Synthesis of Acyltrialkylgermanes and Reactions with Carbon Nucleophiles

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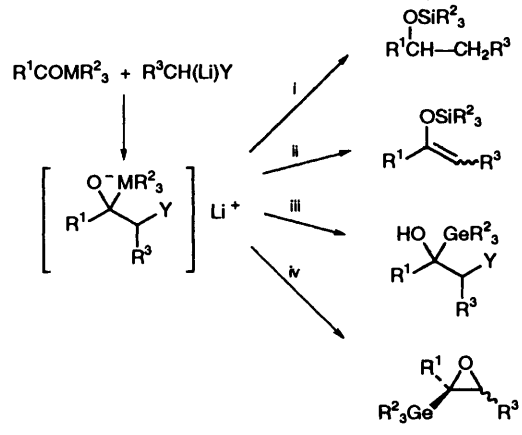
Acyltrialkylgermanes **4** have been obtained in good yields by the Swern oxidation of trialkyl(1-hydroxyalkyl)germanes **3** which were prepared from aldehydes **1** and trialkylgermyllithium **2**. Reaction of **4** with butyllithium **5**, *tert*-butyl lithioacetate **7** or 2-lithiopropionitrile **9** gave the respective 1,2-addition products **6**, **8** and **10**. However, reaction with 1-lithioethyl phenyl sulfone **11** gave α-(trialkylgermyl) ketones **12**, and with the lithium enolate of *tert*-butyl bromoacetate **14** gave (trialkylgermyl)oxiranes **15** as the main products, respectively. The results of the treatment of **15** with Lewis acids are also discussed.

Although the chemistry of acyltrialkylsilanes has been investigated in detail because of the unusual spectroscopic properties of the compounds and their interesting chemical behaviour,[1] studies on acyltrialkylgermanes are limited. Some acyltriphenylgermanes have been prepared directly by reaction of triphenylgermyllithium with acyl halides[2] or esters,[3] but roundabout methods have been employed for the preparation of acyltrialkylgermanes: *e.g.* hydrolysis of trialkylgermyl-1,3-dithianes,[4] reaction of *N,N*-dialkylcarboxamide with triethylgermyllithium prepared from bis(triethylgermyl)mercury[5] and palladium-catalysed reaction of hexamethyldigermane with acyl halides.[6]

In the reaction of acyltrialkylsilanes with carbon nucleophiles (M = Si, Y = H in Scheme 1), the silyl groups of the 1,2-



Scheme 1 i, MR^2_3 = $SiMe_3$, Y = H; ii, MR^2_3 = $SiMe_3$, Y = CN, SO_2Ph; iii, MR^2_3 = $GeEt_3$, H_2O; iv, MR^2_3 = $GeEt_3$, −LiY

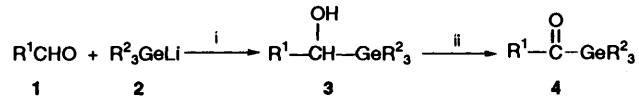
adducts, which are initially formed, quickly rearrange into oxy anions to give the silyl ethers (route i, Brook rearrangement),[7] however silyl enol ethers are formed when Y is a group which can be eliminated (CN, SO_2Ph, *etc.*) (route ii).[8] Trialkylgermyl groups tend to link with carbon rather than oxygen, in contrast to trialkylsilyl groups which have a high affinity with oxygen.[9] We previously prepared (1-hydroxyalkyl)triorganogermanes by the reaction of triorganogermyl anions with aldehydes under non-basic conditions.[10]

Reaction of acyltrialkylgermanes with carbon nucleophiles can give 1,2-addition products (route iii), and (trialkylgermyl)-oxirane can be formed when Y is an eliminating group (route iv). We report herein the synthesis of acyltrialkylgermanes and their reactions with some carbon nucleophiles.

The reaction of aldehydes **1** with trialkylgermyllithium[11] **2**, prepared from trialkylchlorogermane with lithium in hexamethylphosphoramide (HMPA), gave trialkyl(1-hydroxyalkyl)germanes **3** in good yields (Scheme 2, Table 1). Swern oxidation[12] of **3** afforded high yields of acyltrialkylgermanes **4**.

Table 1 Preparation of (1-hydroxyalkyl)triethylgermanes **3** and acyltriethylgermanes **4**

Entry		R^1	R^2	Yield of **3** from **1** (%)	Yield of **4** from **3** (%)
1	**a**	Pr^i	Me	48	72
2	**b**	Pr^i	Et	70	90
3	**c**	c-C_6H_{11}	Et	48	87
4	**d**	$Ph(CH_2)_2$	Et	76	72
5	**e**	Ph	Et	57	86



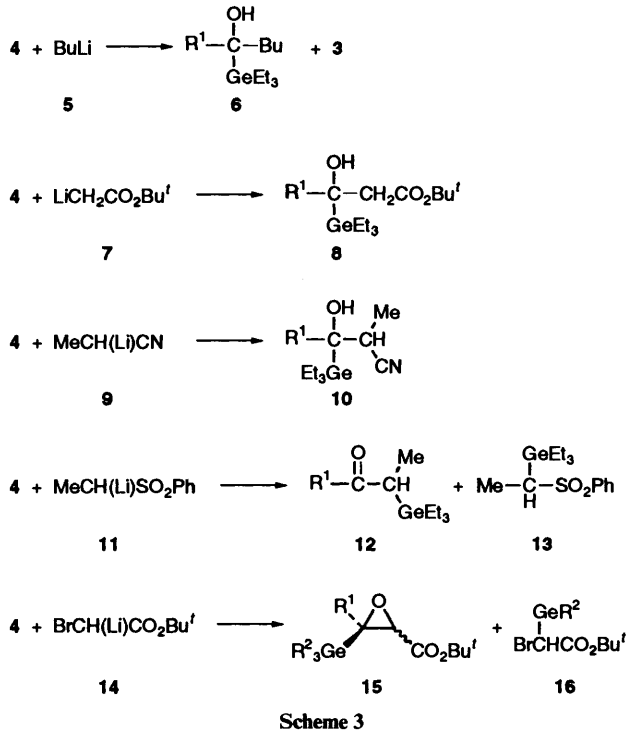
Scheme 2 *Reagents and conditions:* i, THF, 0 °C to room temp., 4 h; ii, DMSO–$(COCl)_2$, Et_3N

The reaction of **4b, e** with butyllithium **5** in tetrahydrofuran (THF) gave the expected 1-(triethylgermyl)alkanols **6b, e** in good yields (Scheme 3, entries 1, 2 in Table 2), although competitive formation of **3e** was observed in the reaction with **4e**. The reaction of **4b, e** with *tert*-butyl lithioacetate **7** or 2-lithiopropionitrile **9** also gave the corresponding 1,2-addition products: *tert*-butyl 3-hydroxy-3-(triethylgermyl)alkanoates **8b, e** (entries 3, 4) or 3-hydroxy-2-methyl-3-(triethylgermyl)-alkanenitriles **10b–e** (entries 5–8), respectively. In the latter case, there was no elimination of the cyano group from the 1,2-adducts even at higher temperatures.

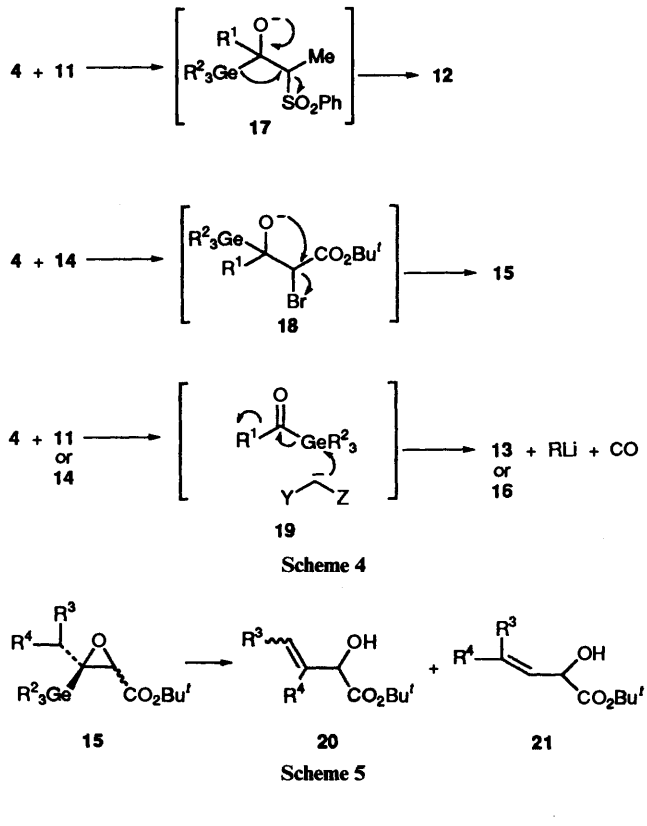
The reaction of **4b–e** with 1-lithioethyl phenyl sulfone **11** gave mixtures of 2-(triethylgermyl)alkan-3-ones **12b, c** and phenyl 2-(triethylgermyl)ethyl sulfone **13** (entries 9–12). Reaction with the lithium enolate of *tert*-butyl bromoacetate afforded a mixture of *cis* and *trans* isomers of *tert*-butyl 3-alkyl-3-(trialkylgermyl)oxirane-2-carboxylates *cis*-**15a–c** and *trans*-**15a–c** accompanied by *tert*-butyl 2-bromo-2-(trialkylgermyl)-acetate **16** (entries 13–15). The stereochemistry of **15** was confirmed by the observation of NOEs.

Compounds **12** or **15** can be formed by the elimination of a phenylsulfonyl or bromide group from the 1,2-addition products **17** or **18** (see Scheme 4). Competitive nucleophilic attack of **11** or **14** on the trialkylgermyl groups of **4** can form **13** or **16** accompanied by elimination of RLi and CO.

Oxiranes are versatile intermediates in organic synthesis,[13]



Scheme 3



Scheme 4

Scheme 5

Table 2 Reaction of ketones **4a–c** with carbon nucleophiles

Entry	Acylgermane	Nucleophile	Products (% yield) [ratio of diastereoisomeric isomers]
1	**4b**	**5**	**6b** (76)
2	**4e**	**5**	**6e** (82) and **3e** (10)[a]
3	**4b**	**7**	**8b** (81)
4	**4e**	**7**	**8e** (82)
5	**4b**	**9**	**10b** (73) [57:43]
6	**4c**	**9**	**10c** (67) [55:45]
7	**4d**	**9**	**10d** (72) [69:31]
8	**4e**	**9**	**10e** (80) [73:27]
9	**4b**	**11**	**12b** (81), **13** (10)
10	**4c**	**11**	**12c** (78), **13** (11)
11	**4d**	**11**	**12d** (80), **13** (13)
12	**4e**	**11**	**12e** (82), **13** (12)
13	**4a**	**14**	*cis*-**15a** (32), *trans*-**15a** (28)
14	**4b**	**14**	*cis*-**15b** (34), *trans*-**15b** (31), **16** (25)
15	**4c**	**14**	*cis*-**15c** (35), *trans*-**15c** (33), **16** (21)

[a] Compound **4e** was added to a butyllithium solution.

and rearrangement assisted by protic or Lewis acids has been extensively investigated.[14] In a preliminary experiment using a mixture of the stereoisomers of **15b** it was noticed that the TLC-spot of *cis*-**15b** disappeared more quickly than that of *trans*-**15b** in the presence of boron trifluoride–diethyl ether (BF_3·OEt_2) in dichloromethane. Thus, the isomers were separated and treated individually with an equimolar amount of boron trifluoride–diethyl ether. After 0.5 h of stirring, *cis*-**15b** was converted into a mixture of *tert*-butyl esters of (*E*)- and (*Z*)-2-hydroxy-3-methylpent-3-enoic acids **20b** and *tert*-butyl 2-hydroxy-4-methylpent-3-enoate **21b** (Scheme 5, Table 3, entry 2). Consumption of *trans*-**15b** was slower and gave (*E*)-**20b** selectively after 2 h (entry 5).

Yields of **20b** and **21b** were improved when we inadvertently used non-redistilled boron trifluoride–diethyl ether. In fact, the use of boron trifluoride–diethyl ether mixed with an equimolar amount of water (deactivated-BF_3) improved the yields (entries 3, 6), although the use of 0.4 mol equivalent of redistilled boron trifluoride–diethyl ether led to a lower yield. The results from the treatment of **15a, c** with deactivated-BF_3 are summarized in entries 1, 8 and 9. A small amount of conversion of *trans*-**15c** was observed under the conditions in which *cis*-**15c** was transformed into **21c** in high yield (entries 8, 9). Products **20** and **21** can be formed *via* routes *a* and *b* from **22**, respectively (Scheme 6). Both routes are possible for *cis*-**22** (Newman formulas **A** and **B**), but only formula **C** may be suitable for the *trans* isomer which results in selective formation of **20**.

Different reactivities were observed for the two stereoisomers *cis*- and *trans*-**15b** when they were treated with sulfuric acid in methanol: the *cis*-isomer of **15b** changed mainly to **20b** (entry 4), however most of the *trans*-isomer remained in the reaction mixture although transesterification occurred. The two isomers also showed different reactivities when they were treated with ethylaluminium dichloride or diethylaluminium chloride.

Experimental

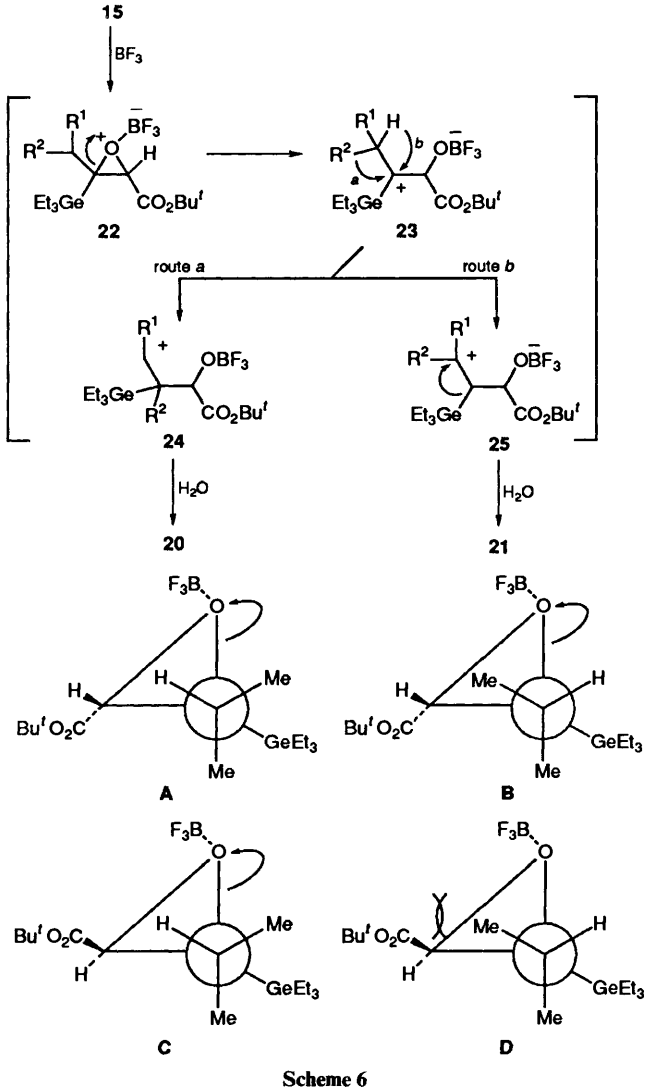
All reactions were carried out under an argon atmosphere. Diethyl ether and THF were distilled from sodium benzophenone ketyl. HMPA was distilled under reduced pressure from sodium. Dimethyl sulfoxide (DMSO) was dried by distillation under reduced pressure from calcium hydride. Dichloromethane and triethylamine were distilled from calcium hydride. All boiling points given are the oven temperature of the Büchi Kugelrohr distillation apparatus and are uncorrected. Ether refers to diethyl ether.

Isobutyryltrimethylgermane **4a**.—A mixture of chlorotrimethylgermane (12.3 g, 80 mmol) and finely cut lithium (2.15 g, 310 mmol) in HMPA (54 cm^3, 312 mmol) was stirred for 20 h

Table 3 Isomerization of (trialkylgermyl)oxirane **15a–c** catalysed by Lewis acids

Entry	Oxirane	R^1	R^2	Lewis acid (1.1 equiv.)	Reaction conditions °C/min	Product (%) **20** (*E*:*Z*)[a]	**21**
1	*cis*-**15a**	Me	Me	BF_3·OEt_2–H_2O	−23/60 then 0/30	47 (53:47)	26
2	*cis*-**15b**	Me	Me	BF_3·OEt_2	−78/5 then −23/30	22 (35:65)	37
3				BF_3·OEt_2–H_2O (1:1)	−23/60 then 0/30	40 (37:63)	47
4				conc. H_2SO_4	0/180 then room temp./60	55 (14:86)	8
5	*trans*-**15b**	Me	Me	BF_3·OEt_2	−78/5 then −23/120	28 (99:1)	—
6				BF_3·OEt_2–H_2O (1:1)	−23/60 then 0/30	30 (96:4)	5
7				conc. H_2SO_4	0/60 then room temp./120	*trans*-**15b**, 49%	*b*
8	*cis*-**15c**	$-[CH_2]_5-$		BF_3·OEt_2–H_2O (1:1)	−23/60 then 0/60	trace	78
9	*trans*-**15c**	$-[CH_2]_5-$		BF_3·OEt_2–H_2O (1:1)	−23/60 then 0/60	6	3

[a] Determined from the integrated values of protons in the ^1H NMR spectrum. [b] The remaining *trans*-**15b** was recovered as methyl ester.



Scheme 6

at room temperature and then diluted with THF (100 cm^3) according to the method of Wickham *et al.*[11] The solution of trimethylgermyllithium thus prepared was added to a solution of isobutyraldehyde (5.80 g, 80 mmol) in THF (50 cm^3) at −50 °C. The mixture was stirred for 1 h at −50 °C followed by 0.5 h at 0 °C, the reaction was then quenched with 3% HCl and the mixture was extracted with ether. The combined extracts were washed first with water, then with saturated aqueous NaCl, dried ($MgSO_4$), and then concentrated. The residue (19.1 g) was chromatographed on a silica gel column with hexane–ethyl acetate (20:1) to give (*1-hydroxy-2-methylpropyl*)*trimethylgermane* **3a** (crude, 7.31 g, 48%), ν_{max}/cm^{-1} 3397 (OH), 824 and 598; δ_H(500 MHz; $CDCl_3$) 0.20 (9 H, s, $GeMe_3$), 0.94 (3 H, d, *J* 6.7, CH_3), 0.97 (3 H, d, *J* 6.7, CH_3), 1.26 (1 H, br s, OH), 1.91 (1 H, octet, *J* 6.7, Me_2CH) and 3.36 (1 H, d, *J* 6.7, $CHOH$); δ_C(125.7 MHz; $CDCl_3$) −2.9 (CH_3), 19.1 (CH_3), 20.0 (CH_3), 33.2 (CH) and 74.5 (CH).

A solution of DMSO (6.52 g, 83.4 mmol) in dichloromethane (20 cm^3) was added to a solution of oxalyl chloride (5.32 g, 41.9 mmol) in dichloromethane (60 cm^3) at −50 to −60 °C. The mixture was stirred for 2 min and then a solution of **3a** (7.18 g, 37.6 mmol) in dichloromethane (20 cm^3) was added during 5 min, the mixture was stirred for 15 min, and then triethylamine (26.2 cm^3, 188 mmol) was added. After 5 min the mixture was allowed to warm to room temperature and stirring was continued for 3 h. The reaction was then quenched with water. The organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined extracts were washed with water and saturated aqueous NaCl, dried ($MgSO_4$), and concentrated. The residue (12.1 g) was chromatographed on a silica gel column with hexane–ethyl acetate (50:1) to give the *title compound* **4a** (5.14 g, 72%), b.p. 78.0–78.5 °C/60 mmHg (Found: C, 44.3; H, 8.2. $C_7H_{16}GeO$ requires C, 44.5; H, 8.5%); ν_{max}/cm^{-1} 1655 (CO), 829 and 604; δ_H(400 MHz; $CDCl_3$) 0.36 (9 H, s, $GeMe_3$), 1.04 (6 H, d, *J* 7.0, CH_3) and 2.83 (1 H, septet, *J* 7.0, CH); δ_C(100.4 MHz; $CDCl_3$) −2.1 (CH_3), 16.2 (CH_3), 46.5 (CH) and 247.3 (CO).

Isobutyryltriethylgermane **4b**.—In a manner similar to that described above, a solution of triethylgermyllithium **2** which was prepared from chlorotriethylgermane (11.7 g, 60 mmol), finely cut lithium (1.67 g, 240 mmol), HMPA (42 cm^3, 240 mmol) and THF (80 cm^3), was added to a solution of isobutyraldehyde (72 mg, 1.0 mmol) in THF (30 cm^3) at 0 °C. The mixture was stirred for 4 h at room temperature and then the reaction was quenched and treated to give (*1-hydroxy-2-methylpropyl*)*triethylgermane* **3b** (163 mg, 70%), b.p. 125 °C/27 mmHg (Found: C, 51.2; H, 10.7. $C_{10}H_{24}GeO$ requires C, 51.6; H, 10.4%); ν_{max}(film)/cm^{-1} 3450 (OH), 1020, 700 and 570; δ_H(100 MHz; $CDCl_3$) 0.60–1.16 (21 H, m), 1.25 (1 H, s), 1.61–2.00 (1 H, m) and 3.45 (1 H, d, *J* 7.5).

In the same way, **3b** (4.66 g, 20 mmol) was treated with DMSO (3.4 cm^3, 44 mmol), oxalyl chloride (2.0 cm^3, 22 mmol) and triethylamine (14.0 cm^3, 100 mmol) in dichloromethane (100 cm^3), and worked up to give the *title compound* **4b** (4.17 g, 90%), b.p. 120 °C/35 mmHg (Found: C, 51.75; H, 9.4. $C_{10}H_{22}GeO$ requires C, 52.0; H, 9.6%); ν_{max}(film)/cm^{-1} 1651 (CO), 1462, 1381, 1022, 968, 704 and 577; δ_H(400 MHz; $CDCl_3$) 0.94–1.01 (6 H, m), 1.01 (6 H, d, *J* 7.0), 1.04–1.09 (9 H, m) and 2.77 (1 H, sept, *J* 7.0).

Cyclohexylcarbonyltriethylgermane **4c**.—Cyclohexanecarbaldehyde **1c** (6.17 g, 55 mmol) and triethylgermyllithium **2** (60 mmol) were treated in the same way to give (*cyclohexylhy-*

droxymethyl)triethylgermane **3c** (7.21 g, 48%), b.p. 118 °C/2.0 mmHg (Found: C, 56.8; H, 10.45. $C_{13}H_{28}GeO$ requires C, 57.2; H, 10.3%); ν_{max}(film)/cm^{-1} 3440 (OH), 1450, 1050, 705 and 570; δ_H(100 MHz; $CDCl_3$) 0.62–2.00 (27 H, m) and 3.59 (1 H, d, *J* 6.3).

Compound **3c** (3.82 g, 14 mmol) was treated in a manner similar to that described above to give the *title compound* **4c** (3.31 g, 87%), b.p. 120 °C/2.0 mmHg (Found: C, 57.4; H, 9.0. $C_{13}H_{25}GeO$ requires C, 57.85; H, 9.3%); ν_{max}(film)/cm^{-1} 1650 (CO), 1450, 965, 705 and 570; δ_H(270 MHz; $CDCl_3$) 0.91–1.30 (21 H, m), 1.62–1.82 (4 H, m) and 2.49–2.60 (1 H, m).

(3-*Phenylpropionyl*)*triethylgermane* **4d**.—3-Phenylpropanal **1d** (138 mg, 1.0 mmol) and triethylgermyllithium **2** (1.2 mmol) were treated in the same way to give (1-*hydroxy*-3-*phenylpropyl*)*triethylgermane* **3d** (225 mg, 76%), b.p. 124 °C/0.8 mmHg (Found: C, 61.0; H, 9.2. $C_{15}H_{26}GeO$ requires C, 61.1; H, 8.9%); ν_{max}(film)/cm^{-1} 3420 (OH), 1020, 700 and 570.

Compound **3d** (3.70 g, 12.5 mmol) was oxidized in a similar manner to give **4d** (2.53 g, 72%), b.p. 90 °C//0.7 mmHg (Found: C, 61.2; H, 8.3. $C_{15}H_{24}GeO$ requires C, 61.5; H, 8.3%); ν_{max}(film)/cm^{-1} 1655 (CO), 1454, 1022, 698 and 581; δ_H(270 MHz; $CDCl_3$) 0.90–0.99 (6 H, m), 1.02–1.10 (9 H, m), 2.80–2.86 (2 H, m), 2.89–2.95 (2 H, m), 7.15–7.20 (3 H, m) and 7.24–7.30 (2 H, m).

Benzoyltriethylgermane **4e**.—Benzaldehyde (3.18 g, 30 mmol) and triethylgermyllithium **2** (36 mmol) were treated in the same way to give (α-*hydroxybenzyl*)*triethylgermane* **3e** (4.53 g, 57%), b.p. 140 °C/3.0 mmHg (Found: C, 58.4; H, 8.2. $C_{13}H_{22}GeO$ requires C, 58.5; H, 8.3%); ν_{max}(film)/cm^{-1} 3400 (OH), 1010, 765, 700 and 575; δ_H(400 MHz; $CDCl_3$) 0.73–0.84 (6 H, m), 0.92–1.02 (9 H, m), 1.67 (1 H, br s), 4.91 (1 H, s), 7.12–7.16 (1 H, m), 7.19–7.21 (2 H, m) and 7.28–7.32 (2 H, m).

Compound **3e** (1.38 g, 5.2 mmol) was converted into **4e** (1.18 g, 86%) in a similar manner, b.p. 118 °C/1.5 mmHg (lit.,[4] b.p. 82–83 °C/0.15 mmHg).

Reaction of Ketone **4b** *with Butyllithium*.—A solution of butyllithium (1.58 mol dm^{-3} in hexane; 0.8 cm^3, 1.3 mmol) was added to a solution of **4b** (229 mg, 1.0 mmol) in THF (10 cm^3) at −78 °C. The mixture was stirred for 1 h and then quenched with saturated aqueous NH_4Cl. The organic layer was separated and the aqueous layer was extracted with ether. The combined extracts were washed with water and saturated aqueous NaCl, dried ($MgSO_4$), and concentrated. The residue was chromatographed on a silica gel column with hexane–ethyl acetate (20:1) to give 2-*methyl*-3-(*triethylgermyl*)*heptan*-3-*ol* **6b** (221 mg, 76%), b.p. 100 °C/0.8 mmHg (Found: C, 58.0; H, 11.3. $C_{14}H_{32}GeO$ requires C, 58.2; H, 11.2%); ν_{max}(film)/cm^{-1} 3500 (OH), 1470, 1020, 695 and 565; δ_H(400 MHz; $CDCl_3$) 0.84–0.94 (15 H, m), 1.07–1.11 (9 H, m), 1.22–1.35 (5 H, m), 1.54–1.60 (2 H, m) and 1.94 (1 H, septet, *J* 6.8).

Reaction of Ketone **4e** *with Butyllithium*.—In the same way, a solution of **4e** (260 mg, 1.0 mmol) in THF (10 cm^3) was added to butyllithium (0.8 cm^3, 1.3 mmol) and then the mixture was treated to give **3e** (111 mg, 42%) and 1-(*triethylgermyl*)-1-*phenylpentan*-1-*ol* **6e** (161 mg, 52%), an undistillable oil (Found: M$^+$ 324.1485. $C_{17}H_{30}GeO$ requires *M*, 324.1507); ν_{max}(film)/cm^{-1} 3450 (OH), 1450, 1010, 695 and 560; δ_H(400 MHz; $CDCl_3$) 0.71–0.80 (6 H, m), 0.85 (3 H, t, *J* 6.9), 0.93–0.99 (9 H, m), 1.23–1.33 (4 H, m), 1.55 (1 H, s), 1.94–2.19 (2 H, m) and 7.10–7.32 (5 H, m).

Reaction of Ketone **4b** *with* tert-*Butyl Lithioacetate* **7**.—A solution of *tert*-butyl acetate (140 mg, 1.2 mmol) in THF (3 cm^3) was added to a solution of lithium diisopropylamide (LDA, 1.2 mmol) in THF (4 cm^3) at −78 °C. The mixture was stirred for 0.5 h and then a solution of **4b** (228 mg, 1.0 mmol) in THF (3 cm^3) was added and stirring was continued for 10 min at −78 °C and then for 0.5 h at 0 °C. The reaction was quenched with saturated aqueous NH_4Cl. The organic layer was separated and the aqueous layer was extracted with ether. The combined extracts were washed with water and saturated NaCl, dried ($MgSO_4$), and then concentrated. The residue was distilled to give tert-*butyl* 3-*hydroxy*-4-*methyl*-3-(*triethylgermyl*)*valerate* **8b** (282 mg, 81%), b.p. 135 °C/2.0 mmHg (Found: C, 55.4; H, 9.95. $C_{16}H_{34}GeO_3$ requires C, 55.4; H, 9.9%); ν_{max}(film)/cm^{-1} 3480 (OH), 1710 (CO), 1375, 1155 and 570; δ_H(400 MHz; $CDCl_3$) 0.86–0.93 (6 H, m), 0.92 (3 H, d, *J* 7.0), 0.93 (3 H, d, *J* 7.0), 1.07–1.11 (9 H, m), 1.46 (9 H, s), 2.01 (1 H, septet, *J* 7.0), 2.47 and 2.51 (2 H, AB-q, *J* 15.7) and 3.91 (1 H, s).

Reaction of Ketone **4e** *with* tert-*Butyl Lithioacetate* **7**.—Ketone **4e** (260 mg, 1.0 mmol) and LDA (1.2 mmol) were treated in the same way to give tert-*butyl* 3-*hydroxy*-3-*phenyl*-3-(*triethylgermyl*)*propionate* **8e** (312 mg, 82%), b.p. 139 °C/1.0 mmHg (Found: C, 59.85; H, 8.7. $C_{19}H_{32}GeO_3$ requires C, 59.9; H, 8.5%); ν_{max}(film/cm^{-1}) 3450 (OH), 1700 (CO), 1370, 1145, 700 and 570; δ_H(400 MHz; $CDCl_3$) 0.75–0.81 (6 H, m), 0.94–0.98 (9 H, m), 1.18 (9 H, s), 2.93 and 3.06 (2 H, AB-q, *J* 15.8), 3.94 (1 H, s) and 7.25–7.30 (5 H, m).

Reaction of Ketone **4b** *with* 2-*Lithiopropionitrile* **9**.—A solution of propionitrile (55 mg, 1.0 mmol) in THF (3 cm^3) was added dropwise at −78 °C to a solution of LDA (1.58 mol dm^{-3}) in THF (4 cm^3) at 0 °C. The mixture was stirred for 0.5 h and then a solution of **4b** (234 mg, 1.0 mmol) in THF (3 cm^3) was added and the mixture was stirred at −78 °C for 10 min then at 0 °C for 0.5 h. The reaction was quenched with saturated aqueous NH_4Cl. The organic layer was separated and the aqueous layer was extracted with ether. The combined extracts were washed with water and saturated aqueous NaCl, dried ($MgSO_4$), and then concentrated. The residue was chromatographed on a silica gel column with hexane–ethyl acetate (20:1 to 10:1) to give 2,4-*dimethyl*-3-*hydroxy*-3-(*triethylgermyl*)-*valeronitrile* **10b** (212 mg, 73%), b.p. 133 °C/1.0 mmHg (Found: C, 54.7; H, 9.55; N, 4.5. $C_{13}H_{27}GeNO$ requires C, 54.6; H, 9.5; N, 4.9%); ν_{max}(film)/cm^{-1} 3450 (OH), 2240 (CN), 1460, 1015 and 565; δ_H(400 MHz; $CDCl_3$) 0.91–1.03 (9 H, m), 1.06–1.15 (12 H, m), 1.30 (d, *J* 7.2, minor isomer) and 1.35 (d, *J* 7.3, major isomer) (total 3 H), 1.49 (br s, major) and 1.61 (br s, minor) (total 1 H), 2.02–2.17 (1 H, m) and 3.00 (q, *J* 7.3, major) and 3.09 (q, *J* 7.2, minor) (total 1 H).

Reaction of Ketone **4d** *with* 2-*Lithiopropionitrile* **9**.—Ketone **4d** (293 mg, 1.0 mmol) and **9** (55 mg, 1.0 mmol) were treated in the same way to give 3-*hydroxy*-2-*methyl*-5-*phenyl*-3-(*triethylgermyl*)*valeronitrile* **10d** (251 mg, 72%), b.p. 160 °C/1.5 mmHg (Found: C, 62.2; H, 8.4; N, 3.7. $C_{18}H_{29}GeNO$ requires C, 62.1; H, 8.4; N, 4.0%); ν_{max}(film)/cm^{-1} 3450 (OH), 2240 (CN), 1460, 1020, 700 and 570; δ_H(400 MHz; $CDCl_3$) 0.96–1.06 (6 H, m), 1.08–1.19 (9 H, m), 1.29 (d, *J* 7.3, major) and 1.39 (d, *J* 7.2, minor) (total 3 H), 1.56 (s, minor) and 1.62 (s, major) (total 1 H), 1.96–2.11 (2 H, m), 2.50–2.71 (1 H, m), 2.75–2.87 (1 H, m), 3.01 (q, *J* 7.2, minor) and 3.09 (q, *J* 7.3, major) (total 1 H) and 7.19–7.34 (5 H, m).

Reaction of Ketone **4e** *with* 2-*Lithiopropionitrile* **9**.—Ketone **4e** (265 mg, 1.0 mmol) and **9** (66 mg, 1.2 mmol) were treated in the same way to give 3-*hydroxy*-2-*methyl*-3-*phenyl*-3-(*triethylgermyl*)*propionitrile* **10e** (256 mg, 80%), b.p. 130 °C/1.0 mmHg (Found: C, 59.8; H, 8.0; N, 4.3. $C_{16}H_{25}GeNO$ requires C, 60.1; H, 7.9; N, 4.4%); ν_{max}(film)/cm^{-1} 3400 (OH), 2200 (CN), 690 and 560; δ_H(400 MHz; $CDCl_3$) 0.89–1.04 (15 H, m), 1.05 (d, *J* 7.0,

major) and 1.48 (d, *J* 7.1, minor) (total 3 H), 1.86 (br s, minor) and 2.00 (br s, major) (total 1 H), 3.28 (q, *J* 7.0, major) and 3.38 (q, *J* 7.1, minor) (total 1 H) and 7.16–7.36 (5 H, m).

Reaction of Ketone **4b** *with* 1-*Lithioethyl Phenyl Sulfone* **11**.—A solution of ethyl phenyl sulfone (207 mg, 1.2 mmol) in THF (3 cm^3) was added to a solution of LDA (1.2 mmol) in THF (4 cm^3) at −78 °C. The mixture was stirred for 15 min and then a solution of **4b** (228 mg, 1.0 mmol) in THF (3 cm^3) was added and the mixture was stirred for 10 min at −78 °C and 0.5 h at 0 °C. The reaction was quenched with saturated aqueous NH_4Cl. The organic layer was separated and the aqueous layer was extracted with ether. The combined extracts were washed with water and saturated NaCl, dried ($MgSO_4$), and then concentrated. The residue was chromatographed on a silica gel column with hexane–ethyl acetate (20:1) to give 4-*methyl*-2-(*triethylgermyl*)*pentan*-3-*one* **12b** (210 mg, 81%) and *phenyl* 1-(*triethylgermyl*)*ethyl sulfone* **13** (33 mg, 10%).

Compound **12b**: b.p. 86 °C/1.5 mmHg (Found: C, 55.7; H, 10.3. $C_{12}H_{26}GeO$ requires C, 55.7; H, 10.1%); ν_{max}(film)/cm^{-1} 1690 (CO), 1465, 1385, 1155, 1133, 1000 and 700; δ_H(400 MHz; $CDCl_3$) 0.81–0.88 (6 H, m), 1.02–1.09 (15 H, m), 1.21 (3 H, d, *J* 6.8), 2.51 (1 H, septet, *J* 6.9) and 2.78 (1 H, q, *J* 6.8).

Compound **13**: b.p. 175 °C/1.1 mmHg (Found: C, 51.4; H, 7.3. $C_{14}H_{24}GeO_2S$ requires C, 51.1; H, 7.35%); ν_{max}(film)/cm^{-1} 1450, 1305, 1140, 1085, 1020, 735, 700, 690, 600 and 570; δ_H(400 MHz; $CDCl_3$) 1.07–1.15 (15 H, m), 1.19 (3 H, d, *J* 7.3), 2.80 (1 H, q, *J* 7.3), 7.51–7.55 (2 H, m), 7.57–7.61 (1 H, m) and 7.84–7.87 (2 H, m).

Reaction of Ketone **4c** *with* 1-*Lithioethyl Phenyl Sulfone* **11**.—Ketone **4c** (270 mg, 1.0 mmol) and **11** (200 mg, 1.2 mmol) were treated in the same way to give **13** (39 mg, 11%) and 1-*cyclohexyl*-2-(*triethylgermyl*)*propan*-1-*one* **12c** (236 mg, 78%), b.p. 95 °C/0.35 mmHg (Found: C, 60.1; H, 10.2. $C_{15}H_{30}GeO$ requires C, 60.3; H, 10.1%); ν_{max}(film)/cm^{-1} 1680 (CO), 1450, 1150, 990 and 570; δ_H(400 MHz; $CDCl_3$) 0.81–0.87 (6 H, m), 1.02–1.07 (9 H, m), 1.19 (3 H, d, *J* 6.8), 1.14–1.38 (3 H, m), 1.47–1.58 (1 H, m), 1.59–1.69 (2 H, m), 1.76–1.84 (4 H, m), 2.21 (1 H, tt, *J* 11.4, 3.3) and 2.76 (1 H, q, *J* 6.8).

Reaction of Ketone **4d** *with* 1-*Lithioethyl Phenyl Sulfone* **11**.—Ketone **4d** (293 mg, 1.0 mmol) and **11** (203 mg, 1.2 mmol) were treated in the same way to give **13** (43 mg, 13%) and 1-*phenyl*-4-(*triethylgermyl*)*pentan*-3-*one* **12d** (129 mg, 80%), an undistillable oil (Found: M^+, 322.1336. $C_{17}H_{28}GeO$ requires *M*, 322.1349); ν_{max}(film)/cm^{-1} 1680 (CO), 1455, 700 and 575; δ_H(400 MHz; $CDCl_3$) 0.73–0.85 (6 H, m), 1.01–1.06 (9 H, m), 1.19 (3 H, d, *J* 7.0), 2.59 (1 H, q, *J* 7.0), 2.59–2.63 (2 H, m), 2.85–2.93 (2 H, m), 7.15–7.19 (3 H, m) and 7.25–7.29 (2 H, m).

Reaction of Ketone **4e** *with* 1-*Lithioethyl Phenyl Sulfone* **11**.—Ketone **4c** (260 mg, 1.0 mmol) and **11** (206 mg, 1.2 mmol) were treated in the same way to give **13** (36 mg, 12%) and 2-(*triethylgermyl*)*propiophenone* **12e** (110 mg, 82%), an undistillable oil (Found: M^+, 294.1028. $C_{15}H_{24}GeO$ requires *M*, 294.1036); ν_{max}(film)/cm^{-1} 1675 (CO), 1315, 1285 and 710; δ_H(400 MHz; $CDCl_3$) 0.68–0.74 (6 H, m), 0.93–0.97 (9 H, m), 1.40 (3 H, d, *J* 6.6), 3.58 (1 H, q, *J* 6.6), 7.53–7.58 (3 H, m) and 7.83–7.86 (2 H, m).

Reaction of Ketone **4a** *with the Lithium Enolate of* tert-*Butyl Bromoacetate* **14**.—A solution of LDA (25 mmol) in THF (75 cm^3) was added to a solution of *tert*-butyl bromoacetate (4.88 g, 25 mmol) in THF (30 cm^3) and then a solution of **4a** (3.60 g, 19 mmol) in THF (30 cm^3) was added. The mixture was stirred for 0.5 h at −78 °C and then 1 h at 0 °C. Saturated aqueous NH_4Cl solution was added and the organic layer was separated. The aqueous layer was extracted with ethyl acetate. The combined extracts were washed with water and saturated aqueous NaCl, dried ($MgSO_4$), and then concentrated. The residue (6.32 g) was chromatographed on a silica gel column with hexane–benzene (1:1) to give tert-*butyl* 3-*isopropyl*-c-3-(*trimethylgermyl*)*oxirane*-2-*carboxylate cis*-**15a** (1.85 g, 32%) and *trans*-**15a** (1.62 g, 28%).*

Compound *cis*-**15a**: b.p. 75 °C/1.0 mmHg (Found: C, 51.7; H, 8.5. $C_{13}H_{26}GeO_3$ requires C, 51.5. H, 8.65%); ν_{max}/cm^{-1} 1748, 1225, 1159 and 833; δ_H(270 MHz; $CDCl_3$) 0.31 (9 H, s, $GeMe_3$), 0.79 (3 H, d, *J* 6.8, CH_3), 0.98 (3 H, d, *J* 6.8, CH_3), 1.49 (3 H, s, Bu^t), 2.05 (1 H, septet, *J* 6.8, CH) and 3.18 (1 H, s, 2-H); δ_C(100.4 MHz; $CDCl_3$) −1.0 (CH_3), 15.4 (CH_3), 19.4 (CH_3), 28.2 (CH_3), 32.8 (CH), 54.3 (CH), 66.3 (C), 81.9 (C) and 169.1 (C). An NOE enhancement of CH_3 (5.3%) and CH (3.1%) protons of the isopropyl group was observed upon irradiation of 2-H.

Compound *trans*-**15a**: b.p. 70 °C/0.45 mmHg (Found: C, 51.7; H, 8.5. $C_{13}H_{26}GeO_3$ requires C, 51.5. H, 8.65); ν_{max}/cm^{-1} 1748, 1227, 1155 and 829; δ_H(270 MHz; $CDCl_3$) 0.27 (9 H, s, $GeMe_3$), 0.93 (3 H, d, *J* 7.3, CH_3), 1.12 (3 H, d, *J* 6.9, CH_3), 1.49 (9 H, s, Bu^t), 1.81 (1 H, ap. septet, *J* 7.0, CH) and 3.24 (1 H, s, 2-H); δ_C(67.8 MHz; $CDCl_3$) −1.4 (CH_3), 18.9 (CH_3), 20.5 (CH_3), 28.1 (CH_3), 32.5 (CH), 57.3 (CH), 66.9 (C), 81.9 (C) and 168.2 (C).

Reaction of Ketone **4b** *with the Lithium Enolate of* tert-*Butyl Bromoacetate* **14**.—In the same way, a solution of **4b** (6.03 g, 26 mmol) in THF (30 cm^3) was treated with LDA (34 mmol) in THF (100 cm^3) to give tert-*butyl* 3-*isopropyl*-c-3-(*triethylgermyl*)*oxirane*-r-2-*carboxylate cis*-**15b** (3.08 g, 34%), *trans*-**15b** (2.74 g, 31%) and tert-*butyl* 2-*bromo*-2-(*triethylgermyl*)*acetate* **16** (2.3 g, 25%).

Compound *cis*-**15b**: b.p. 85 °C/0.3 mmHg (Found: C, 55.6; H, 9.2. $C_{16}H_{32}GeO_3$ requires C, 55.7; H, 9.35%); ν_{max}(film)/cm^{-1} 1748 (CO), 1368, 1225 and 1157; δ_H(270 MHz; $CDCl_3$) 0.77 (3 H, d, *J* 6.9), 0.88–0.96 (6 H, m), 0.96 (3 H, d, *J* 6.9), 1.01–1.10 (9 H, m), 1.50 (9 H, s), 1.99 (1 H, septet, *J* 6.9) and 3.14 (1 H, s).

Compound *trans*-**15b**: b.p. 90 °C/0.6 mmHg (Found: C, 55.7; H, 9.2. $C_{16}H_{32}GeO_3$ requires C, 55.7; H, 9.35%); ν_{max}(film)/cm^{-1} 1748 (CO), 1719, 1368, 1225 and 1155; δ_H(270 MHz; $CDCl_3$) 0.84–0.95 (6 H, m), 0.92 (3 H, d, *J* 6.9), 1.04–1.11 (9 H, m), 1.10 (3 H, d, *J* 6.9), 1.48 (9 H, s), 1.73 (1 H, septet, *J* 6.9) and 3.27 (1 H, s).

Compound **16**: b.p. 110 °C/1.5 mmHg (Found: C, 40.5; H, 7.2. $C_{12}H_{25}BrGeO_2$ requires C, 4.07; H, 7.1%) ν_{max}(film)/cm^{-1} 1730 (CO), 1250 and 1120; δ_H(270 MHz; $CDCl_3$) 1.01 (6 H, q, *J* 7.0), 1.10 (9 H, t, *J* 7.0), 1.47 (9 H, s) and 3.83 (1 H, s).

Reaction of Ketone **4c** *with the Lithium Enolate of* tert-*Butyl Bromoacetate* **14**.—In the same way, a solution of **4c** (6.42 g, 24 mmol) in THF (30 cm^3) was treated with LDA (31 mmol) in THF (100 cm^3) to give tert-*butyl* 3-*cyclohexyl*-c-3-(*triethylgermyl*)*oxirane*-r-2-*carboxylate cis*-**15c** (3.17 g, 35%), *trans*-**15c** (3.00 g, 33%) and acetate **16** (1.78 g, 21%).

Compound *cis*-**15c**: b.p. 100 °C/0.2 mmHg (Found: C, 59.4, H, 9.3. $C_{19}H_{36}GeO_3$ requires C, 59.3; H, 9.4%); ν_{max}/cm^{-1} 1747 (CO), 1395, 1368, 1223 and 1157; δ_H(270 MHz; $CDCl_3$) 0.70–1.30 (20 H, m), 1.49 (9 H, s), 1.58–1.80 (6 H, m) and 3.21 (1 H, s).

Compound *trans*-**15c**: b.p. 100 °C/0.25 mmHg (Found: C, 59.5; H, 9.3. $C_{19}H_{36}GeO_3$ requires C, 59.3; H, 9.4%); ν_{max}/cm^{-1} 1748, 1717 (CO), 1368, 1223 and 1155; δ_H(270 MHz; $CDCl_3$) 0.83–0.92 (6 H, m), 1.04–1.31 (14 H, m), 1.37–1.56 (2 H, m), 1.49 (9 H, s), 1.62–1.80 (3 H, m), 1.87–1.97 (1 H, m) and 3.26 (1 H, s).

* The prefixes *cis* and *trans* are used here and elsewhere to designate the position of the trialkylgermyl substituent relative to the carboxylate group.

Treatment of Oxirane **15a–c** *with Boron Trifluoride–Diethyl Ether. General Procedure.*—To a solution of **15a–c** (0.5 mmol) in dichloromethane (10 cm^3) was added dropwise boron trifluoride–diethyl ether or deactivated catalyst * (0.55 mmol), and the mixture was stirred under the conditions listed in Table 3. The reaction was quenched by sequential addition of triethylamine (1 cm^3) and MeOH (2 cm^3), and the resulting mixture was mixed with ethyl acetate (80 cm^3) and 5% aqueous HCl (20 cm^3). The organic layer was separated and washed with saturated aqueous $NaHCO_3$ (25 cm^3) and NaCl (25 cm^3), dried ($MgSO_4$), and then concentrated. The residue was chromatographed on a silica gel column with hexane–ethyl acetate (10:1) to give the following products. The results are summarized in Table 3 (entries 2, 3, 5, 6).

A mixture of tert-*butyl* (E)- and (Z)-2-*hydroxy*-3-*methylpent*-3-*enoates* (*E*)-**20a**, **b** and (*Z*)-**20a**, **b**: b.p. 60 °C/12 mmHg (Found: C, 64.4; H, 9.8. $C_{10}H_{18}O_3$ requires C, 64.5; H, 9.7%); ν_{max}(film)/cm^{-1} 3505 (OH), 1725, 1370, 1258, 1159 and 1100; δ_H(400 MHz; $CDCl_3$) 1.4768 (s, Bu^t, *Z*), 1.471 (s, Bu^t, *E*) (total 9 H), 1.58 (quint, *J* 1.1, Me, *E*), 1.62 (quintet, *J* 1.5, Me) (total 3 H), 1.65 (dq, *J* 6.8, 1.1, Me, *E*), 1.71 (dq, *J* 7.0, 1.5, Me, *Z*) (total 3 H), 3.08 (d, *J* 5.3, OH, *Z*), 3.14 (d, *J* 5.3, OH, *E*) (total 1 H), 4.36 (d, *J* 5.3, C*H*OH, *E*), 4.93 (d, *J* 5.3, C*H*OH, *Z*) (total 1 H), 5.51 (m, *J* 7.0, 0.7, –CH=, *Z*) and 5.61 (m, *J* 6.8, 0.7, –CH=, *E*) (total 1 H); δ_C(100.4 MHz; $CDCl_3$) 11.3 (CH_3, *E*), 13.3 (CH_3, *Z*), 13.4 (CH_3, *E*), 17.6 (CH_3, *Z*), 27.91 (CH_3, *Z*), 27.94 (CH_3, *E*), 68.9 (CH, *Z*), 76.6 (CH, *E*), 82.49 (C, *Z*), 82.53 (C, *E*), 124.81 (CH, *Z*), 124.83 (CH, *E*), 132.7 (C, *Z*), 133.0 (C, *E*), 173.4 (C, *E*) and 173.5 (C, *Z*). The ratio of (*E*)- and (*Z*)-isomers was determined from the integrated values of protons from the ^1H NMR spectrum.

tert-*Butyl* 2-(*cyclohept*-1-*enyl*)-2-*hydroxyacetate* **20c**: ν_{max}($CHCl_3$)/cm^{-1} 3422, 1719, 1372, 1155 and 669; δ_H(270 MHz; $CDCl_3$) 1.00–1.80 (6 H, m, c-heptyl), 1.47 (9 H, s, Bu^t), 2.05–2.20 (4 H, m, c-heptyl), 3.17 (1 H, d, *J* 5.0, OH), 4.34 (1 H, d, *J* 5.0, C*H*OH) and 5.94 (1 H, t, *J* 6.4, –CH=); δ_C(100.4 MHz; $CDCl_3$) 26.7 (CH_2), 27.0 (CH_2), 28.0 (CH_3), 28.3 (CH_2), 28.4 (CH_2), 32.4 (CH_2), 77.2 (CH), 82.5 (C), 132.3 (CH), 141.1 (C) and 173.4 (C).

tert-*Butyl* 2-*hydroxy*-4-*methylpent*-3-*enoate* **21a**, **b**: b.p. 85 °C/22 mmHg (Found: C, 64.6; H, 9.8. $C_{10}H_{18}O_3$ requires C, 64.5; H, 9.7%); ν_{max}(film)/cm^{-1} 3466, 1728 and 1159; δ_H(270 MHz; $CDCl_3$) 1.47 (9 H, s, Bu^t), 1.76 (6 H, d, *J* 1.3, Me), 2.95 (1 H, d, *J* 5.6, OH), 4.69 (1 H, dd, *J* 8.6, 5.6, C*H*OH) and 5.11 (1 H, d, septet, *J* 8.6, 1.3, –CH=); δ_C(100.4 MHz; $CDCl_3$) 18.6 (CH_3), 25.8 (CH_3), 28.0 (CH_3), 68.5 (CH), 82.4 (C), 122.4 (CH), 138.6 (C) and 173.7 (C).

tert-*Butyl* 3-*cyclohexylidene*-2-*hydroxypropanoate* **21c**: b.p. 70 °C/0.5 mmHg (Found: C, 69.1; H, 9.8. $C_{13}H_{22}O_3$ requires C, 69.0; H, 9.8%); ν_{max}(film)/cm^{-1} 3468, 1726, 1370, 1256, 1159 and 1084; δ_H(400 MHz; $CDCl_3$) 1.47 (9 H, s, Bu^t), 1.47–1.68 (6 H, m, c-hexyl), 2.07–2.17 (2 H, m, c-hexyl), 2.18–2.24 (1 H, m, c-hexyl), 2.27–2.33 (1 H, m, c-hexyl), 2.64 (1 H, br s, OH), 4.75 (1 H, d, *J* 8.6, C*H*OH) and 5.04 (1 H, dt, *J* 8.6, 1.1, –CH=); δ_C(67.8 MHz; $CDCl_3$) 26.5 (CH_2), 27.7 (CH_2), 28.0 (CH_3), 28.4 (CH_2), 29.6 (CH_2), 36.9 (CH_2), 67.7 (CH), 82.2 (C), 119.2 (CH), 145.9 (C) and 173.7 (C).

* Freshly distilled boron trifluoride–diethyl ether (2.84 g, 20 mmol) was mixed with water (360 mg, 20 mmol) at 0 °C and then dichloromethane was added to make the total volume 20 cm^3. The solution was allowed to stand overnight and the clear upper layer was used.

Reaction of Oxirane **15b** *with Sulfuric acid.*—To a solution of *cis*-**15b** (179 mg, 0.52 mmol) or *trans*-**15b** (170 mg, 0.49 mmol) in MeOH (10 cm^3) was added 98% sulfuric acid (0.5 cm^3) at 0 °C. The mixture was stirred under the conditions described in Table 3. Ethyl acetate (80 cm^3) and water (20 cm^3) were added to the mixture and the organic layer was separated and washed with saturated aqueous $NaHCO_3$ (25 cm^3) and saturated NaCl (25 cm^3), dried ($MgSO_4$), and then concentrated. The residue was chromatographed on a silica gel column with hexane–ethyl acetate (10:1). The results are listed in Table 3.

Remaining **15b** was recovered as *methyl* 3-*isopropyl*-t-3-(*triethylgermyl*)*oxirane*-r-2-*carboxylate* (41 mg, 28%), b.p. 75 °C/0.15 mmHg (Found: C, 51.7; H, 8.5. $C_{13}H_{26}GeO_3$ requires C, 51.5; H, 8.65); ν_{max}(film)/cm^{-1} 1757, 1732, 1209 and 1016; δ_H(270 MHz; $CDCl_3$) 0.85–0.94 (6 H, m, $GeCH_2$), 0.89 (3 H, d, *J* 7.3, CH_3 of Pr^i), 1.05–1.15 (9 H, m, $GeCH_2CH_3$), 1.12 (3 H, d, *J* 6.9, CH_3 of Pr^i), 1.68 (1 H, septet, *J* 7.0, CH), 3.39 (s, 1 H, 3-H) and 3.78 (s, 3 H, OCH_3); δ_C(67.8 MHz; $CDCl_3$) 4.7 (CH_2), 8.9 (CH_3), 18.4 (CH_3), 20.3 (CH_3), 32.8 (CH), 52.1 (CH_3), 56.8 (CH), 67.3 (C) and 169.7 (C).

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