

Scandium Trifluoromethanesulfonate-Catalyzed Chemoselective Allylation Reactions of Carbonyl Compounds with Tetraallylgermane in Aqueous Media

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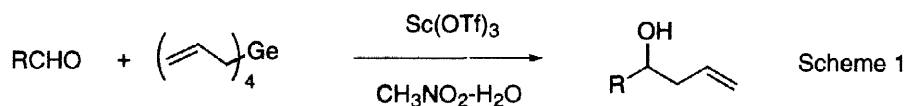
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Abstract: Scandium(III) triflate-catalyzed allylation of carbonyl compounds with tetraallylgermane proceeded readily in aqueous nitromethane to afford homoallyl alcohols in excellent to good yields. The presence of H₂O is indispensable for the allylation of aldehydes to proceed smoothly. Aldehydes were allylated highly chemoselectively in the presence of ketone moieties. © 1999 Elsevier Science Ltd. All rights reserved.

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Introduction

Lewis acid mediated allylations of carbonyl compounds constitute one of the most important class of synthetic reactions leading to homoallylic alcohols. Application of the method for the preparation of poly-oxygenated natural compounds have been studied extensively. Numerous kinds of allylic organometallics as well as various kinds of effective Lewis acids have been developed so far.¹ In particular, allylic metals bearing 14 group elements, such as allylsilanes and allylstannanes have been thoroughly investigated as useful allylic organometallics.² For example, allylstannanes react with aldehydes under varieties of conditions;³ catalyzed by Lewis acid,⁴ transition metal,⁵ heat,⁶ high pressure,⁷ Brønsted acid,⁸ or protic solvent.⁹ Highly enantioselective allylation has also been achieved.¹⁰ They currently enjoy wide application in organic synthesis. Although allylsilanes are less reactive than allylstannanes,¹¹ they attracted much attention as allylic metals¹² and Lewis acid mediated stereoselective as well as enantioselective¹³ allylation of aldehydes have been reported. Lewis base promoted allylations with allyltrichlorosilane have been reported recently.¹⁴ Generally, allyltins showed higher reactivity than allylsilanes. The practical usage of organotin compounds, however, has been



plagued by its inherent toxicity. In striking contrast, little attention has been paid to organogermanium compounds by synthetic organic chemists¹⁵ irrespective of its lower toxicity.¹⁶ With respect to allylgermanium compounds, Sano et al. studied the Lewis acid mediated allylation reaction of aldehydes with allylgermane¹⁷ for the first time and Yamamoto et al. studied the conjugate addition of functionalized allylgermanes.¹⁸ Barbier type reaction using germanium(II) iodide has been investigated by Hashimoto and Saigo et al.^{19,20}

Recently, lanthanide trifluoromethanesulfonates [lanthanide triflates, $\text{Ln}(\text{OTf})_3$] and scandium(III) triflate have attracted attention as a water tolerant Lewis acid exhibiting catalytic ability in numerous carbon-carbon bond forming reactions,²¹ such as Diels-Alder reactions,²² Michael addition,²³ Lanthanide triflate mediated allylation reactions of aldehydes with allylstannanes²⁴ and allylsilanes²⁵ have been recently reported. Allylation of aldimines by allylstannanes also proceeded in good yields.²⁶ Kobayashi et al. have reported lanthanide(III) triflate promoted allylation reactions of aldehydes with tetraallylstannane in aqueous media.²⁷ Lanthanide triflate mediated allylation of allylgermane, however, had not been reported so far. As part of our continued interest in developing synthetic utility of allylic metals of group 14 elements,²⁸ we started our program toward developing synthetic utility of allylgermanium compounds,²⁹ and focused on tetraallylgermane³⁰ as a stable allylic metal for the first time. It was found that scandium(III) trifluoromethanesulfonate-promoted allylation reactions of carbonyl compounds with tetraallylgermane in aqueous nitromethane proceeded smoothly to afford homoallylic alcohols in high yields.³¹ Furthermore, highly chemoselective allylation toward aldehydes in the presence of ketones was achieved.

Results and Discussion

Tetraallylgermane was prepared in one step by the reaction of allylmagnesium bromide and germanium(IV) chloride in high yields.³⁰ We have found that addition of benzaldehyde to a nitromethane solution of scandium(III) triflate (10 mol%) and tetraallylgermane at room temperature afforded a homoallylic alcohol (**1**) in good yield. The effect of the solvent was studied and the results are shown in Table 1. Polar solvents such as acetonitrile and nitromethane promoted the allylation reaction smoothly to afford **1** in good yields, but bis-allylated ether (**2**) was obtained in low yield as a by-product. Quite recently, Aggarwal and co-workers also recently observed the formation of an ether of the similar type as a by-product in $\text{Sc}(\text{OTf})_3$ catalyzed allylation reaction of aldehyde with allylsilane.^{25c} Interestingly, addition of water significantly improved the yield of the

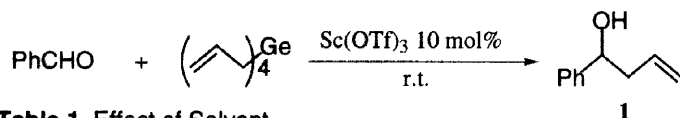
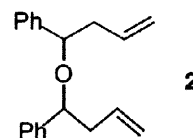


Table 1. Effect of Solvent

Entry	Solvent	no water		35 equiv. of water ^{a)}	
		Time	Yield of 1 / %	Time	Yield of 1 / %
1	Et_2O	10 min	40	3 d	25
2	CH_2Cl_2	5 min	39	5 d	49
3	CH_3CN	1 min	73	10 h	85
4	CH_3NO_2	1 min	72	45 min	94
5	DMSO	7 d	no reaction	—	—

a) Molar equivalent based on $\text{Sc}(\text{OTf})_3$



adduct and formation of **2** was suppressed though the rate of the reaction got slower. High yields were obtained when 30–40 mol equiv of water based on $\text{Sc}(\text{OTf})_3$ was employed in nitromethane. Thus, use of 35 molar equivalent of water in CH_3NO_2 afforded **1** in 99% yield. This effect on the yields appears to level off at about 40 mol equivalent of water based on $\text{Sc}(\text{OTf})_3$. Further increase of the amount of water considerably retarded the reaction.

Recently development of carbon-carbon bond forming reactions in aqueous media is a challenging target in organic synthesis.³² Yanagisawa and Yamamoto disclosed a chemoselective allylation of carbonyl compounds in acidic aqueous media.⁸ Kobayashi reported the improvement of the yields by addition of water in the lanthanide triflate mediated reactions.^{21a} We speculate that addition of water decreased the Lewis acidity of $\text{Sc}(\text{OTf})_3$ thereby suppressing the formation of the by-product.

Other lanthanide triflates were examined and the results are shown in Table 2. Although other lanthanide triflates such as $\text{Yb}(\text{OTf})_3$ and $\text{Sm}(\text{OTf})_3$ also promoted the allylation reaction, $\text{Sc}(\text{OTf})_3$ turned out to be most effective as a Lewis acid in our system.

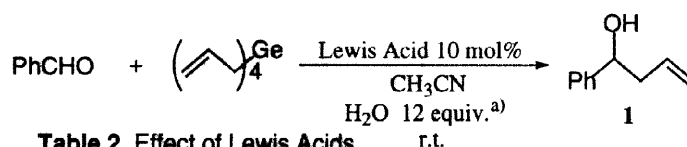


Table 2. Effect of Lewis Acids

Entry	Lewis Acid	Time	Yield of 1 / %
1	$\text{Sc}(\text{OTf})_3$	45 min	81
2	$\text{Yb}(\text{OTf})_3$	30.5 h	84
3	$\text{Sm}(\text{OTf})_3$	6 d	83

a) Molar equivalent based on $\text{Sc}(\text{OTf})_3$

Tetraallylgermane possess four allyl moieties. How many allyl groups will work as allyl anion? The effect of the loading of tetraallylgermane was studied and the results are shown in Table 3. At least 2 moles of the allyl group worked efficiently as allylating reagents though the first allyl moiety is much more reactive than the second one.

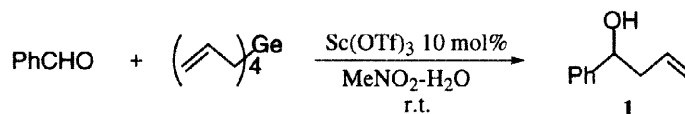
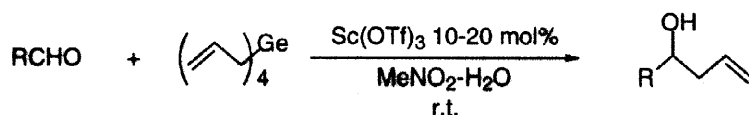


Table 3. Effect of the loading of tetraallylgermane

Entry	Tetraallylgermane / equiv.	Time	Yield of 1 / %
1	1.00	45 min	99
2	0.75	7 h	88
3	0.50	27 h	73
4	0.25	4 d	39

**Table 4.** Allylation of Various Aldehydes^a

Entry	Carbonyl Compounds	Product		Amount of Sc(OTf) ₃ ^b	Amount of H ₂ O ^c	Reaction time/h	Yield/% ^d
1	PhCHO		1	0.10	35	0.75	99(72)
2			3	0.10	36	2.7	99
3			4	0.10	36	2.0	quant
4	PhCH ₂ CH ₂ CHO		5	0.15	43	3.5	92(33)
5	<i>n</i> -C ₁₁ H ₂₃ CHO		6	0.20	43	4	92(45)
6			7	0.20	39	2.5	75
7	PhC(=O)CHO·H ₂ O		8	0.20	28	0.5	87
8			9	0.20	0	114	0(92)
9			10	0.10	35	5	82

a) The reactions were carried out using tetraallylgermane (1.0 equiv) and a carbonyl compound at room temperature in CH₃NO₂. b) mol equivalent based on carbonyl compounds. c) mol equivalent of H₂O based on Sc(OTf)₃. d) Parenthesis refers to the yield of the reaction without water.

The results of the scandium(III) triflate catalyzed allylation of several carbonyl compounds with tetraallylgermane are summarized in Table 4. The yields in parenthesis refer to the yield of the reaction carried out under anhydrous conditions. Allylation of both aromatic and aliphatic aldehydes proceeded smoothly to afford the corresponding homoallylic alcohols in excellent to good yields. Whereas 10 mol% of the catalyst sufficed for the aromatic aldehydes, use of 15–20 mol% of the catalyst was requisite for the aliphatic aldehydes (entries 4, 5, and 6). The effect of water is also prominently observed with aliphatic aldehydes such as 3-phenyl propanal and lauraldehyde, wherein removal of the water noticeably reduced the yields of the corresponding homoallyl alcohols (entries 4 and 5). Phenylglyoxal monohydrate, which possesses water of crystallization, afforded the mono-allylated product predominantly in 87% yield (entry 7). Ketones were usually inert under the standard conditions. For example, acetophenone did not give the corresponding homoallyl alcohol. An activated ketone afforded the corresponding adduct. While allylation of an α -keto ester under the optimized reaction conditions did not take place, allylation of an α -keto ester completed without water after 114 h to furnish the adduct (**9**) in 92% yield (entry 8). Cyclohexanone underwent allylation readily to afford the adduct (**10**) in a good yield (entry 9).

The effect of germyl substituents is noteworthy. Allyltriethylgermane did not react with benzaldehyde under the optimized reaction conditions. Thus treatment of allyltriethylgermane and benzaldehyde in the presence of $\text{Sc}(\text{OTf})_3$ (10 mol%) in nitromethane at room temperature for 2 days, **1** was obtained less than 5 % yield.³³

Chemoselectivity

Discrimination of aldehydes and ketones in the allylation reaction is not always a trivial issue. For example, chemoselective allylation of benzaldehyde in preference to acetophenone proceeded in modest selectivity using several allylic organometallics.³⁴ Quite recently, Yamamoto et al. reported extremely highly selective allylation reactions by tetraallyltin promoted by a Brønsted acid.⁸ A high level of chemoselectivity has not been achieved except in a few instances.³⁵ It is worth noting that the present system exhibited high chemoselectivity toward aldehydes. Competitive allylation reactions of aldehyde and ketone were thus examined under the influence of 10 mol% of $\text{Sc}(\text{OTf})_3$ based on benzaldehyde in CH_3NO_2 in the presence of water (35 mol equivalent) and the results are shown in Table 5. In the presence of equimolar amounts of benzaldehyde, acetophenone, and tetraallylgermane, benzaldehyde exclusively underwent allylation to afford **1** in 94% yield (entry 1). Chemoselective allylation of benzaldehyde also proceeded in the presence of an α -keto ester (entry 2). 1-Octanal was also allylated highly selectively in the presence of several ketones (entries 4, 5, and 6).

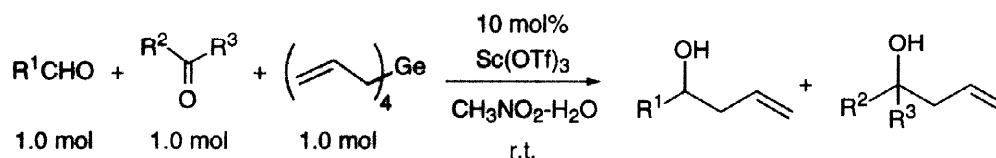
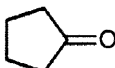
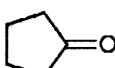


Table 5. Chemoselectivity to aldehyde and ketone

Entry	Carbonyl Compounds		Yield/% ^{a)}	Ratio
1	PhCHO	+ PhCOCH ₃	94	54:1
2	PhCHO	+ PhCOCOOEt	96	>99:<1
3	PhCHO	+ 	90	70:1
4	<i>n</i> -C ₇ H ₁₅ CHO	+ PhCOCH ₃	64	>99:<1
5	<i>n</i> -C ₇ H ₁₅ CHO	+ <i>n</i> -C ₅ H ₁₁ COCH ₃	79	57:1
6	<i>n</i> -C ₇ H ₁₅ CHO	+ 	86	>99:<1

a) combined yields of the alcohols.

Comparison with Sn and Si

Reactivity of allylgermane were compared with those of allylstannane and allylsilane, and the results are shown in Table 6. Although tetraallylstannane underwent allylation much faster than tetraallylgermane, allylation reaction of tetraallylsilane was sluggish under the identical reaction conditions. Thus the

nucleophilicity of the tetraallylic metals are in the order allylstannane > allylgermane > allylsilane, which is in good agreement with the nucleophilicity elucidated by the kinetic study on the reactions of allylmethyl with diaryl carbenium ions.¹¹ Advantage of allylgermane over allylstannane lies in its chemoselectivity toward aldehyde, which is ascribed to its moderate reactivity.

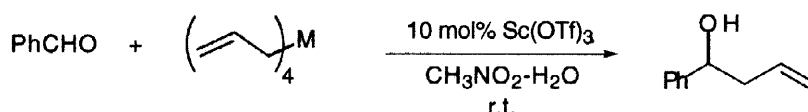


Table 6. Effect of the center metal

Entry	M	Time	Yield/%
1	Sn	5 min	86
2	Ge	45 min	99
3	Si	25 h	18

a) 35 mol equiv of water based on Sc(OTf)₃ was employed.

Conclusions

The present allylation reactions of aldehydes required 30–40 equiv of H₂O based on Sc(OTf)₃ for the reaction to proceed smoothly. Appropriate Lewis acidity appears to be essential to achieve the smooth reaction. H₂O would coordinate to scandium and lower the Lewis acidity of the catalyst. Addition of further amount of water decreased the Lewis acidity of Sc(OTf)₃ significantly, thus retarding the allylation reaction remarkably.

In summary, we have developed a novel allylation reaction utilizing tetraallylgermane. Salient features of the present allylation reaction are: 1) the less toxic organogermanium compounds have been utilized as allylmethyl, 2) allylation took place smoothly in the presence of water, 3) readily accessible tetraallylgermane was employed as an allylating reagent for the first time, 4) high chemoselectivity toward aldehydes was observed in the presence of ketones.

Experimental Section

General Methods. ¹H and ¹³C NMR spectra were recorded on a Varian Inova 400 spectrometer in CDCl₃. Tetramethylsilane (TMS) served as internal standard ($\delta = 0$) for ¹H NMR, and CDCl₃ was used as internal standard ($\delta = 77.0$) for ¹³C NMR. Purification of the products was performed by column chromatography on silica gel (Fuji sylisia D60L) or preparative TLC on silica gel (Wako gel B-5F). All solvents were purified according to the standard procedures.

Tetraallylgermane:³⁰ Allyl bromide (23.2 mL, 0.268 mol) was added dropwise to a mixture of Mg (6.51 g, 0.268 mol) in Et₂O (83 mL) for 1 h at 0 °C. To the solution of allylmagnesium bromide was added dropwise a solution of GeCl₄ (3.8 mL, 33.3 mmol) in Et₂O (17 mL) for 1 h at the temperature. After being heated to reflux for 3 h, the mixture was cooled to 0 °C and was quenched by addition of 1N HCl. After filtration over Celite, the aqueous layer was extracted with ethyl acetate and the combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, and concentrated to dryness. Purification of the crude mixture by distillation (bp. 70 °C/ 4 mmHg) afforded tetraallylgermane (6.76 g) in 86% yield. ¹H NMR(CDCl₃) δ = 5.82 (ddd, 1H, *J* = 17.0, 10.1, 8.4 Hz), 4.89 (ddd, 1H, *J* = 17.0, 1.3, 1.3 Hz), 4.84 (dddd,

1H, $J=13.1, 13.1, 1.0, 1.0$ Hz), 1.77 (ddd, 2H, $J= 8.2, 1.0, 1.0$ Hz); ^{13}C NMR (CDCl_3) $\delta= 135.06, 113.19, 19.05$.

Allyltriethylgermane:³⁶ ^1H NMR(CDCl_3) $\delta= 5.82$ (dddd, 1H, $J=16.9, 10.0, 8.3, 8.3$ Hz), 4.82 (dd, 1H, $J=16.9, 1.2$ Hz), 4.72 (dd, 1H, $J=10.0, 0.9$ Hz), 1.51 (dd, 2H, $J= 10.0, 0.9$ Hz), 1.00 (t, 3H, $J=7.9$ Hz), 0.76 (q, 2H, $J=7.9$ Hz); ^{13}C NMR (CDCl_3) $\delta= 136.50, 111.58, 18.84, 8.88, 3.83$.

A typical experimental procedure for the allylation of aldehydes (Table 4, Entry 1); To a suspension of scandium trifluoromethanesulfonate (9.9 mg, 0.020 mmol) in nitromethane (0.70 mL) and H_2O (13 μL , 0.721 mmol) was added successively tetraallylgermane (47 μL , 0.202 mmol) and benzaldehyde (20.5 μL , 0.202 mmol) at room temperature. After being stirred at that temperature for 1.5 h, the reaction was quenched by addition of 1N HCl solution. The aqueous layer was extracted with ethyl acetate and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 , and concentrated to dryness. Purification of the crude mixture by column chromatography (SiO_2 , hexane: ethyl acetate = 6 : 1, v/v) gave **1** (29.7 mg) in 99% yield.

1-Phenyl-3-buten-1-ol (1):³⁷ ^1H NMR(CDCl_3) $\delta= 7.41\text{--}7.23$ (m, 5H), 5.81 (ddt, 1H, $J=17.2, 10.2, 6.9$ Hz), 5.19–5.12 (m, 2H), 4.73 (dd, 1H, $J= 7.5, 5.3$ Hz), 2.53–2.47 (2H, m), 2.09 (s, 1H); ^{13}C NMR (CDCl_3) $\delta= 143.82, 134.43, 128.39, 127.52, 125.78, 118.43, 73.25, 43.83$.

1-(4-Nitrophenyl)-3-buten-1-ol (3):³⁷ ^1H NMR(CDCl_3) $\delta= 8.19$ (d, 2H, $J=7.0$ Hz), 7.41 (d, 2H, $J=7.0$ Hz), 5.78 (dddd, 1H, $J= 17.8, 9.9, 7.5, 6.4$ Hz), 5.18 (dd, 1H, $J= 17.8, 9.9$ Hz), 5.17 (dd, 1H, $J= 9.9, 1.5$ Hz), 4.86 (dd, 1H, $J=7.9, 5.3$ Hz), 2.56 (ddd, 1H, $J= 14.5, 6.4, 5.3$ Hz), 2.47 (s, 1H), 2.46 (ddd, 1H, $J= 14.5, 7.9, 7.5$ Hz); ^{13}C NMR (CDCl_3) $\delta= 151.12, 147.18, 133.18, 126.51, 123.53, 119.44, 72.16, 43.80$.

1-(4-Chlorophenyl)-3-buten-1-ol (4):³⁷ ^1H NMR(CDCl_3) $\delta= 7.32\text{--}7.26$ (m, 5H), 5.77 (dddd, 1H, $J= 17.3, 10.5, 7.3, 7.2$ Hz), 5.15 (d, 1H, $J=17.3$ Hz), 5.15 (d, 1H, $J=10.5$ Hz), 4.71 (dd, 1H, $J=7.7, 5.1$ Hz), 2.53–2.41 (m, 2H), 2.10 (brds, 1H); ^{13}C NMR (CDCl_3) $\delta= 142.24, 133.94, 133.13, 128.50, 127.17, 118.83, 72.53, 43.83$.

5-Phenyl-1-hexen-3-ol (5):³⁷ ^1H NMR(CDCl_3) $\delta= 7.30\text{--}7.16$ (m, 5H), 5.81 (dddd, 1H, $J= 17.2, 10.6, 7.9, 6.4$ Hz), 5.14 (d, 1H, $J= 17.2$ Hz), 5.14 (d, 1H, $J= 10.6$ Hz), 3.67 (brs, 1H), 2.81 (ddd, 1H, $J= 14.6, 7.5, 6.6$ Hz), 2.68 (ddd, 1H, $J= 14.6, 7.5, 6.6$ Hz), 2.29 (m, 1H), 2.13 (m, 1H), 2.04–1.75 (m, 2H), 1.65 (s, 1H); ^{13}C NMR (CDCl_3) $\delta= 142.02, 134.60, 128.41, 128.38, 125.80, 118.33, 69.88, 42.07, 38.44, 32.04$.

1-Pentadecen-4-ol (6):³⁸ ^1H NMR(CDCl_3) $\delta= 5.83$ (dddd, 1H, $J= 16.6, 10.2, 8.0, 6.8$ Hz), 5.13 (d, 1H, $J= 16.6$ Hz), 5.13 (d, 1H, $J= 10.2$ Hz), 3.64 (brs, 1H), 2.30 (m, 1H), 2.14 (ddd, 1H, $J= 14.4, 7.9, 6.8$

Hz), 1.65 (brs, 1H), 1.46 (m, 1H), 1.26 (m, 1H), 0.88 (t, 3H, $J=6.8$ Hz); ^{13}C NMR (CDCl_3) $\delta=$ 134.90, 118.03, 70.96, 41.95, 36.83, 31.92, 29.67, 29.64, 29.62, 29.36, 25.68, 22.69, 19.06, 14.12.

1-Cyclohexyl-3-buten-1-ol (7):³⁷ ^1H NMR(CDCl_3) $\delta=$ 5.84 (dddd, 1H, $J=$ 17.7, 9.7, 8.2, 6.2 Hz), 5.15 (d, 1H, $J=$ 17.7 Hz), 5.14 (d, 1H, $J=$ 9.7 Hz), 3.39 (brs, 1H), 2.37–2.30 (m, 1H), 2.16–2.09 (m, 1H), 1.88–1.00 (m, 11H); ^{13}C NMR (CDCl_3) $\delta=$ 135.44, 117.93, 74.71, 43.08, 38.82, 29.09, 28.11, 26.51, 26.28, 26.14.

1-Phenyl-1-oxo-4-penten-2-ol (8):³⁹ ^1H NMR(CDCl_3) $\delta=$ 7.96–7.43 (m, 5H), 5.80 (dddd, 1H, $J=$ 17.1, 10.2, 7.0, 7.0 Hz), 5.16 (ddd, 1H, $J=$ 6.8, 6.6, 4.0 Hz), 5.04 (brd, 1H, $J=$ 10.2 Hz), 5.01 (ddd, 1H, $J=$ 17.1, 1.5, 1.5 Hz), 3.75 (d, 1H, $J=$ 6.6 Hz), 2.67 (dddd, 1H, $J=$ 14.5, 7.0, 6.8, 1.4, 1.3 Hz), 2.36 (dddd, 1H, $J=$ 14.5, 7.0, 4.0, 1.3, 1.1 Hz); ^{13}C NMR (CDCl_3) $\delta=$ 201.15, 133.95, 132.41, 128.87, 128.49, 118.39, 72.63, 40.03.

Ethyl 2-hydroxy-2-phenyl-4-pentenoate (9):⁴⁰ ^1H NMR(CDCl_3) $\delta=$ 7.62–7.26 (m, 5H), 5.80 (dddd, 1H, $J=$ 17.1, 10.1, 7.6, 6.6 Hz), 5.17 (d, 1H, $J=$ 17.1 Hz), 5.13 (d, 1H, $J=$ 10.1 Hz), 4.27 (dq, 1H, $J=$ 10.8, 7.1 Hz), 4.19 (dq, 1H, $J=$ 10.8, 7.1 Hz), 3.76 (s, 1H), 2.97 (dd, 2H, $J=$ 14.0, 7.6 Hz), 2.76 (dd, 2H, $J=$ 14.0, 6.6 Hz), 1.27 (t, 3H, $J=$ 7.1 Hz); ^{13}C NMR (CDCl_3) $\delta=$ 174.57, 141.41, 132.40, 128.22, 127.75, 125.51, 119.26, 77.87, 62.46, 44.17, 14.10.

1-Allylcyclohexanol (10):³⁷ ^1H NMR(CDCl_3) $\delta=$ 5.88 (dddd, 1H, $J=$ 17.2, 10.1, 7.5, 7.3 Hz), 5.14 (d, 1H, $J=$ 10.1 Hz), 5.10 (d, 1H, $J=$ 17.2 Hz), 2.21 (d, 2H, $J=$ 7.7 Hz), 1.65–1.24 (m, 11H); ^{13}C NMR (CDCl_3) $\delta=$ 133.72, 118.69, 70.91, 46.72, 37.40, 25.77, 22.17.

2-Undecen-4-ol (11):⁴¹ ^1H NMR(CDCl_3) $\delta=$ 5.83 (dddd, 1H, $J=$ 17.2, 10.8, 7.9, 6.4 Hz), 5.14 (d, 1H, $J=$ 17.2 Hz), 5.13 (d, 1H, $J=$ 10.8 Hz), 3.60–3.68 (m, 1H), 2.33–2.27 (m, 1H), 2.17–2.10 (m, 1H), 1.66 (brs, 1H), 1.47–1.29 (m, 12H), 0.88 (t, 3H, $J=$ 7.0 Hz); ^{13}C NMR (CDCl_3) $\delta=$ 134.90, 118.07, 70.68, 41.94, 36.82, 31.82, 29.62, 29.28, 25.38, 22.44, 14.10.

Bis(1-phenyl-3-buten-1-yl)ether (2) (1:1 mixture of diastereomers): ^1H NMR(CDCl_3) $\delta=$ 7.38–7.14 (m, 10H), 5.82–5.61 (m, 1H), 5.05–4.88 (m, 2H), 4.42 (dd, 1H(one isomer), $J=$ 6.3, 6.3 Hz), 4.09 (dd, 1H(another isomer), $J=$ 7.3, 6.2 Hz), 2.65–2.29 (m, 4H); ^{13}C NMR (CDCl_3) $\delta=$ 142.28, 141.98, 134.91, 134.73, 128.26, 127.98, 127.57, 127.15, 126.74, 117.00, 116.70, 79.33, 78.26, 42.87, 41.63; Found: C, 86.42; H, 8.30 %. Calcd for $\text{C}_{20}\text{H}_{22}\text{O}$: C, 86.28; H, 7.96%.

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References and Notes

1. Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207.

2. Roush, W. R. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: Oxford, 1991; Vol. 2, pp. 1. Fleming, I. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I. Eds.; Pergamon Press: Oxford, 1991; Vol. 2, pp. 563.
3. Nishigaichi, Y.; Takuwa, A.; Naruta, Y.; Maruyama, K. *Tetrahedron* **1993**, *49*, 7395. Davies, A. G. *Organotin Chemistry*, VCH: Weinheim, 1997 pp. 102.
4. Aspinall, H. C.; Browning, A. F.; Greeves, N.; Ravenscroft, P. *Tetrahedron Lett.* **1994**, *35*, 4639. Keck, G. E.; Tarbet, K. H.; Geraci, L. S. *J. Am. Chem. Soc.* **1993**, *115*, 8467. Kobayashi, S.; Nishio, K. *Tetrahedron Lett.* **1995**, *36*, 6729. Whitesell, J. K.; Apodaca, R. *Tetrahedron Lett.* **1996**, *37*, 3955.
5. Nakamura, H.; Asao, N.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1995**, 1273. Nakamura, H.; Iwama, H.; Yamamoto, Y. *J. Am. Chem. Soc.* **1996**, *118*, 6641.
6. Hull, C.; Mortlock, S. V.; Thomas, E. J. *Tetrahedron* **1989**, *45*, 1007.
7. Yamamoto, Y.; Maruyama, K.; Matsumoto, K. *J. Chem. Soc., Chem. Commun.* **1983**, 489.
8. a) Yanagisawa, A.; Inoue, H.; Morodome, M.; Yamamoto, H. *J. Am. Chem. Soc.* **1993**, *115*, 10356. b) Yanagisawa, A.; Morodome, M.; Nakashima, H.; Yamamoto, H. *Synlett* **1997**, 1309.
9. Cokley, T. M.; Marshall, R. L.; McCluskey, A.; Young, J. J. *Tetrahedron Lett.* **1996**, *39*, 1905. Cokley, T. M.; Harvey, P. J.; Marshall, R. L.; McCluskey, A.; Young, D. J. *J. Org. Chem.* **1997**, *62*, 1961. Yasuda, M.; Fujibayashi, T.; Baba, A. *J. Org. Chem.* **1998**, *63*, 6401. Asao, N.; Abe, N.; Tan, Z.; Maruoka, K. *Synlett* **1998**, 377.
10. Keck, G. E.; Geraci, L. S. *Tetrahedron Lett.* **1993**, *34*, 7827. Keck, G. E.; Tarbet, K. H.; Geraci, L. S. *J. Am. Chem. Soc.* **1993**, *115*, 8467. Yanagisawa, A.; Nakashima, H.; Ishida, A.; Yamamoto, H. *J. Am. Chem. Soc.* **1996**, *118*, 4723. Casolari, S.; Cozzi, P. G.; Orioli, P.; Tagliavini, E.; U.-Ronchi, A. *J. Chem. Soc., Chem. Commun.* **1997**, 2123. Yu, C.-H.; Choi, H.-S.; Yoon, S.-K.; Kung, W.-H. *Synlett* **1997**, 889-890. Yasuda, M.; Kitahara, N.; Fujibayashi, T.; Baba, A. *Chem. Lett.* **1988**, 743. Motoyama, Y.; Narusawa, H.; Nishiyama, H. *J. Chem. Soc., Chem. Commun.* **1999**, 131.
11. Hagen, G.; Mayr, H. *J. Am. Chem. Soc.* **1991**, *113*, 4954. Mayr, H.; Patz, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 938.
12. Majetich, G. In *Organic Synthesis, Theory and Applications*; Hudlicky Ed.; JAI Press, Inc.: Greenwich, CT, 1989; pp. 173. Fleming, I.; Dunogues, J.; Smithers, R. *Org. React. (N.Y.)* **1989**, *37*, 57.
13. Furuta, K.; Mouri, M.; Yamamoto, H. *Synlett* **1991**, 561. D. R. Gauthier, J.; Carreira, E. M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2363.
14. Denmark, S. E.; Coe, D. M.; Pratt, N. E.; Griedel, B. D. *J. Org. Chem.* **1994**, *59*, 6161. Nakajima, M.; Saito, M.; Shiro, M.; Hashimoto, S. *J. Am. Chem. Soc.* **1998**, *120*, 6419. Iseki, K.; Mizuno, S.; Kuroki, Y.; Kobayashi, Y. *Tetrahedron* **1999**, *55*, 977.
15. For organogermanium compounds in organic synthesis: Curran, D. P.; Diederichsen, U.; Palovich, M. *J. Am. Chem. Soc.* **1997**, *119*, 4797. Yokoyama, Y.; Mochida, K. *J. Chem. Soc., Chem. Commun.* **1998**, 1093-1094. See also references cited therein.
16. Barnes, J. M.; Magos, L. *Organometal. Chem. Rev.* **1968**, *3*, 137.
17. Sano, H.; Miyazaki, Y.; Okawara, M.; Ueno, Y. *Synthesis* **1986**, 776.
18. Yamamoto, Y.; Hatsuya, S.; Yamada, J. *J. Org. Chem.* **1990**, *55*, 3118. Yamamoto, Y.; Okano, H.; Yamada, J. *Tetrahedron Lett.* **1991**, *32*, 4749.
19. For the use of allylgermane as an allylmetal: Sato, T.; Otera, J.; Nozaki, H. *J. Org. Chem.* **1990**, *55*, 6116. Denmark, S. E.; Almstead, N. G. *J. Org. Chem.* **1991**, *56*, 6485.
20. Hashimoto, Y.; Kagoshima, H.; Saigo, K. *Tetrahedron Lett.* **1994**, *35*, 4805.

21. a) Kobayashi, S. *Synlett* **1994**, 689. b) Kobayashi, S. *Eur. J. Org. Chem.* **1999**, 15. c) Kobayashi, S. *Chem. Soc. Rev.* **1999**, 28, 1.
22. Kobayashi, S.; Hachiya, I.; Araki, M.; Ishitani, H. *Tetrahedron Lett.* **1993**, 34, 3755. Kobayashi, S.; Hachiya, I.; Ishitani, H.; Araki, M. *Tetrahedron Lett.* **1993**, 34, 4535.
23. Kobayashi, S.; Hachiya, I.; Ishitani, H.; Araki, M. *Synlett* **1993**, 472.
24. Aspinall, H. C.; Browning, A. F.; Greeves, N.; Ravenscroft, P. *Tetrahedron Lett.* **1994**, 35, 4639. Aspinall, H. C.; Greeves, N.; McIver, E. G. *Tetrahedron Lett.* **1998**, 39, 9283.
25. a) Aggarwal, V. K.; Vennall, G. P. *Tetrahedron Lett.* **1996**, 37, 3745. b) Yang, Y.; Wang, M.; Wang, D. *J. Chem. Soc., Chem. Commun.* **1997**, 1651. c) Aggarwal, V. K.; Vennall, G. P. *Synthesis* **1998**, 1822.
26. Kobayashi, S.; Nagayama, S. *J. Am. Chem. Soc.* **1997**, 119, 10049. Kobayashi, S.; Iwamoto, S.; Nagayama, S. *Synlett* **1997**, 1099. Kobayashi, S.; Busujima, T.; Nagayama, S. *J. Chem. Soc., Chem. Commun.* **1998**, 19.
27. a) Hachiya, I.; Kobayashi, S. *J. Org. Chem.* **1993**, 58, 6958. Kobayashi, S.; Hachiya, I.; Yamanoi, Y. *Bull. Chem. Soc. Jpn.* **1994**, 67, 2342. Kobayashi, S.; Nagayama, S. *J. Org. Chem.* **1996**, 61, 2256.
28. Akiyama, T.; Ishikawa, K.; Ozaki, S. *Synlett* **1994**, 275. Akiyama, T.; Ishikawa, K.; Ozaki, S. *Chem. Lett.* **1994**, 627. Akiyama, T.; Yasusa, T.; Ishikawa, K.; Ozaki, S. *Tetrahedron Lett.* **1994**, 35, 8401. Akiyama, T.; Kirino, M. *Chem. Lett.* **1995**, 723. Akiyama, T.; Yamanaka, M. *Synlett* **1996**, 1095. Akiyama, T.; Nakano, M.; Kanatani, J.; Ozaki, S. *Chem. Lett.* **1997**, 385. Akiyama, T.; Hoshi, E.; Fujiyoshi, S. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2121. Akiyama, T.; Yamanaka, M. *Tetrahedron Lett.* **1998**, 39, 7885. Akiyama, T.; Ishida, Y. *Synlett* **1998**, 1150. Akiyama, T.; Asayama, K.; Fujiyoshi, S. *J. Chem. Soc., Perkin Trans. 1* **1998**, 3655.
29. Akiyama, T.; Suzuki, M. *J. Chem. Soc., Chem. Commun.* **1997**, 2357.
30. O'Brien, S.; Fishwick, M.; McDermott, B.; Wallbridge, M. G. H.; Wright, G. A. *Inorg. Synth.* **1971**, 13, 73. Tetraallylgermane is fairly stable in acidic aqueous media.
31. A preliminary communication: Akiyama, T.; Iwai, J. *Tetrahedron Lett.* **1997**, 38, 853.
32. Reissig, H. -U. In *Organic Synthesis Highlights*; VCH: Weinheim, 1991; pp. 71. Li, C.-J. *Chem. Rev.* **1993**, 93, 2023. Li, C.-J.; Chan, T.-H. *Organic Reactions in Aqueous Media*, John Wiley: New York, 1997.
33. We have recently found that scandium(III) triflate catalyzed allylation of aldimines with allyltriethylgermane took place smoothly to furnish homoallylic amines in high yields: Akiyama, T.; Iwai, J. *Synlett* **1998**, 273.
34. Okude, Y.; Hirano, S.; Nozaki, H. *J. Am. Chem. Soc.* **1977**, 99, 3179. Reetz, M. T.; Wendderoth, B. *Tetrahedron Lett.* **1982**, 23, 5259.
35. Asao, N.; Liu, P.; Maruoka, K. *Angew. Chem., Int. Ed. Engl.* **1997**, 36, 2507.
36. Korshak, V. V.; Polyakova, A. M.; Petrov, A. D.; Mironov, V. F. *Dokl. Akad. Nauk SSSR, Ser. Sci., Khim.* **1957**, 112, 436. Jones, R. G.; Partington, P.; Rennie, W. J.; Roberts, R. M. G. *J. Organomet. Chem.* **1972**, 35, 291.
37. Davis, A. P.; Jaspars, M. *J. Chem. Soc., Perkin Trans. 1* **1992**, 2111.
38. Hanessian, S.; Tehim, A.; Chen, P. *J. Org. Chem.* **1993**, 58, 7768.
39. Takuwa, A.; Nishigaichi, Y.; Yamashita, K.; Iwamoto, H. *Chem. Lett.* **1990**, 1761.
40. Moorlag, H.; Kellog, R. M.; Kloosterman, M.; Kaptein, B.; Kamphuis, J.; Shoemaker, H. E. *J. Org. Chem.* **1990**, 55, 5874.
41. Sames, D.; Liu, Y.; DeYoung, L.; Polt, R. *J. Org. Chem.*, **1995**, 60, 2153.