Peterson Olefination Reaction Using (Trimethylgermyl)acetate. Stereoselective Synthesis of (*E*)-2-Alkenoic Acid Esters

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Received May 14, 1990

Peterson-type reaction of (trimethylgermyl)acetates **1** with aldehydes and ketones **2** gave stereoselectively (*E*)-2-alkenoic acid esters (*E*)-**4** after stirring at −78 °C and warming to room temperature. High yields of the reaction intermediates *threo*- and *erythro*-3-hydroxy-2-(trimethylgermyl)alkanoic acid esters **3** were obtained when the reaction was quenched at −78 °C. The paths for conversion of *threo*-**3** and *erythro*-**3** to (*E*)-**4** are discussed.

Introduction

The lithium enolates of (trimethylsilyl)acetates have been widely employed for the synthesis of 2-alkenoic acid esters from aldehydes and ketones (Peterson reaction).[1] In the course of our investigations on organogermanium compounds, we noticed that the Peterson-type reaction of ethyl (trimethylgermyl)acetate with some aldehydes gave (*E*)-2-alkenoic acid esters stereoselectively,[2] whereas the use of the silyl analogues gave mixtures of the geometrical isomers.[3] This result let us investigate the role of germanium in the induction of stereoselectivity in the Peterson reaction.

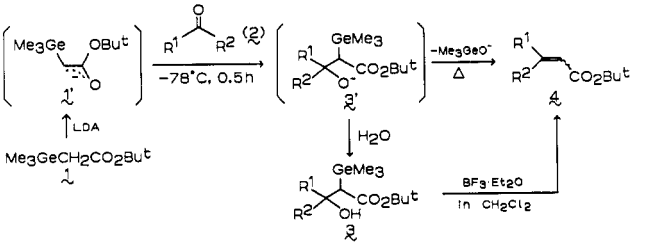
Results and Discussion

tert-Butyl (trimethylgermyl)acetate (**1**) was treated with lithium diisopropylamide (LDA) and an equimolar amount of aldehydes or ketones **2** was added at −78 °C in tetrahydrofuran (THF) (Scheme I). The reaction was quenched after warming to room temperature and stirring for the times listed in Table I. Moderate yields of mixtures of the geometrical isomers *tert*-butyl 2-alkenoates (*E*)-**4** and (*Z*)-**4** were obtained, accompanied by small amounts of the starting materials and 3-hydroxy-2-(trimethylgermyl)alkanoates **3** (column 6 in Table I). However, the *E* selectivity of **4** was surprisingly high compared with that of the Peterson reaction using (trimethylsilyl)acetates.[3]

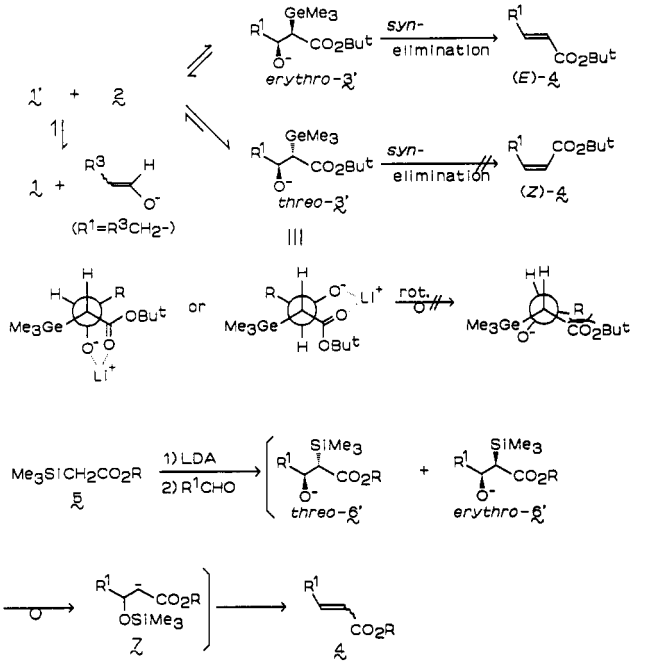
The lithium enolates of **1** (**1'**) reacted initially with **2** to form mixtures of the diastereomers of 3-hydroxy-2-(trimethylgermyl)alkanoates (*erythro*-**3** and *threo*-**3**),[5] which were converted into (*E*)-**4** and (*Z*)-**4** with the elimination of the (trimethylgermyl)oxy group. Because syn elimination of the germyloxy group occurs in the basic medium in a manner similar to elimination of the (trimethylsilyl)oxy group in the Peterson reaction,[6] the major isomer (*E*)-**4** must be formed from *erythro*-**3** (Scheme II).

Quenching of the reaction at −78 °C before elevation of the reaction temperature gave mixtures of the diastereomers of **3** in high yields (next to last column in Table I). High diastereoselectivity was observed in the products from *sec*- and *tert*-alkyl aldehydes **2d,e,g** and phenyl ketones **2m,n** (entries 4, 5, 7, 13, and 14), and *n*-alkyl aldehydes **2a–c,f**, benzaldehyde (**2h**), and alkyl ketones **2k,l** gave mixtures of about 8:2 (entries 1–3, 6, 8, 11, and 12).

Scheme I



Scheme II



The diastereomers from *n*-octanal (**2a**) or benzaldehyde (**2h**) were separated on a silica gel column. The major isomer from **2a** was stereoselectively converted to (*E*)-*tert*-butyl 2-decenoate ((*E*)-**4a**, 96%) and that from **2h** to (*E*)-*tert*-butyl cinnamate ((*E*)-**4h**, 96%) by treatment with boron trifluoride etherate in dichloromethane. Under similar conditions, the minor isomer from **2a** was eliminated to (*Z*)-*tert*-butyl 2-decenoate ((*Z*)-**4a**, 99%) and that from **2h** to (*Z*)-cinnamate ((*Z*)-**4h**, 97%). In the acidic medium, anti elimination of hydroxytrimethylgermane occurs in the conversion from **3** to **4**, similar to the elimination of hydroxytrimethylsilane in the silyl analogues. Thus the major isomers are assigned to *threo*-**3** and the minor isomers to *erythro*-**3**. Selected ^{1}H NMR spectral data for *threo*-**3a,h** and *erythro*-**3a,h** are listed in Table

(1) For reviews of the Peterson reaction, see, (a) Ager, D. J. *Org. React.* **1990**, *38*, 1. (b) Ager, D. J. *Synthesis* **1984**, 384. (c) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983; p 58.

(2) Inoue, S.; Sato, Y. *Organometallics* **1988**, *7*, 739.

(3) The reaction of lithium enolate of ethyl (trimethylsilyl)acetate with carbonyl compounds gave 2-alkenoates in the following yields (ratios of *E* and *Z*):[4] *n*-nonanal, 81% (1:1); benzaldehyde, 84% (3:1 to 9:1); acetophenone, 63% (2:1).

(4) Taguchi, H.; Shimoji, K.; Yamamoto, H.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2529.

(5) In this paper the stereochemical descriptions threo and erythro are employed in the following sense. The main chain of the aldol is written in an extended zigzag fashion. If the bonds to the α-trimethylgermyl and the β-hydroxy groups both project either toward or away from the viewer, this is the erythro diastereomer.

(6) Hudrlik, P. F.; Peterson, D. *J. Am. Chem. Soc.* **1975**, *97*, 1464.

0022-3263/91/1956-0347$02.50/0

Table I. Preparation of *tert*-Butyl 3-Hydroxy-2-(trimethylgermyl)alkanoates 3 and 2-Alkanoates 4

		aldehydes and ketones 2		quenched at room temperature		quenched at −78 °C	quenched at −78 °C and then treated with BF_3·OEt_2
entry		R^1	R^2	reactn time, h	% yield of 4 (E/Z)[a]	% yield of 3 (threo/erythro)[b]	% yield of 4 (E/Z)[a]
1	**a**	$Me(CH_2)_6$	H	4	64 (93:7)	80 (80:20)	83 (79:21)
2	**b**	$Ph(CH_2)_2$	H	3	65 (90:10)	81 (79:21)	73 (69:31)
3	**c**	t-$BuCH_2CHMeCH_2$	H	5	66 (95:5)	77 (79:21)[c]	68 (78:22)
4	**d**	i-Pr	H	3	54 (>99:<1)	91 (97:3)	75 (99:1)
5	**e**	c-C_6H_{11}	H	2	78 (96:4)	84 (95:5)	83 (96:4)
6	**f**	n-PrCH=CH	H	2	92 (97:3)	95 (81:19)	82 (81:19)
7	**g**	t-Bu	H	3	41 (>99:<1)[d]	61 (98:2)	42 (>99:<1)
8	**h**	Ph	H	6	83 (>99:<1)	99 (80:20)[e]	81 (81:19)
9	**i**	$-(CH_2)_4-$		1	53	77	69
10	**j**	$-(CH_2)_5-$		1	83	92	97
11	**k**	$Me(CH_2)_5$	Me			95 (66:34)	91 (63:37)
12	**l**	t-Bu	Me			39 (87:13)	31 (97:3)
13	**m**	Ph	Me	1	17 (>99:<1)[f]	96 (93:7)	91 (93:7)
14	**n**	Ph	Et			97 (91:9)	97 (96:4)

[a] Determined from the integrated values of GLC analyses. [b] Determined on the basis of the integrated values of protons of ^1H NMR. [c] *threo*-**3c** and *erythro*-**3c** were mixtures of C-5 epimers (1:1 and 3:1), respectively. [d] *threo-tert*-Butyl 3-hydroxy-4,4-dimethyl-2-(trimethylgermyl)pentanoate (*threo*-**3g**, 29%) remained in the reaction mixture. [e] Ratio of isolated isomers. [f] Acetophenone (**2m**, 64%) was recovered.

Table II. Selected ^1H NMR Spectral Data for 3 ($RCH_b(OH_c)CH_a(GeMe_3)CO_2Bu^t$)

	chemical shift, δ						coupling constant, Hz			
	H_a		H_b		H_c		J_{ab}		J_{bc}	
compd	threo	erythro	threo	erythro	threo	erythro	threo	erythro	threo	erythro
3a	2.19	2.25	3.68	4.09	3.45	2.55	3.7	5.1	10.1	4.6
3b	2.20	2.28	3.71	4.12	3.61	2.64	3.5	4.8	10.3	4.6
3c[a]	2.22	2.20	3.72	4.12	3.53	2.38	3.3	5.3	10.6	4.6
3c[a]	2.13	2.21	3.77	*b*	3.38	*b*	3.8	5.0	10.1	
3d	2.35	2.37	3.25	3.85	3.61	2.31	2.9	6.4	10.6	4.5
3e	2.35	2.40	3.29	3.87	3.48	2.49	2.9	5.7	10.8	4.4
3f	2.25	2.32	4.23	4.52	3.44	2.52	4.9	6.1	9.0	4.2
3g	2.29	2.39	3.33	3.97	4.99	1.52	0	9.7	9.7	6.2
3h	2.65	2.62	4.91	5.23	3.87	2.90	5.6	6.4	8.6	2.9

[a] A C-5 epimer. [b] Signals of the minor epimer could not be assigned due to an overlap with other signals.

II. The chemical shifts of the β-hydrogens (H_b) are consistently less for the threo than for the erythro isomer and conversely those of the hydroxyl groups (H_c) are larger for the threo than the erythro isomer. The vicinal coupling constant J_{ab} is less for the threo (3–6 Hz) than for the erythro isomer (5–7 Hz), and J_{bc} is larger for the threo (9–11 Hz) than for erythro isomer (3–5 Hz). The diastereomers of **3b–g** were separated on silica gel columns and their stereochemistry was assigned by comparison of their ^1H NMR spectra in this sense. Mixtures of the diastereomers were also treated with boron trifluoride to give mixtures of (*E*)-**4** and (*Z*)-**4**. Their *E*/*Z* ratios corresponded with the ratios of *threo*-**3** and *erythro*-**3** (last column in Table I).

There seemed to be an inconsistency between *threo*-**3** being the major product when the reactions were quenched at −78 °C and (*E*)-**4** being formed selectively when quenching was at room temperature, because under the basic condition *threo*-**3** must give (*Z*)-**4** by the syn elimination.

The reaction of **1′** with **2h** was quenched after different reaction times and the product ratios were measured. Although the yield of **3h** increased over reaction times at 10 s to 30 min at −78 °C, no notable change of the ratio of diastereomers (threo/erythro = 8:2) was observed (Table III, entries 1–3). After an hour at room temperature, the reaction products became a mixture of almost pure *threo*-**3h** and (*E*)-**4h**; the change to the latter was completed within 6 h (entries 4 and 5). These results suggest that *erythro*-**3h** was quickly converted to (*E*)-**4h**, while

Table III. Reaction of Ester Enolate 1 with Benzaldehyde (2h)

		% yield and ratio	
entry	reaction conditions: time/temp, °C	**3h** (threo/erythro)[a]	**4h** (E/Z)[b]
1	10 s/−78[c]	86 (80:20)	
2	5 min/−78	91 (83:17)	1–3
3	30 min/−78	99 (80:20)[d]	1–3
4	30 min/−78, then 1 h/r.t.[e]	20 (>99:<1)	71 (>99:<1)
5	30 min/−78, then 6 h/r.t.	0	83 (>99:<1)

[a] The ratio was determined by ^1H NMR. [b] The ratio was determined by GLC. [c] Benzaldehyde was added in one portion. [d] Ratio of isolated isomers. [e] r.t. = room temperature.

threo-**3h** was not changed to (*Z*)-**4h** but slowly to (*E*)-**4h** at room temperature.

An equimolar amount of LDA was added to THF solutions of *threo*-**3h** and *erythro*-**3h**. The former was transformed into a mixture of (*E*)-**4h** (71%), **1** (16%), and unchanged *threo*-**3h** (13%) after 1 h at room temperature, whereas no detectable change was observed at −78 °C. In the latter solution, 21% of *erythro*-**3h** was converted to (*E*)-**4h** after 1 h at −78 °C, and the conversion was completed at room temperature.

These results may be explained as follows. Apparently, the syn elimination of the (trimethylgermyl)oxy group occurred smoothly in the conversion from *erythro*-**3** to (*E*)-**4** during the temperature rise. However, the difficulty of an overlap of the R and (*tert*-butyloxy)carbonyl groups in *threo*-**3** interfered with the syn elimination to (*Z*)-**4** (see

Scheme II). Dissociation of *threo*-**3** to a mixture of **1'** and **2** (retro-aldol reaction) takes place with the elevation of temperature, and their recombination gives partially *erythro*-**3**, which is easily converted to (*E*)-**4**. There may be two equilibria between *threo*-**3h** or *erythro*-**3h** and a mixture of **1'** and **2h** at room temperature. This equilibrium may result in the predominant formation of (*E*)-**4**.

In the reaction of the (trimethylsilyl)acetate anion with aldehydes, the trimethylsilyl groups in the two diastereomers (*threo*-**6'** and *erythro*-**6'**) may quickly rearrange to give the same intermediate (**7**),[7] which is subsequently converted to (*E*)- and (*Z*)-olefins. Thus, geometrical selectivity cannot be expected from the Peterson reaction using silicon compounds. Rearrangement of the trimethylgermyl group to the oxy anion in *threo*-**3'** and *erythro*-**3'** does not occur because the trimethylgermyl group has high affinity to carbon rather than oxygen, in contrast to the trimethylsilyl group, which has higher affinity to oxygen.[2,8]

When the reaction mixtures of **1** with **2** quenched at −78 °C were subsequently treated with boron trifluoride etherate, high yields of **4** were obtained, and their *E*/*Z* ratios were controlled by the threo/erythro ratios of **3** (Table I). If **3** has higher threo selectivity, an improved yield of (*E*)-**4** is obtainable by acid treatment. Changing the reaction temperature to −100 °C and varying the solvents (Et_2O, dimethoxyethane, and 20% HMPA in THF) and base (lithium hexamethyldisilazide) did not lead to improvement of the diastereoselectivity.

Larchevêque et al. reported that change of the counter cation from Li^+ to $MgBr^+$ in the Peterson reaction of the (trimethylsilyl)acetate anion with aldehydes brought about selective formation of threo isomers of 3-hydroxy-2-(trimethylsilyl)alkanoates.[9,10] However, application of their method to the reaction of **1** with **2** resulted in poor diastereoselectivity (**3a**, threo/erythro = 66:34; **3h**, threo/erythro = 70:30). No effect of bulkiness of the alkyloxy group of **1** was observed between ethyloxy and *tert*-butyloxy. 2,6-Di-*tert*-butyl-4-methylphenyl (trimethylgermyl)acetate led to selective formation of a threo isomer (>99%) but the yield was low (35%).[11]

It is known that the lithium enolate of *tert*-butyl propionate has the *E* geometry in THF; however, the aldol products from the reaction with aldehydes were 1:1 mixtures of the diastereomers.[12] Fairly high threo selectivities were observed in the aldol products from **1'** and also from the magnesium enolates of (trimethylsilyl)acetates.[9] In order to determine the geometry of **1'**, we tried to quench to enolate with chlorotrimethylsilane; however, the expected *O*-*tert*-butyl-*O*-(trimethylsilyl)(trimethylgermyl)-ketene acetal was not obtained and *tert*-butyl (trimethylgermyl)(trimethylsilyl)acetate was the sole product.[13]

It is well known that the Emmons–Wadsworth–Horner reaction using phosphonate carbanions is useful for the stereoselective synthesis of (*E*)-olefins;[14] however, the application is limited for readily enolizable ketones.[4,15] The reaction using (trimethylgermyl)acetate is widely applicable for various aldehydes and ketones.

Experimental Section

All reactions were carried out under a nitrogen atmosphere. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone ketyl prior to use. Dimethoxyethane was distilled from calcium hydride. Hexamethylphosphoric triamide (HMPA) was distilled under reduced pressure from sodium. All melting points and boiling points are uncorrected. ^1H NMR spectra were recorded at 60, 100, or 400 MHz. Silica gel (BW-200 or BW-300, purchased from Fuji-Davison) was used for column chromatography. Gas chromatographic analyses were carried out on a 2-m, 3% silicone SE-30 column.

***tert*-Butyl (Trimethylgermyl)acetate (1).** A solution of *n*-butyllithium in hexane (1.58 M, 35 mL, 55 mmol) was added to a solution of diisopropylamine (5.57 g, 55 mmol) in THF (60 mL) at 0 °C, and the mixture was stirred for 15 min. The solution of lithium diisopropylamide (LDA) thus prepared was cooled at −78 °C and *tert*-butyl acetate (6.39 g, 55 mmol) in THF (30 mL) was added dropwise with additional stirring for 0.5 h. The chilled solution was added to a solution of chlorotrimethylgermane (7.66 g, 50 mmol) in THF (50 mL) at −78 °C through a cannula. After 1 h of stirring, saturated aqueous NH_4Cl was added. The organic layer was separated and the aqueous layer was extracted with diethyl ether. The combined extracts were washed with water and saturated aqueous NaCl, dried ($MgSO_4$), and concentrated. Distillation of the residual oil gave **1** (9.70 g, 83%): bp 65.5–66.0 °C (10 mmHg); IR (film) 1710, 1260, 1170, 1090, 825, 605 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.27 (s, 9 H), 1.43 (s, 9 H), 1.84 (s, 2 H). Anal. Calcd for $C_9H_{20}GeO_2$: C, 46.42; H, 8.66. Found: C, 46.15; H, 8.57.

2,6-Di-*tert*-butyl-4-methylphenyl (Trimethylgermyl)-acetate. In a manner similar to that described above for **1**, 2,6-di-*tert*-butyl-4-methylphenyl acetate[16] (8.66 g, 33 mmol) was treated with a solution of LDA (33 mmol) and chlorotrimethylgermane (4.59 g, 30 mmol). The ethereal extract was distilled to give 8.34 g (73%) of 2,6-di-*tert*-butyl-4-methylphenyl (trimethylgermyl)acetate: bp 139.0–142.0 °C (0.9 mmHg); mp 62.5–63.5 °C; IR (Nujol) 1765, 1210, 1100, 850, 630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.37 (s, 9 H), 1.34 (s, 18 H), 2.25 (s, 2 H), 2.31 (s, 3 H), 7.11 (s, 2 H). Anal. Calcd for $C_{20}H_{34}GeO_2$: C, 63.37; H, 9.04. Found: C, 63.63; H, 9.30.

Preparation of *tert*-Butyl 2-Alkenoates 4 from 1 and Aldehydes or Ketones 2. General Procedure. A solution of **1** (279 mg, 1.2 mmol) in THF (3 mL) was added dropwise at −78 °C to a solution of LDA, prepared from *n*-butyllithium (1.58 M in hexane, 0.76 mL, 1.2 mmol) and diisopropylamine (121 mg, 1.2 mmol) in THF (4 mL). After 0.5 h of stirring, a solution of **2** (1 mmol) in THF (3 mL) was added. Stirring was continued for 0.5 h at −78 °C and then at room temperature for the times indicated in Table I. The reaction mixture was cooled in an ice bath and then mixed with a saturated aqueous NH_4Cl solution. The organic layer was separated and the aqueous layer was extracted with diethyl ether. The combined extracts were washed with water and saturated NaCl, dried ($MgSO_4$), and evaporated under reduced pressure. The residue was purified by distillation or column chromatography on silica gel (hexane–benzene). The ratio of *E* and *Z* isomers was determined by GLC. The yields and ratios are shown in the middle column of Table I.

***tert*-Butyl (*E*)-5-phenyl-2-pentenoate ((*E*)-4b):** bp 90 °C (0.15 mmHg, Kugelrohr); IR (film) 1710, 1650, 1145, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.47 (s, 9 H), 2.33–2.61 (m, 2 H), 2.64–2.88 (m, 2 H), 5.77 (dt, J = 15.5, 1.5 Hz, 1 H), 6.89 (dt, J = 15.5, 6.5 Hz, 1 H), 7.05–7.40 (m, 5 H). Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.43; H, 8.87.

(7) Yamamoto, K.; Tomo, Y.; Suzuki, S. *Tetrahedron Lett.* **1980**, *21*, 2861.

(8) (a) Inoue, S.; Sato, Y. *Organometallics* **1986**, *5*, 1197; **1987**, *6*, 2568. (b) Urayama, S.; Inoue, S.; Sato, Y. *J. Organomet. Chem.* **1988**, *354*, 155.

(9) Larchevêque, M.; Debal, A. *J. Chem. Soc., Chem. Commun.* **1981**, 877.

(10) We examined the reaction of benzaldehyde with methyl (trimethylsilyl)acetate magnesium enolate according to Larchevêque's report,[9] but the ratio of diastereomers was 90:10 (83% yield), not 100:0 as reported.

(11) Aldol reaction using 2,6-di-*tert*-butyl-4-methylphenyl esters led predominantly to threo aldols: Heathcock, C. H.; Pirrung, M. C.; Montgomery, S. H.; Lampe, J. *Tetrahedron* **1981**, *37*, 4087.

(12) Heathcock, C. H.; Buse, C. T.; Kleschick, W. A.; Pirrung, M. C.; Sohn, J. E.; Lampe, J. *J. Org. Chem.* **1980**, *45*, 1066.

(13) Silylation of the lithium enolate of *tert*-butyl (trimethylsilyl)-acetate gave a mixture of *tert*-butyl bis(trimethylsilyl)acetate and *O*-(trimethylsilyl)ketene *tert*-butyl trimethylsilyl acetal in the ratio of 70:30. Hartzell, S. L.; Rathke, M. W. *Tetrahedron Lett.* **1976**, 2737.

(14) Reviews: Wadsworth, W. S. *Org. React.* **1977**, *25*, 73. Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863.

(15) Corey, E. J.; Shulman, J. I. *J. Org. Chem.* **1970**, *35*, 777.

(16) Heathcock, C. H.; Young, S. D.; Hagen, J. P.; Pirrung, M. C.; White, C. T.; VanDerveer, D. *J. Org. Chem.* **1980**, *45*, 3846 and references cited therein.

***tert*-Butyl (*Z*)-5-phenyl-2-pentenoate ((*Z*)-4b)**: bp 70 °C (0.1 mmHg, Kugelrohr); IR (film) 1710, 1640, 1150, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.48 (s, 9 H), 2.62–3.04 (m, 4 H), 5.68 (dt, J = 11.5, 1.5 Hz, 1 H), 6.13 (dt, J = 11.5, 7.0 Hz, 1 H), 7.02–7.39 (m, 5 H). Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.34; H, 8.89.

***tert*-Butyl (*E*)-5,7,7-trimethyl-2-octenoate ((*E*)-4c)**: bp 130 °C (13 mmHg, Kugelrohr); IR (film) 1710, 1650, 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (s, 9 H), 0.96 (d, J = 7 Hz, 3 H), 1.06–1.80 (m, 3 H), 1.48 (s, 9 H), 1.94–2.28 (m, 2 H), 5.71 (d, J = 16 Hz, 1 H), 6.81 (dt, J = 16, 7 Hz, 1 H). Anal. Calcd for $C_{15}H_{28}O_2$: C, 74.95; H, 11.74. Found: C, 75.20; H, 11.77.

***tert*-Butyl (*Z*)-5,7,7-trimethyl-2-octenoate ((*Z*)-4c)**: bp 105 °C (9 mmHg, Kugelrohr); IR (film) 1715, 1635, 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (s, 9 H), 0.95 (d, J = 7 Hz, 3 H), 1.06–1.84 (m, 3 H), 1.49 (s, 9 H), 2.55 (td, J = 7, 1.5 Hz, 2 H), 5.70 (dd, J = 12, 1.5 Hz, 1 H), 6.10 (dt, J = 12, 7 Hz, 1 H). Anal. Calcd for $C_{15}H_{28}O_2$: C, 74.95; H, 11.74. Found: C, 74.84; H, 12.10.

***tert*-Butyl (*E*)-4-methyl-2-pentenoate ((*E*)-4d)**: bp 80 °C (60 mmHg, Kugelrohr) [lit.[19] bp 98 °C (41 mmHg)]; IR (film) 1710, 1645, 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.06 (d, J = 6.8 Hz, 6 H), 1.49 (s, 9 H), 2.20–2.62 (m, 1 H), 5.67 (d, J = 15.6 Hz, 1 H), 6.83 (dd, J = 15.6 and 6.8 Hz, 1 H).

***tert*-Butyl (2*E*,4*E*)-octa-2,4-dienoate ((*E*)-4f)**: bp 120 °C (10 mmHg, Kugelrohr); IR (film) 1705, 1640, 1610, 1135 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (t, J = 7.4 Hz, 3 H), 1.45 (sextet, J = 7.4 Hz, 2 H), 1.48 (s, 9 H), 2.13 (app q, J = 7.0 Hz, 2 H), 5.71 (d, J = 15.4 Hz, 1 H), 6.07 (dt, J = 15.4, 6.6 Hz, 1 H), 6.15 (dd, J = 15.4, 10.1 Hz, 1 H), 7.16 (dd, J = 15.4, 10.1 Hz, 1 H). Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.30. Found: C, 73.34; H, 10.22.

***tert*-Butyl (2*Z*,4*E*)-octa-2,4-dienoate ((*Z*)-4f)**: bp 80 °C (8 mmHg, Kugelrohr); IR (film) 1710, 1640, 1600, 1155 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92 (t, J = 7.4 Hz, 3 H), 1.47 (sextet, J = 7.4 Hz, 2 H), 1.50 (s, 9 H), 2.17 (m, 2 H), 5.48 (d, J = 11.4 Hz, 1 H), 6.02 (dt, J = 15.3, 7.2 Hz, 1 H), 6.47 (t, J = 11.4 Hz, 1 H), 7.34 (dddd, J = 15.3, 11.4, 2.6, 1.5 Hz, 1 H). Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.30. Found: C, 73.23; H, 10.22.

***tert*-Butyl (*E*)-4,4-dimethyl-2-pentenoate ((*E*)-4g)**: bp 80 °C (27 mmHg, Kugelrohr); mp 70.0–71.0 °C; IR (Nujol) 1715, 1645, 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.06 (s, 9 H), 1.48 (s, 9 H), 5.57 (d, J = 15 Hz, 1 H), 6.80 (d, J = 15 Hz, 1 H); mass spectrum, m/e 169 (2.5, $M^+ - CH_3$), 129 (52), 128 (100), 113 (55), 111 (87), 83 (33), 57 (82); exact mass for $M^+ - 15$ ion, found 169.12317, calcd for $C_{10}H_{17}O_2$ 169.12283.

***tert*-Butyl cyclopentylideneacetate (4i)**: bp 65 °C (16 mmHg, Kugelrohr); IR (film) 1705, 1650, 1170, 1120 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.49 (s, 9 H), 1.49–1.92 (m, 4 H), 2.14–3.02 (m, 4 H), 5.60–5.80 (m, 1 H). Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.44; H, 10.23.

***tert*-Butyl cyclohexylideneacetate (4j)**: bp 120 °C (12 mmHg, Kugelrohr); IR (film) 1705, 1640, 1145 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.32–1.74 (m, 6 H), 1.48 (s, 9 H), 2.04–2.26 (m, 2 H), 2.66–2.88 (m, 2 H), 5.53 (s, 1 H). Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.30; H, 10.61.

***tert*-Butyl (*E*)-3-methyl-2-nonenoate ((*E*)-4k)**: bp 65 °C (0.3 mmHg, Kugelrohr); IR (film) 1705, 1640, 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 6.8 Hz, 3 H), 1.25–1.33 (m, 6 H), 1.41–1.48 (m, 2 H), 1.48 (s, 9 H), 2.09 (t, J = 7.9 Hz, 2 H), 2.11 (d, J = 1.3 Hz, 3 H), 5.58 (q, J = 1.3 Hz, 1 H). Anal. Calcd for $C_{14}H_{26}O_2$: C, 74.29; H, 11.58. Found: C, 74.21; H, 11.49.

***tert*-Butyl (*Z*)-3-methyl-2-nonenoate ((*Z*)-4k)**: bp 65 °C (0.3 mmHg, Kugelrohr); IR (film) 1705, 1640, 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 6.9 Hz, 3 H), 1.25–1.37 (m, 6 H), 1.40–1.49 (m, 2 H), 1.47 (s, 9 H), 1.84 (d, J = 1.3 Hz, 3 H), 2.57 (t, J = 7.8 Hz, 2 H), 5.56 (s, 1 H). Anal. Calcd for $C_{14}H_{26}O_2$: C, 74.29; H, 11.58. Found: C, 74.19; H, 11.38.

***tert*-Butyl (*E*)- and (*Z*)-3,4,4-trimethyl-2-pentenoate (4l)**: bp 75 °C (10 mmHg, Kugelrohr); IR (film) 1700, 1625, 1145 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.09 (s, *E*) and 1.20 (s, *Z*) (total 9 H), 1.48 (s, 9 H), 1.80 (d, J = 1.5 Hz, *Z*) and 2.12 (d, J = 1.2 Hz, *E*) (total 3 H), 5.57 (q, J = 1.5 Hz, *Z*), and 5.65 (q, J = 1.2 Hz, *E*) (total 1 H). Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.94; H, 11.05.

***tert*-Butyl (*E*)-3-phenyl-2-pentenoate ((*E*)-4n)**: bp 65 °C (0.05 mmHg, Kugelrohr); IR (film) 1705, 1620, 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.07 (t, J = 7.6 Hz, 3 H), 1.52 (s, 9 H), 3.05 (q, J = 7.6 Hz, 2 H), 5.91 (s, 1 H), 7.29–7.53 (m, 5 H). Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.60; H, 8.80.

***tert*-Butyl (*Z*)-3-phenyl-2-pentenoate ((*Z*)-4n)**: IR (film) 1700, 1630, 1145, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.03 (t, J = 7.6 Hz, 3 H), 1.21 (s, 9 H), 2.42 (qd, J = 7.6 and 1.5 Hz, 2 H), 5.77 (t, J = 1.5 Hz, 1 H), 7.03–7.43 (m, 5 H); mass spectrum, m/e 232 (3, M^+), 176 (92), 159 (44), 158 (100), 57 (33); exact mass for M^+ ion, found 232.14731, calcd for $C_{15}H_{20}O_2$ 232.14630.

The structures of **4a**,[17] **4e**,[17] **4h**,[17] and **4m**[18] were confirmed by comparing their ^1H NMR spectra with the reported values.

***tert*-Butyl 3-Hydroxy-2-(trimethylgermyl)alkanoates 3. General Procedure.** Reaction of **1** and **2** was carried out according to the general preparation of **4** described above and quenched with 5% aqueous citric acid after stirring at −78 °C for 0.5 h, without the elevation of temperature. The mixture was extracted with ether. The organic layer was washed with water and saturated aqueous NaCl, dried ($MgSO_4$), and concentrated in vacuo. The residue was chromatographed on a silica gel column (hexane/ethyl acetate) to give *threo*-**3** and *erythro*-**3**. The ratio of the diastereomers was determined from the integrated values of hydrogens at C-3 carbons in ^1H NMR of the residual oil. The yields and ratios are summarized in the next to last column in Table I.

***threo-tert*-Butyl 3-hydroxy-2-(trimethylgermyl)decanoate (*threo*-3a)**: bp 100 °C (0.7 mmHg, oven temperature of a Büchi Kugelrohr distillation apparatus); IR (film) 3500, 1685, 1150, 830, 605 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.30 (s, 9 H), 0.88 (t, J = 7.0 Hz, 3 H), 1.22–1.38 (m, 9 H), 1.43–1.52 (m, 2 H), 1.46 (s, 9 H), 1.62–1.68 (m, 1 H), 2.19 (d, J = 3.7 Hz, 1 H), 3.45 (d, J = 10.1 Hz, 1 H), 3.64–3.72 (m, 1 H). Anal. Calcd for $C_{17}H_{36}GeO_3$: C, 56.55; H, 10.05. Found: C, 56.49; H, 9.85.

***erythro-tert*-Butyl 3-hydroxy-2-(trimethylgermyl)decanoate (*erythro*-3a)**: bp 100 °C (0.5 mmHg, Kugelrohr); IR (film) 3450, 1685, 1150, 830, 605 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.31 (s, 9 H), 0.88 (t, J = 6.9 Hz, 3 H), 1.23–1.36 (m, 9 H), 1.36–1.61 (m, 3 H), 1.45 (s, 9 H), 2.25 (d, J = 5.1 Hz, 1 H), 2.55 (d, J = 4.6 Hz, 1 H), 4.05–4.12 (m, 1 H). Anal. Calcd for $C_{17}H_{36}GeO_3$: C, 56.55; H, 10.05. Found: C, 56.31; H, 9.78.

***threo-tert*-Butyl 3-hydroxy-5-phenyl-2-(trimethylgermyl)pentanoate (*threo*-3b)**: bp 100 °C (0.6 mmHg, Kugelrohr); IR (film) 3470, 1680, 1140, 830, 600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.29 (s, 9 H), 1.46 (s, 9 H), 1.72–1.80 (m, 1 H), 1.94–2.03 (m, 1 H), 2.20 (d, J = 3.5 Hz, 1 H), 2.66 (ddd, J = 13.7, 10.0, 6.4 Hz, 1 H), 2.82 (ddd, J = 13.7, 10.2, 5.3 Hz, 1 H), 3.61 (d, J = 10.3 Hz, 1 H), 3.68–3.74 (m, 1 H), 7.15–7.20 (m, 3 H), 7.26–7.30 (m, 2 H). Anal. Calcd for $C_{18}H_{30}GeO_3$: C, 58.91; H, 8.24. Found: C, 58.79; H, 8.24.

***erythro-tert*-Butyl 3-hydroxy-5-phenyl-2-(trimethylgermyl)pentanoate (*erythro*-3b)**: bp 95 °C (0.15 mmHg, Kugelrohr); mp 56.5–58.5 °C, IR (Nujol) 3450, 1685, 1140, 830, 605 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.31 (s, 9 H), 1.44 (s, 9 H), 1.67–1.75 (m, 1 H), 1.86–1.96 (m, 1 H), 2.28 (d, J = 4.8 Hz, 1 H), 2.64 (d, J = 4.6 Hz, 1 H), 2.65 (ddd, J = 13.7, 9.8, 6.8 Hz, 1 H), 2.85 (ddd, J = 13.7, 10.2, 5.2 Hz, 1 H), 4.09–4.15 (m, 1 H), 7.16–7.20 (m, 3 H), 7.26–7.30 (m, 2 H). Anal. Calcd for $C_{18}H_{30}GeO_3$: C, 58.91; H, 8.24. Found: C, 58.67; H, 8.49.

***threo-tert*-Butyl 3-hydroxy-5,7,7-trimethyl-2-(trimethylgermyl)octanoate (*threo*-3c, 1:1 mixture of C-5 epimers)**: bp 125 °C (0.8 mmHg, Kugelrohr); IR (film) 3480, 1680, 1145, 830, 605 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.31 and 0.30 (s, 9 H), 0.90 (s, 9 H), 0.92 and 0.93 (d, J = 6.4 and 6.6 Hz, 3 H), 1.03–1.23 (m, 2 H), 1.45 and 1.46 (s, 9 H), 1.49–1.84 (m, 3 H), 2.22 and 2.13 (d, J = 3.3 and 3.8 Hz, 1 H), 3.58 and 3.38 (d, J = 10.6 and 10.1 Hz, 1 H), 3.72 and 3.77 (m, 1 H). Anal. Calcd for $C_{18}H_{38}GeO_3$: C, 57.64; H, 10.21. Found: C, 57.77; H, 10.12.

(17) Sato, Y.; Takeuchi, S. *Synthesis* **1983**, 734.

(18) Takai, K.; Hotta, Y.; Oshima, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1698. They assigned the geometrical isomers of *tert*-butyl 3-methylcinnamate (**4m**) by ^1H NMR analysis as follows: a vinylic proton of the *E* isomer appeared at 5.72 ppm and that of the *Z* isomer at 5.96 ppm. However, we assigned the signal at 5.72 ppm to the *Z* isomer and that of 5.96 ppm to the *E* isomer, the reverse of their conclusion based on comparison of the NOE effect (9% for *Z* isomer, 0% for *E* isomer) between the 3-methyl and vinylic protons.

(19) Hartzell, S. L.; Sullivan, D. F.; Rathke, M. W. *Tetrahedron Lett.* **1974**, 1403.

***erythro-tert*-Butyl 3-hydroxy-5,7,7-trimethyl-2-(trimethylgermyl)octanoate (*erythro*-3c, 3:1 mixture of C-5 epimers)**: bp 90 °C (0.15 mmHg, Kugelrohr); mp 66.0–68.0 °C; IR (Nujol) 3450, 1690, 1145, 830, 600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.31 (s, 9 H), 0.91 and 0.90 (s, 9 H), 0.97 and 0.94 (d, J = 6.6 and 6.6 Hz, 3 H), 0.99–1.21 (m, 1 H), 1.24–1.32 (m, 2 H), 1.38–1.50 (m, 1 H), 1.46 and 1.45 (s, 9 H), 1.58–1.79 (m, 1 H), 2.20 and 2.21 (d, J = 5.3 and 5.0 Hz, 1 H), 2.38 (d, J = 4.6 Hz, 1 H), 4.11–4.17 (m, 1 H). Anal. Calcd for $C_{18}H_{38}GeO_3$: C, 57.64; H, 10.21. Found: C, 57.37; H, 10.49.

***threo-tert*-Butyl 3-hydroxy-4-methyl-2-(trimethylgermyl)pentanoate (*threo*-3d)**: bp 90 °C (9 mmHg, Kugelrohr); IR (film) 3475, 1680, 1145, 825, 600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.30 (s, 9 H), 0.87 (d, J = 6.8 Hz, 3 H), 1.00 (d, J = 6.6 Hz, 3 H), 1.46 (s, 9 H), 1.78–1.86 (m, 1 H), 2.35 (d, J = 2.9 Hz, 1 H), 3.25 (ddd, J = 10.6, 8.0, 2.9 Hz, 1 H), 3.61 (d, J = 10.6 Hz, 1 H). Anal. Calcd for $C_{13}H_{28}GeO_3$: C, 51.20; H, 9.25. Found: C, 51.11; H, 9.40.

***erythro-tert*-Butyl 3-hydroxy-4-methyl-2-(trimethylgermyl)pentanoate (*erythro*-3d)**: mp 67.5–68.5 °C; IR (Nujol) 3425, 1680, 1150, 825, 600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.31 (s, 9 H), 0.90 (d, J = 7.0 Hz, 3 H), 0.92 (d, J = 6.6 Hz, 3 H), 1.45 (s, 9 H), 1.67–1.78 (m, 1 H), 2.31 (d, J = 4.5 Hz, 1 H), 2.37 (d, J = 6.4 Hz, 1 H), 3.85 (dt, J = 6.4, 4.5 Hz, 1 H). Anal. Calcd for $C_{13}H_{28}GeO_3$: C, 51.20; H, 9.25. Found: C, 51.16; H, 9.18.

***threo*- and *erythro-tert*-Butyl 3-cyclohexyl-3-hydroxy-2-(trimethylgermyl)propanoate (3e)**: bp 140 °C (2 mmHg, Kugelrohr); IR (film) 3500, 1685, 1150, 830, 605 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.30 (s, threo) and 0.31 (s, erythro) (total 9 H), 0.86–0.99 (m, 2 H), 1.06–1.30 (m, 3 H), 1.45 (s, erythro) and 1.46 (s, threo) (total 9 H), 1.42–1.55 (m, 1 H), 1.60–1.68 (m, 2 H), 1.69–1.80 (m, 2 H), 2.02–2.09 (m, 1 H), 2.35 (d, J = 2.9 Hz, threo) and 2.40 (d, J = 5.7 Hz, erythro) (total 1 H), 3.29 (ddd, J = 10.8, 8.1, 2.9 Hz, threo) and 3.85–3.89 (m, erythro) (total 1 H), 3.48 (d, J = 10.8 Hz, threo) and 2.49 (d, J = 4.4 Hz, erythro) (total 1 H). Anal. Calcd for $C_{16}H_{32}GeO_3$: C, 55.70; H, 9.35. Found: C, 55.78; H, 9.27.

***threo-tert*-Butyl (*E*)-3-hydroxy-2-(trimethylgermyl)-4-octenoate (*threo*-3f)**: bp 75 °C (0.65 mmHg, Kugelrohr); IR (film) 3450, 1685, 1150, 828, 600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.30 (s, 9 H), 0.90 (t, J = 7.3 Hz, 3 H), 1.39 (sextet, J = 7.3 Hz, 2 H), 1.45 (s, 9 H), 2.00 (td, J = 7.3, 6.6 Hz, 2 H), 2.25 (d, J = 4.9 Hz, 1 H), 3.44 (d, J = 9.0 Hz, 1 H), 4.23 (m, 1 H), 5.55 (dd, J = 15.4, 6.0 Hz, 1 H), 5.65 (dt, J = 15.4, 6.6 Hz, 1 H). Anal. Calcd for $C_{15}H_{30}GeO_3$: C, 54.43; H, 9.14. Found: C, 54.23; H, 9.10.

***erythro-tert*-Butyl (*E*)-3-hydroxy-2-(trimethylgermyl)-4-octenoate (*erythro*-3f)**: bp 75 °C (0.2 mmHg, Kugelrohr); IR (film) 3425, 1685, 1150, 825, 600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.30 (s, 9 H), 0.90 (t, J = 7.3 Hz, 3 H), 1.39 (sextet, J = 7.3 Hz, 2 H), 1.44 (s, 9 H), 2.00 (td, J = 7.3, 6.6 Hz, 2 H), 2.32 (d, J = 6.1 Hz, 1 H), 2.52 (d, J = 4.2 Hz, 1 H), 4.52 (m, 1 H), 5.55 (dd, J = 15.4, 6.6 Hz, 1 H), 5.67 (dt, J = 15.4, 6.6 Hz, 1 H). Anal. Calcd for $C_{15}H_{30}GeO_3$: C, 54.43; H, 9.14. Found: C, 54.50; H, 9.15.

***threo-tert*-Butyl 3-hydroxy-4,4-dimethyl-2-(trimethylgermyl)pentanoate (*threo*-3g)**: bp 105 °C (3 mmHg, Kugelrohr); IR (film), 3450, 1680, 1140, 830, 610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.31 (s, 9 H), 0.90 (s, 9 H), 1.45 (s, 9 H), 2.29 (s, 1 H), 3.33 (d, J = 9.7 Hz, 1 H), 4.99 (d, J = 9.7 Hz, 1 H). Anal. Calcd for $C_{14}H_{30}GeO_3$: C, 52.71; H, 9.48. Found: C, 52.97; H, 9.51.

***erythro-tert*-Butyl 3-hydroxy-4,4-dimethyl-2-(trimethylgermyl)pentanoate (*erythro*-3g)**: mp 105.0–106.5 °C, sublimed at 70 °C (0.25 mmHg); IR (Nujol) 3525, 1685, 1145, 830, 610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.29 (s, 9 H), 0.90 (s, 9 H), 1.43 (s, 9 H), 1.52 (d, J = 6.2 Hz, 1 H), 2.39 (d, J = 9.7 Hz, 1 H), 3.97 (dd, J = 9.7 and 6.2 Hz, 1 H). Anal. Calcd for $C_{14}H_{30}GeO_3$: C, 52.71; H, 9.48. Found: C, 52.59; H, 9.52.

***threo-tert*-Butyl 3-hydroxy-3-phenyl-2-(trimethylgermyl)propanoate (*threo*-3h)**: bp 150 °C (1 mmHg, Kugelrohr); IR (film) 3420, 1705, 1140, 830, 700, 605 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.24 (s, 9 H), 1.38 (s, 9 H), 2.65 (d, J = 5.6 Hz, 1 H), 3.87 (d, J = 8.6 Hz, 1 H), 4.91 (dd, J = 8.6, 5.6 Hz, 1 H), 7.22–7.38 (m, 5 H). Anal. Calcd for $C_{16}H_{26}GeO_3$: C, 56.69; H, 7.73. Found: C, 56.46; H, 7.55.

***erythro-tert*-Butyl 3-hydroxy-3-phenyl-2-(trimethylgermyl)propanoate (*erythro*-3h)**: mp 79.0–80.0 °C (recrystallized from hexane); IR (Nujol) 3420, 1680, 1145, 825, 695, 600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.21 (s, 9 H), 1.36 (s, 9 H), 2.62 (d, J = 6.4 Hz, 1 H), 2.90 (d, J = 2.9 Hz, 1 H), 5.23 (dd, J = 6.4, 2.9 Hz, 1 H), 7.22–7.41 (m, 5 H). Anal. Calcd for $C_{16}H_{26}GeO_3$: C, 56.69; H, 7.73. Found: C, 56.87; H, 7.84.

***tert*-Butyl 2-(1-hydroxycyclopentyl)-2-(trimethylgermyl)acetate (3i)**: bp 90 °C (2 mmHg, Kugelrohr); IR (film) 3500, 1685, 1145, 830, 605 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.32 (s, 9 H), 1.22–2.03 (m, 8 H), 1.48 (s, 9 H), 2.25 (s, 1 H), 3.69 (s, 1 H). Anal. Calcd for $C_{14}H_{28}GeO_3$: C, 53.05; H, 8.90. Found: C, 53.09; H, 9.19.

***tert*-Butyl 2-(1-hydroxycyclohexyl)-2-(trimethylgermyl)acetate (3j)**: bp 110 °C (0.55 mmHg, Kugelrohr); IR (film) 3475, 1680, 1140, 830, 595 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.34 (s, 9 H), 1.08–1.80 (m, 10 H), 1.48 (s, 9 H), 2.28 (s, 1 H), 3.82 (s, 1 H). Anal. Calcd for $C_{15}H_{30}GeO_3$: C, 54.43; H, 9.14. Found: C, 54.63; H, 9.29.

***threo*- and *erythro-tert*-butyl 3-hydroxy-3-methyl-2-(trimethylgermyl)nonanoate (3k)**: bp 110 °C (0.15 mmHg, Kugelrohr); IR (film) 3490, 1680, 1130, 830, 605 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.32 (s, erythro) and 0.33 (s, threo) (total 9 H), 0.88 (t, J = 6.9 Hz, 3 H), 1.18 (s, threo) and 1.25 (s, erythro) (total 3 H), 1.20–1.80 (m, 8 H), 1.47 (s, threo) and 1.48 (s, erythro) (total 9 H), 1.54–1.60 (m, 2 H), 2.29 (s, erythro) and 2.30 (s, threo) (total 1 H), 3.79 (s, erythro) and 3.92 (s, threo) (total 1 H). Anal. Calcd for $C_{17}H_{36}GeO_3$: C, 56.55; H, 10.05. Found: C, 56.40; H, 10.02.

***threo*- and *erythro-tert*-butyl 3-hydroxy-3,4,4-trimethyl-2-(trimethylgermyl)pentanoate (3l)**: bp 100 °C (0.7 mmHg, Kugelrohr); IR (film) 3430, 1705, 1670, 1160, 1120, 830, 605 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.30 (s, erythro) and 0.37 (s, threo) (total 9 H), 0.95 (s, threo) and 0.96 (s, erythro) (total 9 H), 1.20 (s, threo) and 1.42 (s, erythro) (total 3 H), 1.43 (s, erythro) and 1.47 (s, threo) (total 9 H), 2.48 (s, threo) and 2.73 (s, erythro) (total 1 H), 5.21 (s, threo) and 1.35 (s, erythro) (total 1 H). Anal. Calcd for $C_{15}H_{32}GeO_3$: C, 54.10; H, 9.69. Found: C, 54.23; H, 9.79.

***threo-tert*-Butyl 3-hydroxy-3-phenyl-2-(trimethylgermyl)butanoate (*threo*-3m)**: bp 115 °C (0.5 mmHg, Kugelrohr); mp 41.5–43.5 °C; IR (Nujol) 3440, 1670, 1160, 1120, 825, 695, 600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.41 (s, 9 H), 1.12 (s, 9 H), 1.46 (s, 3 H), 2.86 (s, 1 H), 4.48 (s, 1 H), 7.15–7.46 (m, 5 H). Anal. Calcd for $C_{17}H_{28}GeO_3$: C, 57.84; H, 8.00. Found: C, 57.89; H, 8.04.

***erythro-tert*-Butyl 3-hydroxy-3-phenyl-2-(trimethylgermyl)butanoate (*erythro*-3m)**: bp 80 °C (0.3 mmHg, Kugelrohr); IR (film) 3450, 1675, 1150, 830, 700, 605 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.09 (s, 9 H), 1.53 (s, 9 H), 1.59 (s, 3 H), 2.67 (s, 1 H), 4.79 (s, 1 H), 7.10–7.50 (m, 5 H). Anal. Calcd for $C_{17}H_{28}GeO_3$: C, 57.84; H, 8.00. Found: C, 57.80; H, 7.96.

***threo-tert*-Butyl 3-hydroxy-3-phenyl-2-(trimethylgermyl)pentanoate (*threo*-3n)**: mp 84.5–86.0 °C (from *n*-hexane); IR (Nujol) 3440, 1670, 1140, 1125, 830, 695, 610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.42 (s, 9 H), 0.63 (t, J = 7.3 Hz, 3 H), 1.11 (s, 9 H), 1.67 (dqd, J = 13.6, 7.5, 1.8 Hz, 1 H), 1.89 (dq, J = 13.6, 7.3 Hz, 1 H), 2.86 (s, 1 H), 4.39 (d, J = 1.8 Hz, 1 H), 7.15–7.40 (m, 5 H). Anal. Calcd for $C_{18}H_{30}GeO_3$: C, 58.91; H, 8.24. Found: C, 58.83; H, 8.52.

***erythro-tert*-Butyl 3-hydroxy-3-phenyl-2-(trimethylgermyl)pentanoate (*erythro*-3n)**: bp 80 °C (0.1 mmHg, Kugelrohr), IR (film) 3470, 1680, 1160, 830, 700, 605 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.10 (s, 9 H), 0.60 (t, J = 7.2 Hz, 3 H), 1.53 (s, 9 H), 1.81–1.95 (m, 2 H), 2.68 (s, 1 H), 4.48 (s, 1 H), 7.15–7.40 (m, 5 H). Anal. Calcd for $C_{18}H_{30}GeO_3$: C, 58.91; H, 8.24. Found: C, 58.93; H, 8.25.

Treatment of *threo*-3h with LDA. To a solution of LDA (0.47 mmol) in THF (5 mL) was added dropwise a solution of *threo*-**3h** (160 mg, 0.47 mmol) in THF (3 mL) at −78 °C. Stirring was continued at −78 °C for 0.5 h, at −20 °C for 0.5 h, and then at room temperature for 1 h. Aqueous citric acid (5%) was added and the mixture was extracted with ether. The ether layer was washed with water and saturated aqueous NaCl, dried ($MgSO_4$), and evaporated. GLC analysis of the residue revealed **1** (16%), *threo*-**3h** (13%), and (*E*)-**4h** (71%). They were isolated on a silica gel column and respectively identified with authentic samples. When this reaction was quenched after stirring at −78 °C for 1 h, *threo*-**3h** (160 mg, 100%) was recovered.

Treatment of *erythro*-3h with LDA. In a similar manner to that described above, *erythro*-**3h** (160 mg, 0.47 mmol) was treated with an equimolar amount of LDA. Distillation of the

residue gave (*E*)-**4h** (88 mg, 92%). When the reaction was quenched after 1 h at −78 °C, *erythro*-**3h** (122 mg, 77%) and (*E*)-**4h** (20 mg, 21%) were obtained by a silica gel column chromatograph (hexane/ethyl acetate).

Conversion of 3 to 4 in the Presence of BF_3·OEt_2. The residual oil in the general preparation of **3** was dissolved in CH_2Cl_2 (7 mL) and mixed with boron trifluoride etherate (170 mg, 1.2 mmol) in CH_2Cl_2 (3 mL) at 0 °C. After 1 h of stirring, saturated aqueous $NaHCO_3$ was added, and the mixture was extracted with ether. The extract was washed with water and saturated NaCl, dried ($MgSO_4$), and concentrated. Distillation of the residue gave a mixture of the geometrical isomers of **4**. The yields and ratios are summarized in the last column in Table I.

Conversion of *threo*-3a or *erythro*-3a to (*E*)-4a or (*Z*)-4a. In a similar manner as described above, *threo*-**3a** (purity >99%) or *erythro*-**3a** (purity 97%) (361 mg, 1.0 mmol) was treated with BF_3·OEt_2 (170 mg, 1.2 mmol) to give (*E*)-**4a**[17] (217 mg, 96%) or (*Z*)-**4a**[17] (224 mg, 99%, *Z*/*E* = 98:2), respectively.

Conversion of *threo*-3h or *erythro*-3h to (*E*)-4h or (*Z*)-4h. A similar treatment of *threo*-**3h** or *erythro*-**3h** (339 mg, 1.0 mmol) with BF_3·OEt_2 (170 mg, 1.2 mmol) gave (*E*)-**4h** (197 mg, 96% purity >99%) or (*Z*)-**4h** (199 mg, 97%, *Z*/*E* = 95:5).

Reaction of Ethyl (Trimethylgermyl)acetate with 2h. According to the general preparation of **3** described above, ethyl (trimethylgermyl)acetate (246 mg, 1.2 mmol) was lithiated with a solution of LDA (1.2 mmol) and then reacted with **2h** (106 mg, 1.0 mmol) at −78 °C for 0.5 h. The ethereal extract was chromatographed on a silica gel column (hexane/ethyl acetate) to give the following three products.

***threo*-Ethyl 3-hydroxy-3-phenyl-2-(trimethylgermyl)propanoate**: yield, 204 mg (66%); bp 125 °C (0.9 mmHg, Kugelrohr); IR (film) 3420, 1705, 1160, 830, 700, 608 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.18 (s, 9 H), 1.22 (t, *J* = 7.1 Hz, 3 H), 2.77 (d, *J* = 6.6 Hz, 1 H), 3.64 (d, *J* = 7.9 Hz, 1 H), 4.04–4.17 (m, 2 H), 4.99 (dd, *J* = 7.9 and 6.6 Hz, 1 H), 7.24–7.38 (m, 5 H). Anal. Calcd for $C_{14}H_{22}GeO_3$: C, 54.08; H, 7.13. Found: C, 54.21; H, 7.17.

***erythro*-Ethyl 3-hydroxy-3-phenyl-2-(trimethylgermyl)propanoate**: yield, 57 mg (18%); bp 80 °C (0.2 mmHg, Kugelrohr); IR (film) 3450, 1690, 1160, 835, 700, 605 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.21 (s, 9 H), 1.19 (t, *J* = 7.1 Hz, 3 H), 2.73 (d, *J* = 6.6 Hz, 1 H), 2.90 (d, *J* = 2.8 Hz, 1 H), 4.06 (q, *J* = 7.1 Hz, 2 H), 5.29 (dd, *J* = 6.6 and 2.8 Hz, 1 H), 7.22–7.41 (m, 5 H). Anal. Calcd for $C_{14}H_{22}GeO_3$: C, 54.08; H, 7.13. Found: C, 54.10; H, 7.32.

Ethyl cinnamate: yield 8 mg (5%).

Reaction of 2,6-Di-*tert*-butyl-4-methylphenyl (Trimethylgermyl)acetate with 2h. In a similar manner to that described above, 2,6-di-*tert*-butyl-4-methylphenyl (trimethylgermyl)acetate (457 mg, 1.2 mmol), LDA (1.2 mmol), and **2h** (106 mg, 1.0 mmol) gave the following three products.

***threo*-2,6-Di-*tert*-butyl-4-methylphenyl 3-hydroxy-3-phenyl-2-(trimethylgermyl)propanoate**: yield, 170 mg (35%); highly viscous oil; IR (film) 3500, 1710, 1100, 830, 700, 605 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.50 (s, 9 H), 0.99 (s, 9 H), 1.36 (s, 9 H), 2.26 (s, 3 H), 2.90 (d, *J* = 3.3 Hz, 1 H), 4.64 (d, *J* = 10.0 Hz, 1 H), 5.12 (dd, *J* = 10.0 and 3.3 Hz, 1 H), 6.99 (d, *J* = 2 Hz, 1 H), 7.12 (d, *J* = 2 Hz, 1 H), 7.14–7.32 (m, 5 H). Anal. Calcd for $C_{27}H_{40}GeO_3$: C, 66.84; H, 8.31. Found: C, 66.94; H, 8.27.

2,6-Di-*tert*-butyl-4-methylphenol: yield 86 mg.

2,6-Di-*tert*-butyl-4-methylphenyl (trimethylgermyl)acetate: yield 104 mg.

Effect of the Counter Cation of the Enolate. To a solution of the lithium enolate of **1** (279 mg, 1.2 mmol) in THF (3 mL) was added a suspension of magnesium dibromide [prepared from magnesium turnings (40 mg, 1.6 mmol) and dibromoethane (282 mg, 1.5 mmol) in THF (3 mL)] or powder of zinc dichloride (205 mg, 1.5 mmol, dried at 170 °C for 24 h in vacuo). After 1 h of stirring at −78 °C, a solution of **2a** (128 mg, 1.0 mmol) or **2h** (106 mg, 1.0 mmol) in THF (3 mL) was added and stirring was continued for 0.5 h. The reaction mixture was worked up and chromatographed on a silica gel column (hexane–ethyl acetate) to give the following results [aldehyde/additive/yield (threo/erythro)]: **2a**/$MgBr_2$/90% (66:34), **2h**/$MgBr_2$/94% (70:30), **2h**/$ZnCl_2$/57% (83:17).

Reaction of the Lithium Enolate of *tert*-Butyl (Trimethylgermyl)acetate with Chlorotrimethylsilane. A solution of **1** (466 mg, 2.0 mmol) in THF (5 mL) was added to a solution of LDA (2.0 mmol) in THF (7 mL) at −78 °C. After 0.5 h of stirring, chlorotrimethylsilane (290 mg, 2.7 mmol) was added and the temperature was allowed to warm to room temperature. The mixture was concentrated under reduced pressure and hexane (5 mL) was added. Precipitated white solid was filtered off under a nitrogen atmosphere, and the filtrate was concentrated. ^1H NMR of the residual oil showed no presence of vinylic proton.

The same reaction was repeated and the reaction mixture was quenched with aqueous NH_4Cl and extracted with ether. The extract was washed with water, dried, and distilled to give *tert*-butyl (trimethylgermyl)(trimethylsilyl)acetate (557 mg, 91%): bp 77.0–78.0 °C (2.5 mmHg); IR (film) 1690, 1250, 850, 825, 600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.12 (s, 9 H), 0.28 (s, 9 H), 1.44 (s, 9 H), 1.49 (s, 1 H). Anal. Calcd for $C_{12}H_{28}GeO_2Si$: C, 47.25; H, 9.25. Found: C, 47.05; H, 9.25.

Acknowledgment. We are grateful to the Ministry of Education, Science, and Culture, Japan, for a Grant-in-Aid for Encouragement of Young Scientists (No. 01771923) and to the Asai Germanium Research Institute for its generous gift of germanium tetrachloride.