 (M^{+}), 191 (100%). Anal. Calcd for $C_{14}H_{18}O_2Ge$: C, 57.80; H, 6.24. Found: C, 57.75; H, 6.24.

4.4.2. 4-Methyl-2,2,3-triphenyl-2*H*-[1,2]oxagermal-5-one (11a). Colorless plates (ethyl acetate–hexane, mp 166.9–168.3 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.28 (3H, s), 7.24–7.41 (5H, m), 7.43–7.48 (4H, m), 7.50–7.56 (2H, m), 7.58–7.62 (4H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.7 (q), 128.2 (d), 128.5 (d), 128.96 (d), 128.99 (d), 130.7 (s), 131.5 (d), 134.2 (d), 136.5 (s), 140.5 (s), 150.0 (s), 172.8 (s). IR ($CHCl_3$): 1703, 696 cm^{-1}. MS (EI) *m/z* 388 (M^{+}), 227 (100%). Anal. Calcd for $C_{22}H_{18}O_2Ge$: C, 68.25; H, 4.68. Found: C, 68.28; H, 4.69.

4.4.3. 4-Methyl-2,2-diphenyl-3-phenylmethyl-2*H*-[1,2]oxagermal-5-one (11c) (method B). To a solution of (*Z*)-2-methyl-4-phenyl-3-trimethylgermyl-2-butenoic acid (**6ae**, 7.4 mg, 0.025 mmol) in dichloromethane (1 mL) was added NIS (8.5 mg, 0.038 mmol) at room temperature. The reaction mixture was stirred at room temperature for 70 min and then a saturated $Na_2S_2O_3$ solution (2 mL) was added. The resulting mixture was extracted with CH_2Cl_2. The organic phase was washed with brine, dried over $MgSO_4$, filtered, and concentrated to afford pale yellow oil, which was chromatographed over silica gel (20% ethyl acetate in hexane) to yield 4.0 mg (57%) of **11c**. Colorless needles (pentane, mp 85–88 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.33 (6H, s), 2.06 (3H, t, J=1.1 Hz), 3.75 (2H, br s), 7.12–7.17 (2H, m), 7.24–7.30 (1H, m), 7.32–7.38 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 0.3 (q), 12.9 (q), 37.0 (t), 127.2 (d), 128.5 (d), 129.2 (d), 137.8 (s), 139.1 (s), 157.0 (s), 172.5 (s). IR ($CHCl_3$): 1697, 1291, 1160 cm^{-1}. MS (FAB) *m/z* 279 (M^{+}+H). HRMS (FAB)

Calcd for $C_{13}H_{17}O_2Ge$ (M^++H): 279.0440, found: 279.0431. Anal. Calcd for $C_{13}H_{17}O_2Ge$: C, 56.39; H, 5.82. Found: C, 56.31; H, 5.79.

4.5. (*Z*)-3-(Diethylphenylgermyl)-2-methyl-3-phenylpropenoic acid (12)

To a solution of **11** (40 mg, 0.12 mmol) in THF (2 mL) was added dropwise a solution of phenyl magnesium bromide (2.06 mL, 1.03 mmol, 0.5 M in THF) at 0 °C under argon. The reaction mixture was slowly allowed to warm to room temperature. After 19 h, a saturated NH_4Cl solution was added and the resulting mixture was extracted with ethyl acetate. The organic phase was washed with brine, dried over $MgSO_4$, filtered, and concentrated to afford a pale yellow oil, which was chromatographed over silica gel (15% ethyl acetate in hexane) to yield 44 mg (87%) of **12** as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.89–1.04 (10H, m), 1.78 (3H, s), 6.87–6.92 (2H, m), 7.15–7.21 (1H, m), 7.22–7.42 (7H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 6.6 (t), 9.1 (q), 17.4 (q), 125.7 (d), 126.0 (d), 127.6 (d), 127.8 (d), 128.2 (d), 137.1 (s), 139.8 (s), 144.0 (s), 159.9 (s), 173.8 (s). IR (neat): 2872, 1683, 1283 cm^{-1}. MS (FAB) *m*/*z* 370 (M^+), 341 ($M^+-C_2H_5$, 100%). HRMS (FAB) Calcd for $C_{20}H_{24}O_2Ge$ (M^+): 370.0992, found: 370.0993.

Acknowledgements

We thank Professor S. Kanemasa (Kyushu University) for valuable discussions and Dr. J. Tanaka for X-ray crystal structure analysis. This research was supported by a Grant in Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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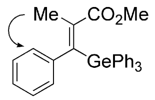
22. The results of the NOE experiments are shown below. Others were tentatively assigned.



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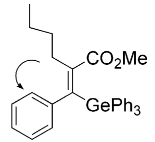

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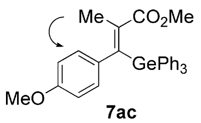

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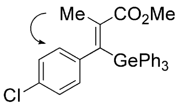

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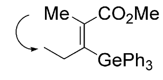

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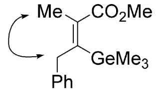

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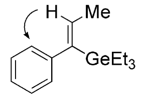

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