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Synthesis of t-butyl (trialkylstannyl)(trimethylgermyl)acetates and application of their anions to the Peterson-type reaction

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Abstract

Three t-butyl (trialkylstannyl)(trimethylgermyl)acetates were synthesized and subjected to the Peterson-type reaction with carbonyl compounds. t-Butyl 2-(trimethylgermyl)-2-alkenoates were obtained as the main products from (tri-n-butylstannyl) (trimethylgermyl)acetate, along with 2-(tri-n-butyl-stannyl)-2-alkenoates and 2-alkenoates as minor products

Introduction

The Peterson-type reaction of lithio(trimethylgermyl)(trimethylsilyl)acetonitrile or ethyl lithio(trimethylgermyl)(trimethylsilyl)acetate with aldehydes was found to give predominantly 2-(trimethylgermyl)-2-alkenenitriles or ethyl 2-(trimethylgermyl)-2-alkenoates, respectively [1, 2]. Zapata et al. [3] and Ager et al. [4] have reported the reaction of t-butyl lithio(tri-n-butylstannyl)(trimethylsilyl)acetate with aldehydes to give 2-(tri-n-butylstannyl)-2-alkenoates in moderate yields.

Both the germyl-silyl-substituted, and the silyl-stannyl-substituted carbanions thus undergo similar Peterson-type reactions, and the trimethylsiloxy group is selectively eliminated from the reaction intermediates. This selectivity may be due to the higher affinity of silicon for oxygen than that of either germanium or tin.

The question then arises of which group remains in the Peterson-type reaction products when a germyl-stannyl-substituted carbanion is treated with carbonyl compound. We prepared three (trialkylstannyl) (trimethylgermyl)acetates and carried out Peterson-type reactions of their anions with carbonyl compounds.

Results and discussion

The trialkylstannylation of t-butyl (trimethylgermyl)acetate (**1**) proceeded smoothly using chlorotrimethylstannane, chlorotriethylstannane, chlorotri-n-butylstannane, and lithium diisopropylamide (LDA) in THF. However, the yields of

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Table 1

Peterson reaction of t-butyl (trialkylstannyl)(trimethylgermyl)acetate (**2**) with carbonyl compounds

Entry	Acetate	R^1	R^2	R^3	Base/Solvent	Products, yield (%), (E/Z) [a]		
1	**2a**	Me	Ph	H	LDA/THF			*E*-**9a**, 43 [b]
2	**2b**	Et	Ph	H	LDA/THF			*E*-**9a**, 20 [b]
3	**2b**	Et	Ph	H	LDA/THF-HMPA			*E*-**9a**, 29 [b]
4	**2c**	n-Bu	Ph	H	LDA/THF	**5a**, 56 (5:2)		*E*-**9a**, 16
5	**2c**	n-Bu	Ph	H	LDA/THF-HMPA	**5a**, 25 (5:7)	*Z*-**6a**, 11	*E*-**9a**, 36
6	**2c**	n-Bu	Ph	H	KDA/THF	**5a**, 70 (5:3)	*Z*-**6a**, 1	*E*-**9a**, 16
7	**2c**	n-Bu	PhCH=CH	H	KDA/THF	**5b**, 44 (10:13)		*E*-**9b**, 7
8	**2c**	n-Bu	Ph	Ph	KDA/THF	**5c**, 21	**6c**, 16	**9c**, 33

[a] Based on integrated GLC values. [b] GLC yield.

t-butyl (trimethylgermyl)(trimethylstannyl)acetate (**2a**) and (triethylstannyl)(trimethylgermyl)acetate (**2b**) isolated were less than expected, since significant amounts of the products were destannylated to **1** during the aqueous work-up. t-Butyl (tri-n-butylstannyl)(trimethylgermyl)acetate (**2c**) was stable to similar aqueous work-up but could not be distilled under reduced pressure without partial decomposition. Therefore, the synthesis of **2c** and the subsequent Peterson-type reaction were carried out continuously in one pot.

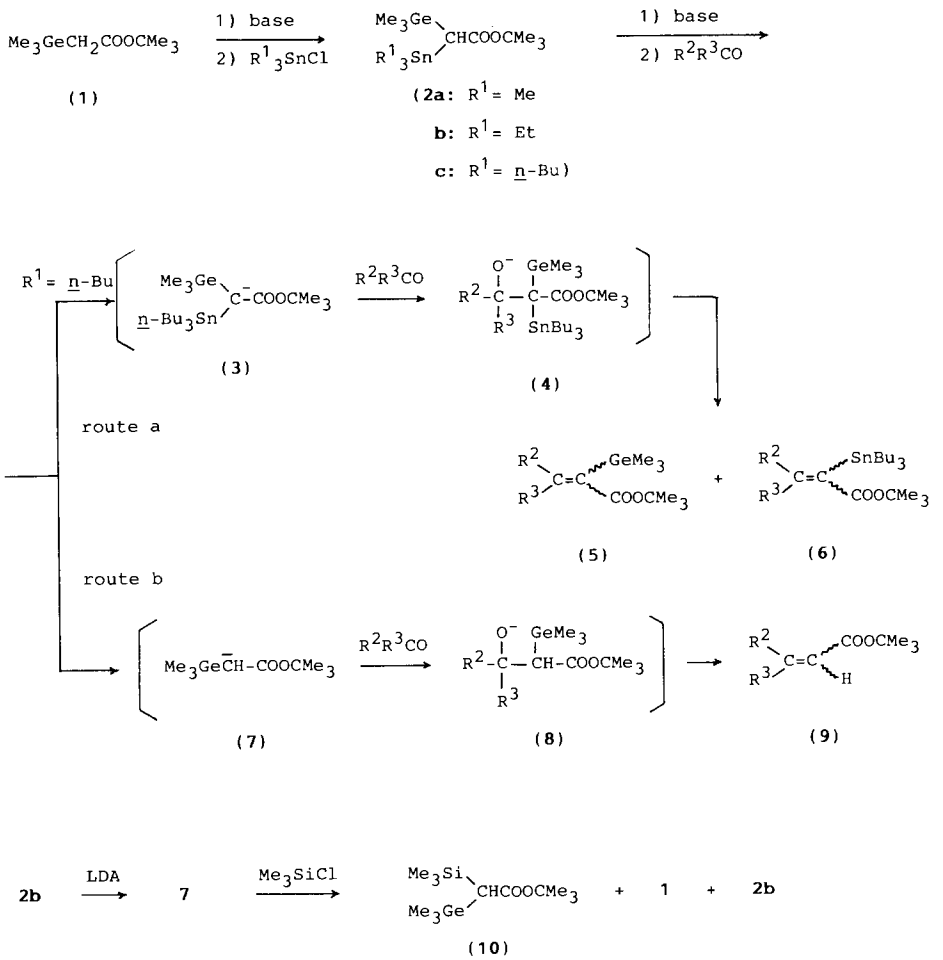
When a solution of **2a** or **2b** in THF or in a mixture of THF and hexamethylphosphoric triamide (HMPA) * was treated with LDA followed by the addition of benzaldehyde, (*E*)-t-butyl 3-phenylpropenoate (*E*-**9a**) was obtained in moderate yield but neither the germyl nor stannyl group could be found in the reaction product (entries 1–3 in Table 1).

Treatment of **2b** with LDA followed by the addition of chlorotrimethylsilane resulted in the formation of t-butyl (trimethylgermyl)(trimethylsilyl)acetate (**10**) in a high yield. It appears that LDA acts only as a destannylation reagent and not as a deprotonation reagent for **2a** or **2b**. The formation of *E*-**9a** may take place via route b in Scheme 1.

However, (*E*)- and (*Z*)-t-butyl 3-phenyl-2-(trimethylgermyl)propenoate (**5a**) were obtained as the main products from the reaction of **2c** with benzaldehyde (entry 4). The addition of HMPA as a co-solvent brought about the formation of (*Z*)-t-butyl 3-phenyl-2-(tri-n-butylstannyl)propenoate (*Z*-**6a**) at the expense of a reduced yield of **5a**. Use of potassium diisopropylamide (KDA) instead of LDA gave the highest yield of **5a** (entry 6). Thus, the stannyl group is eliminated preferentially from the Peterson-type reaction intermediate (**4**), but selectivity decreases with increasing polarity of the solvent used.

Similar treatment of **2c** with (*E*)-cinnamaldehyde gave t-butyl 5-phenyl-2-(trimethylgermyl)-2,4-pentadienoate (**5b**) as the major product. The reaction of **2c** with benzophenone proceeded to give a mixture of t-butyl 3,3-diphenyl-2-(trimethylgermyl)propenoate (**5c**), t-butyl 3,3-diphenyl-2-(tri-n-butylstannyl)propenoate (**6c**), and t-butyl 3,3-diphenylpropenoate (**9c**).

* The reaction of t-butyl (tri-n-butylstannyl)(trimethylsilyl)acetate with aldehydes was carried out in a mixture of THF and HMPA [3,4]



Scheme 1

Thus, the increasing ability to eliminate trialkylelemento groups in the Peterson-type olefination falls in the order $Me_3Si > n\text{-}Bu_3Sn > Me_3Ge$. The stereoselectivity of **9a** and **9b** was high, and their (*Z*)-isomers could not be detected by GLC analysis.

Experimental

All reactions were carried out under nitrogen. Tetrahydrofuran was dried by distillation from sodium benzophenone ketyl and HMPA was distilled from sodium under reduced pressure. ^1H and ^{13}C NMR spectra were recorded on JEOL JNM-MH 100 and JNM-GSX 400 spectrometers with Me_4Si as an internal standard. IR spectra were recorded on a JASCO IRA-2 spectrometer. Mass spectral data were obtained by use of a JEOL JMS-DX 300 GC/MS system (70 eV). Gas chromatographic analyses were carried out on a Gasukuro Kogyo Model-370 equipped with TCD detector using a 1 m, 20% silicone SE-30 column. All melting points and

boiling points are uncorrected. n-Butyllithium, 15% in hexane, was purchased from Nakarai Chemicals, Ltd. Kyoto.

*t-Butyl (trimethylgermyl)acetate (**1**)*

n-Butyllithium (64 ml, 100 mmol) was added dropwise to a solution of diisopropylamine (10.23 g, 101 mmol) in THF (100 ml) at 0 °C and stirred for 0.5 h. The resulting LDA solution was cooled to −78 °C and t-butyl acetate (11.72 g, 101 mmol) was added dropwise. After 1.5 h of stirring, the cold solution of the lithium ester enolate thus obtained was added slowly by cannulation to a solution of chlorotrimethylgermane (15.01 g, 98 mmol) in THF (50 ml) at −78 °C, and stirring was continued for another hour. Aqueous citric acid solution (1 *M*, 200 ml) was added to the reaction mixture and the product was extracted with ethyl ether (200 ml × 3). The ethereal extract was washed with 1% $NaHCO_3$, water (200 ml), dried over anhydrous $MgSO_4$, and concentrated. Distillation of the residue gave **1** (17.33 g, 76%): b.p. 65–67 °C (7–9 Torr); IR (film) 1710 cm^{-1} (CO); ^1H NMR ($CDCl_3$): δ 0.27 (9H, s, Me_3Ge), 1.37 (9H, s, Me_3C), 1.78 (2H, s, CH_2). Anal. Found: C, 46.15; H, 8.57. $C_9H_{20}GeO_2$ calcd.: C, 46.42; H, 8.66%.

*t-Butyl (trimethylgermyl)(trimethylstannyl)acetate (**2a**)*

A solution of **1** (15.23 g, 66 mmol) in THF (20 ml) was added dropwise at −78 °C to a LDA solution, prepared from diisopropylamine (7.11 g, 70 mmol) and n-BuLi (44.8 ml, 70 mmol) in THF (100 ml). After the solution was stirred for 1 h, chlorotrimethylstannane (15.34 g, 77 mmol) was added dropwise and stirring was continued for a further hour at the same temperature. Aqueous citric acid solution (0.1 *M*, 150 ml) was added and the mixture was extracted with ethyl ether (150 ml × 3). The extract was washed with 0.1 *M*-citric acid (150 ml × 2), water (150 ml × 2), dried over anhydrous $MgSO_4$, and concentrated. Fractional distillation of the residue gave **2a** (12.44 g, 48%): b.p. 86–90 °C (2 Torr); IR (film) 1690 cm^{-1} (CO); ^1H NMR ($CDCl_3$): δ 0.20 (9H, s, Me_3Sn), 0.25 (9H, s, Me_3Ge), 1.43 (9H, s, Me_3C), 1.59 (1H, s, CH). Anal. Found: C, 36.21; H, 7.14. $C_{12}H_{28}GeO_2Sn$ calcd.: C, 36.43; H, 7.13%.

*t-Butyl (triethylstannyl)(trimethylgermyl)acetate (**2b**)*

In a manner similar to that described for **2a**, n-BuLi (25.6 ml, 40 mmol), diisopropylamine (5.6 ml, 40 mmol), 1 (8.32 g, 36 mmol), THF (70 ml), and chlorotriethylstannane (8.67 g, 36 mmol) were allowed to react and work-up gave **2b** (7.90 g, 51%): b.p. 96–98 °C (0.2 Torr); IR (film) 1695 cm^{-1} (CO); ^1H NMR ($CDCl_3$): δ 0.23 (9H, s, Me_3Ge), 0.9–1.4 (15H, m, Et_3Sn), 1.51 (9H, s, Me_3C), 1.74 (1H, s, CH). Anal. Found: C, 40.78; H, 7.77. $C_{15}H_{34}GeO_2Sn$ calcd.: C, 41.16; H, 7.83%.

*t-Butyl (tri-n-butylstannyl)(trimethylgermyl)acetate (**2c**)*

Ester **1** (1.16 g, 5 mmol) was added dropwise at −78 °C to a LDA (5 mmol) solution in THF (15 ml). After 1 h of stirring, chlorotri-n-butylstannane (1.63 g, 5 mmol) was added and the mixture was stirred for 1 h at room temperature (this mixture was used in the reaction with carbonyl compounds as the **2c** solution). The mixture was quenched with saturated aqueous NH_4Cl (15 ml) and extracted with ether (15 ml × 3). The extract was washed with saturated aqueous NaCl (15 ml × 3),

dried (Na_2SO_4) and concentrated under reduced pressure at 50°C to give **2c** (2.55 g 98%): IR (film) 1690 cm^{-1} (CO); ^1H NMR ($CDCl_3$): δ 0.24 (9H, s, Me_3Ge), 1.42 (9H, s, Me_3C), 0.65–1.90 (28H, m, Bu_3Sn and CH).

Attempts to purify this compound by distillation under reduced pressure resulted in degradation.

*Reaction of **2a** or **2b** with benzaldehyde*

A solution of 2 mmol of **2a** or **2b** in THF (1 ml) was added at −78°C to a solution of LDA, prepared from n-BuLi (1.4 ml, 2.2 mmol) and diisopropylamine (0.35 ml, 2.5 mmol) in THF (2.5 ml). After 1 h of stirring, benzaldehyde (212 mg, 2 mmol) was added and stirring was continued for a further hour at the same temperature. Saturated aqueous NH_4Cl (10 ml) was added and the mixture was extracted with ethyl ether (10 ml × 3). The ethereal extract was washed successively with aqueous NaCl and water, then dried over anhydrous $MgSO_4$, and concentrated. The structure of the main product in the residue was confirmed by direct comparison with an authentic sample of (*E*)-t-butyl 3-phenylpropenoate (*E*-**9a**) using GLC and GC-MS spectra. The yield was determined on the basis of the integrated GLC value relative to an internal standard (benzoin). The yields are shown in Table 1.

*Reaction of **2c** with carbonyl compounds*

Entry 4 in Table 1. The **2c** solution was added to a LDA solution, prepared from n-BuLi (3.2 ml, 5 mmol) and diisopropylamine (0.7 ml, 5 mmol) in THF (10 ml) at −78°C. After the solution had been stirred for 0.5 h, benzaldehyde (531 g, 5 mmol) was added dropwise and stirring was continued for 15 min at the same temperature, and then at room temperature overnight. Saturated aqueous NH_4Cl solution (25 ml) was added and the mixture was extracted with ethyl ether (25 ml × 3). The ethereal extract was washed successively with saturated NaCl (25 ml), and water (25 ml), then dried over anhydrous $MgSO_4$, and concentrated. The residue was chromatographed on a silica gel column (petroleum ether/dichloromethane 3/1) to give a mixture of (*E*)- and (*Z*)-t-butyl 3-phenyl-2-(trimethylgermyl)propenoate (*E*-**5a** and *Z*-**5a**), and *E*-**9a**. * The ratio of *E*-**5a** and *Z*-**5a** was determined on the basis of integrated GLC values. The yields are listed in Table 1.

E-**5a**: IR (film) 1700 cm^{-1} (CO); ^1H NMR ($CDCl_3$): δ 0.38 (9H, s, Me_3Ge), 1.46 (9H, s, Me_3C), 6.64 (1H, s, =CH), 7.3 (5H, br, ArH). *Z*-**5a**): ^1H NMR ($CDCl_3$): δ 0.20 (9H, s, Me_3Ge), 1.57 (9H, s, Me_3C), 8.10 (1 H, s, =CH), 7.3 (5H, br, ArH). Anal. Found: C, 59.85; H, 7.69. $C_{16}H_{24}GeO_2$ calcd.: C, 59.88; H, 7.54%.

Entry 5 in Table 1. To a solution of LDA (5 mmol) in THF (10 ml) was added HMPA (2 ml). This was followed by the addition of the **2c** solution at −78°C, then the mixture was treated with benzaldehyde in the same manner as described above. Silica gel chromatography of the residue gave **5a**, **9a**, and (*Z*)-t-butyl 3-phenyl-2-(tri-n-butylstannyl)propenoate (*Z*-**6a**) [3]. The yields are listed in Table 1.

* The *E*,*Z* assignment of two geometrical isomers of the products was carried out by published methods [1, 5, 6], and involved the comparison of the chemical shifts of olefinic protons and trimethylgermyl groups in their ^1H NMR spectra and retention times of GLC, or the coupling constant (^3J(C–Hβ) between the olefinic proton and the carbonyl carbon in ^{13}C NMR.

Entries 6 to 8 in Table 1: General procedure. n-BuLi (3.2 ml, 5 mmol) was added to a solution of diisopropylamine (0.70 ml, 5 mmol) and potassium t-butoxide (0.56 g, 5 mmol) in THF (10 ml) at −78°C. After 10 min of stirring, the **2c** solution was added dropwise, and the mixture was stirred for a further hafl hour. To this mixture was added a solution of 5 mmol of benzaldehyde, [(*E*)-cinnamaldehyde, or benzophenone] in THF (3 ml) at the same temperature. After 15 min, the mixture was allowed to warm to room temperature and stirring was continued overnight. Work-up of the mixture was similar to that described for entry 4. The yields are shown in Table 1.

(*2E,4E*)-t-Butyl 5-phenyl-2-(trimethylgermyl)-2,4-pentadienoate (*E*-**5b**): m.p. 79–82°C; IR (Nujol) 1685 cm^{-1}; ^1H NMR ($CDCl_3$); δ 0.33 (9H, s, Me_3Ge), 1.55 (9H, s, Me_3C), 6.69 (1H, d, *J* 11 Hz, =CH), 6.74 (1H, d, *J* 16 Hz, =CH), 7.2–7.5 (5H, m, ArH), 7.73 (1H, dd, *J* 11 Hz, *J* 16 Hz, =CH); ^{13}C NMR ($CDCl_3$); δ 169.0 (^3J(CO–Hβ) 15.4 Hz). Anal. Found: C, 61.98; H, 7.53. $C_{18}H_{26}GeO_2$ calcd.: C, 62.31; H, 7.55%.

(*2Z,4E*)-t-Butyl 5-phenyl-2-(trimethylgermyl)-2,4-pentadienoate (*Z*-**5b**): IR (film) 1695 cm^{-1} (CO); ^1H NMR ($CDCl_3$): δ 0.46 (9H, s, Me_3Ge), 1.52 (9H, s, Me_3C), 6.82 (1H, d, *J* 15 Hz, =CH), 7.13 (1H, dd, *J* 12 Hz, *J* 15 Hz, =CH), 7.2–7.5 (5H, m, ArH), 7.70 (1H, d, *J* 12 Hz, =CH); ^{13}C NMR ($CDCl_3$): δ 170.3 (^3J(CO–Hß) 8.8 Hz). Anal. Found: C, 62.32; H, 7.48. $C_{18}H_{26}GeO_2$ calcd.: C, 62.31; H, 7.55%.

(*2E, 4E*)-t-Butyl 5-phenyl-2, 4-pentadienoate (*E*-**9b**): m.p. 45–48°C; IR (Nujol) 1710 cm^{-1} (CO); ^1H NMR ($CDCl_3$): δ 1.53 (9H, s, Me_3C), 5.92 (1H, d, *J* 15 Hz, =CHCO), 6.8–6.9 (2H, m, =CH × 2), 7.3–7.5 (6H, m, =CH and ArH). Anal. Found: C, 78.02; H, 8.11. $C_{15}H_{18}O_2$ calcd.: C, 78.23; H, 7.88%.

t-Butyl 3,3-diphenyl-2-(trimethylgermyl)propenoate (**5c**): m.p. 66–68°C; IR (film) 1700 cm^{-1} (CO); ^1H NMR ($CDCl_3$): δ 0.10 (9H, s, Me_3Ge), 1.24 (9H, s, Me_3C), 7.0–7.4 (10H, m, ArH). Anal. Found: C, 66.43; H, 6.98. $C_{22}H_{28}GeO_2$ calcd.: C, 66.55; H, 7.11%.

t-Butyl 3,3-diphenyl-2-(tri-n-butylstannyl)propenoate (**6c**): b.p. 95°C (0.02 Torr, oven temperature of a Kugelrohr distillation apparatus); IR (film) 1695 cm^{-1} (CO); ^1H NMR ($CDCl_3$): δ 1.24 (9H, s, Me_3C) *, 0.6–1.8 (27H, m, Bu_3Sn), 7.2–7.3 (10H, m, ArH).

t-Butyl 3,3-diphenylpropenoate (**9c**): m.p. 86–87°C; IR (Nujol) 1715 cm^{-1} (CO); ^1H NMR ($CDCl_3$): δ 1.28 (9H, s, Me_3C), 6.27 (1H, s, =CH), 7.0–7.5 (10H, m, ArH). Anal. Found: C, 81.20; H, 7.29. $C_{19}H_{20}O_2$ calcd.: C, 81.40; H, 7.19%.

*t-Butyl (trimethylgermyl) (trimethylsilyl)acetate (**10**)*

(A). A solution of **2b** (877 mg, 2.0 mmol) in THF (2 ml) was added to a solution of LDA (2.2 mmol) in THF (4 ml) at −78°C. After the solution had been stirred for 1 h, chlorotrimethylsilane (237 g, 2.2 mmol) was added dropwise, and the mixture was stirred for another hour. A saturated aqueous solution of NH_4Cl (10 ml) was added and the mixture was extracted with ethyl ether (10 ml × 3). The extract was dried over anhydrous $MgSO_4$, and concentrated. The residual oil (1.04 g) was subjected to GLC and GC-MS, and the main peak was compared with an

* Ager found the chemical shift of this proton to be 1.52 ppm [6].

authentic sample of **10** prepared by procedure B. The yield (79%) was determined on the basis of the integrated GLC value.

(B). t-Butyl (trimethylsilyl)acetate (370 mg, 2.0 mmol) was added to LDA (2.2 mmol) in THF (5 ml) at −78°C. After 1 h of stirring, chlorotrimethylgermane (294 mg, 1.9 mmol) was added and the mixture was stirred continuously for 1 h. Saturated aqueous NH_4Cl was added and the mixture was extracted with ethyl ether. The extract was dried ($MgSO_4$), concentrated, and distilled to give **10** (487 mg, 83%): b.p. 110–115°C (22 Torr); IR (film) 1690 cm^{-1} (CO); ^1H NMR ($CDCl_3$): δ 0.10 (9H, s, Me_3Si), 0.26 (9H, s, Me_3Ge), 1.42 (9H, s, Me_3C), 1.46 (1H, s, CH). Anal. Found: C, 47.05; H, 9.25. $C_{12}H_{28}GeO_2Si$ calcd.: C, 47.25; H, 9.25%.

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