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Note

New synthetic routes to allylic germatranes

J.W. Faller *, Roman G. Kultyshev, Jonathan Parr

Department of Chemistry, Yale University, 225 Prospect Street, New Haven, CT 06520, USA

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Abstract

Allylic germatranes derived from triethanolamine can be prepared with moderate control of regioselectivity by two complementary routes. The first of these is through the preparation of the precursor allylic germanium trichlorides by a transmetallation reaction between germanium(IV) chloride and the corresponding allylic tributylstannanes followed by alcoholysis and reaction with triethanolamine. The second route is via the palladium-catalyzed hydrogermylation of conjugated dienes by germatrane, $N(CH_2CH_2O)_3GeH$. The former route gives mixtures of *E* and *Z* stereoisomers, whereas the second route gives exclusively *Z* products.

Keywords: Germatrane; Organogermanium

1. Introduction

Organometallic compounds of Group 14 metals (Si, Ge, Sn, Pb) enjoy a wide range of applications in the synthesis of diverse organometallic and organic products. Of these elements, silicon [1] and tin [2] are the more widely explored because these elements show attractive reaction behavior and are readily synthesized or are commercially available. Germanium, situated between these two more commonly used elements in the periodic table is less widely studied, although its location would suggest that its reactivity would be intermediate between silicon and tin.

A number of groups have investigated germanium compounds as reagents [3], and to this body of work we have recently contributed some reports on the use of organogermatranes $N(CH_2CH_2O)_3$ GeR in cross-coupling reactions (R = aryl, alkynyl) [a,b] and in the rhodium and palladium-catalyzed hydrogermylation of alkynes (R = H) [c]. Although numerous germatranes based upon triethanolamine are known [4], we report here some advances in the synthesis of allylic germatranes by two complementary routes. The first of these is by a transmetallation between germanium(IV) chloride and the corresponding (allyl)tributylstannane followed by ethanolysis to yield the (allyl)triethoxygermane and finally complexation by triethanolamine, Fig. 1 and Scheme 1. The second route, Scheme 2, is through the palladium-catalyzed hydrogermylation of a suitable diene using germatrane. These two routes both offer ready access to allylic germatranes in high yield.

2. Experimental

2.1. General procedures

Synthetic manipulations were carried out using standard Schlenk techniques under an inert atmosphere or in a glove-box. Solvents were dried according to standard procedures [5]. The ^1H NMR spectra were recorded on either a Bruker 500 MHz or a Bruker 400 MHz spectrometer, and chemical shifts (δ) are reported in ppm

* Corresponding author. Tel.: +1-2034323954; fax: +1-2034326144.
E-mail address: jack.faller@yale.edu (J.W. Faller).

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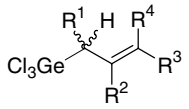


R^1 = Me; R^2 = H; R^3 = H; R^4 = H, **1**
R^1 = H; R^2 = H; R^3 = Me; R^4 = H, *E*-**2**
R^1 = H; R^2 = H; R^3 = H; R^4 = Me, *Z*-**2**
R^1 = H; R^2 = Me; R^3 = Me; R^4 = H, *E*-**3**
R^1 = H; R^2 = Me; R^3 = H; R^4 = Me, *Z*-**3**
R^1 = Me; R^2 = Me; R^3 = H; R^4 = H, **4**

Fig. 1. Allylgermanium trichlorides.

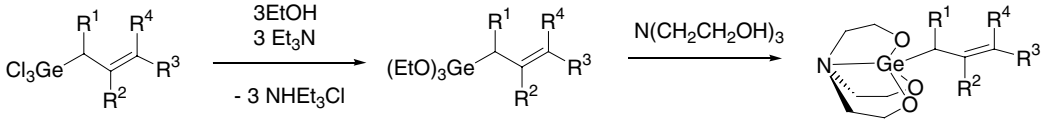
relative to residual solvent resonances ($CD(H)Cl_3$: ^1H 7.27 δ). The $^{13}C\{^1H\}$ NMR spectra were recorded on either a Bruker 500 MHz or a Bruker 400 MHz spectrometer operating at 125.8 or 100.6 MHz, respectively, and referenced to the solvent signals ($CDCl_3$: ^{13}C 77.2 δ. Microanalyses were performed by Atlantic Microlab Inc. Additions of ethanol to the organogermanium trichlorides were carried out at −78 °C in these preparations; however, the additions can be carried out at room temperature.

2.2. 3-Buten-2-yl germanium trichloride (*1*)

In a 50 mL Young's flask crotyltributylstannane (5.28 g, 15.3 mmol) was combined with $GeCl_4$ (3.27 g, 15.3 mmol). The flask was sealed under vacuum and the reaction stirred at room temperature for 21 h, during which time the initial cloudiness disappeared. The reaction mixture was distilled (90 °C bath temperature) under reduced pressure to give 3-buten-2-yl germanium trichloride, **1**. Yield; 1.80 g, 51%. ^1H NMR ($CDCl_3$): δ 5.90 (ddd, J_{trans} = 16, J_{cis} = 10, J = 7, 1H, C*H*═), 5.35 (d, J_{cis} = 10, 1H, CH_2═), 5.33 (d, J_{trans} = 16, 1H, CH_2═), 3.06 (dq, 1H, J = 7, 7, C*H*Ge), 1.49 (d, 3H, J = 7, CH_3CHGe). $^{13}C\{^1H\}$ ($CDCl_3$): δ 132.9, 119.5, 44.5, 13.2. Anal. Calc. for $C_4H_7Cl_3Ge$: C, 20.53; H, 3.01. Found: C, 20.95; H. 3.16.

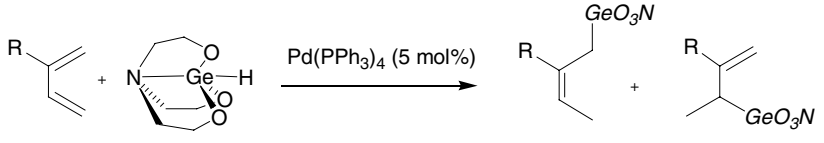
2.3. E,Z-Crotyl germanium trichloride (*2*)

In a 50 mL Young's flask crotyl tributylstannane (5.28 g, 15.3 mmol) was combined with $GeCl_4$ (3.27 g, 15.3 mmol). The flask was sealed under vacuum and the reaction heated to 110 °C for 10 h. The reaction was cooled to room temperature and the mixture distilled (90 °C bath temperature) to give a mixture of **1** and **2** (55:45). Heating this mixture to 135 °C in a sealed flask for a period of 9 h resulted in almost complete isomerization to **2** (*E*:*Z* 65:35). ^1H NMR ($CDCl_3$): *E*-**2** δ 5.77 (dq, 1H, J_{trans} = 15.2, J_{Me-H} = 6.9, C*H*═), 5.48 (m, 1H, C*H*═), 2.83 (d, J = 8.1, 2H, CH_2Ge), 1.73 (dm, J = 6.9, 3H, CH_3CH); *Z*-**2** δ 5.83 (dq, J_{cis} = 10.3, J_{Me-H} = 6.9 H, C*H*═), 5.48 (m, 1H, C*H*═), 2.93 (d, J = 8.1, 2H, CH_2Ge), 1.76 (dm, J = 6.9, 3H, CH_3CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ *E*-**2** 133.5, 118.4, 36.7, 18.4;. *Z*-**2** 131.5, 117.7, 32.1, 13.4.



R^1 = Me; R^2 = H; R^3 = H; R^4 = H, **6**
R^1 = H; R^2 = H; R^3 = Me; R^4 = H, *E*-**7**
R^1 = H; R^2 = H; R^3 = H; R^4 = Me, *Z*-**7**
R^1 = H; R^2 = Me; R^3 = Me; R^4 = H, *E*-**8**
R^1 = H; R^2 = Me; R^3 = H; R^4 = Me, *Z*-**8**
R^1 = Me; R^2 = Me; R^3 = H; R^4 = H, **9**

Scheme 1. Preparation of allylgermatranes via ethanolysis and transalkoxylation.



"HGeO_3N"

Z-7, R = H **6,** R = H
Z-8, R = Me **9,** R = Me

Z-7 : **6** = 28 : 1
Z-8 : **9** = 30 : 1

Scheme 2. Preparation of allylgermatranes via palladium-catalyzed hydrogermylation of dienes.

2.4. E, Z-β-Methylcrotyl germanium trichloride (3) and 3-methyl-3-buten-2-yl germanium trichloride (4)

The β-methylcrotyl tributylstannane needed for this synthesis was prepared by the method of Weigand and Bruckner [6] using the alcohol derived by LAH reduction of tiglic acid. The originally formed *E*-isomer, (^{119}Sn NMR, 186 MHz, $CDCl_3$, δ 14.4; ^{1}H, δ 5.02, q, J=6.6, CMe*H*=) partially isomerized to the *Z*-isomer (^{119}Sn NMR,186 MHz, $CDCl_3$, δ11.7; ^{1}H, δ 4.91, q, J=6.6, CMe*H*=) upon distillation to yield an *E*:*Z* mixture in a ratio of 38:62.

To a 50 mL Young's flask containing a stirring bar and β-methylcrotyl tributylstannane (*E*:*Z* 38:62, 2.73 g, 7.60 mmol) was added $GeCl_4$(0.87 mL, 7.63 mmol). The flask was sealed under vacuum and stirred at room temperature for 27 h. The reaction mixture was distilled to give *E*:*Z*-**3** (*E*:*Z*=65:35) and 3-methyl-3-buten-2-yl germanium trichloride **4** (**3**:**4** 92:8). Yield: 1.51 g, 80%. ^{1}H NMR ($CDCl_3$): *E*-**3** δ 5.52 (q, 1H, J=7.4, C*H*=), 2.88 (s, 2H, CH_2Ge), 1.77 (m, 3H, CH_3C=), 1.66 (d, 3H, J=7.4, CH_3CH=). *Z*-**3** δ 5.56 (q, 1H, J=7.4, C*H*=), 2.94 (s, 2H, CH_2Ge), 1.86 (m, 3H, CH_3C=), 1.52 (d, 3H, J=7.4, CH_3CH=). **4** δ 5.10 (m, 1H, C*H*=), 5.02 (m, 1H, C*H*=), 3.05 (q, 1H, J=7.5, C*H*Ge), 1.90 (m, 3H, CH_3C=), 1.52 (d, 3H, J=7.5, CH_3CH).

2.5. 2-Cyclohexen-1-yl germanium trichloride (5)

To a 50 mL Young's flask containing a stirring bar and 2-cyclohexen-1-yl tributylstannane (1.61 g, 4.34 mmol) was added $GeCl_4$(0.49 mL, 4.3 mmol). The flask was sealed under vacuum and the reaction stirred at room temperature for 20 h. Distillation of the reaction mixture (110 °C) allowed the isolation of **5**. Yield: 0.65 g, 58%. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.07 (m, 1H, C*H*=), 5.77 (m, 1H, C*H*=), 3.09 (m, 1H, C*H*Ge), 2.15–2.07 (m, 4H), 1.88 (m, 1H), 1.74 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 133.5, 120.4, 44.9, 24.7, 23.3, 20.8.

2.6. 3-Buten-2-yl germatrane (6)

In a 100 mL Schlenk flask under nitrogen, **1** (1.73 g, 7.4 mmol) was dissolved in toluene (20 mL). Then ethanol (1.30 mL, 22.2 mmol) and triethylamine (3.09 mL, 22.2 mmol) were added. After standing at room temperature (45 min) the precipitate was filtered off and washed with further toluene (2×25 mL). The combined washings and filtrate were transferred to a 250 mL flask containing triethanolamine (1.127 g, 7.4 mmol). The flask was fitted with a reflux condenser and the mixture was heated to 95 °C for 6 h. The reaction was cooled and the volatiles were removed to yield a white solid melting at 125 °C. Yield: 2.02 g, 99%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.17 (ddd, 1H, J=17, 10.3, 6.9; C*H*=), 4.95 (m, 2H, CH_2=), 3.76 (t, 6H, CH_2O), 2.79 (t, 6H, CH_2N), 2.17 (quintet, 1H, C*H*Ge), 1.29 (d, 3H, J=7.2, CH_3CHGe). ^{13}C{^{1}H} ($CDCl_3$, 125.8 MHz): δ 141.9, 110.7, 57.1, 52.3, 33.1, 14.3. Anal. Calc. for $C_{10}H_{19}O_3NGe$: C, 43.86; H, 6.99; N, 5.11. Found: C, 43.94; H, 7.08, N, 5.19%.

2.7. E,Z-Crotyl germatrane (7)

In a 100 mL Schlenk flask under nitrogen, **2** (0.99 g, 4.2 mmol *E*:*Z* 65:35) was dissolved in toluene (20 mL). The flask was cooled to −78 °C whereupon ethanol (0.74 mL, 13 mmol) and triethylamine (1.77 mL, 12.7 mmol) were added. After warming to room temperature (45 min) the precipitate was filtered off and washed with further toluene (2×25 mL). The combined washings and filtrate were transferred to a 250 mL flask containing triethanolamine (0.64 g, 4.2 mmol). The flask was fitted with a reflux condenser and the mixture was heated to 90 °C for 6 h. The reaction was cooled and the volume reduced to ca. 5 mL. Diethyl ether was added (35 mL) and the resulting solution evaporated giving a white solid. Yield: 1.14 g, 98% (*E*:*Z* 65:35). ^{1}H NMR ($CDCl_3$) (resonances of *E*-**7** and *Z*-**7** overlap except for the methylene); *E*-**7** δ 5.58 (m, 1H, C*H*=), 5.41(m, 1H, C*H*=), 3.76 (m, 6H, CH_2O), 2.80 (m, 6H, CH_2N), 1.83 (m, 2H, CH_2Ge), 1.63 (m, 3H, CH_3CH). *Z*-**7** δ 5.58 (m, 1H, C*H*=), 5.41 (m, 1H, C*H*=), 3.76 (m, 6H, CH_2O), 2.80 (m, 6H, CH_2N), 1.86 (m, 2H, CH_2Ge), 1.63 (m, 3H, CH_3CH). ^{13}C{^{1}H} ($CDCl_3$); *E*-**7** δ 126.9, 124.5, 56.9, 51.9, 24.2, 18.3; *Z*-**7** δ 126.1, 122.7, 57.0, 52.0, 19.4, 12.7. Anal. Calc. for $C_{10}H_{19}NO_3Ge$: C, 43.86; H, 6.99; N, 5.11. Found: C, 43.95; H, 7.12; N, 5.11%.

2.8. E,Z-β-Methylcrotyl germatrane (8) and 3-methyl-3-buten-2-yl germatrane (9)

In a 100 mL Schlenk flask under nitrogen, a mixture of **3** and **4** (11:1, 1.45 g, 5.84 mmol) was dissolved in toluene (20 mL). The flask was cooled to −78 °C whereupon ethanol (1.03 mL, 17.6 mmol) and triethylamine (2.45 mL, 17.1 mmol) were added. After warming to room temperature (40 min) the precipitate was filtered off and washed with further toluene (2×25 mL). The combined washings and filtrate were transferred to a 250 mL flask containing triethanolamine (0.89 g, 5.9 mmol). The flask was fitted with a reflux condenser and the mixture was heated to 90 °C for 6 h. The reaction was cooled and the volatiles removed. The residue was treated with methylene chloride (20 mL). The resulting solution was again taken to dryness and the residue washed with diethyl ether (10 mL) leaving **8** (*E*/*Z*=65:35) and **9** (11:1) as a white powder. Yield: 1.44 g, 86%. *Z*-**8** was distinguished from *E*-**8** by a larger NOE being observed in the vinylic proton resonance upon irradiation of the β-methyl group (the

effect was more readily observed in benzene-d_6, where less overlap of resonances occurred). ^{1}H NMR ($CDCl_3$): *E*-**8** δ 5.24 (q, 1H, $J = 6.5$, $(CH_3)CH$=), 3.71 (m, 6H, CH_2O), 2.78 (m, 6H, CH_2N), 1.89 (s, 2H, $GeCH_2$), 1.71 (s, 3H, CH_3C=), 1.57 (d, 3H, $J = 6.5$, $(CH_3)CH$=). *Z*-**8** δ 5.17 (q, 1H, $J = 6.4$, $(CH_3)CH$=), 3.76 (m, 6H, CH_2O), 2.77 (m, 6H, CH_2N), 1.81 (s, 2H, $GeCH_2$), 1.70 (s, 3H, CH_3C=), 1.61 (d, 3H, $J = 6.4$, $(CH_3)CH$=). **9** δ 4.74 (m, 2H, H_2C=), 3.74 (m, 6H, CH_2O), 2.78 (m, 6H, CH_2N), 2.14 (q, 1H, $J = 7.5$, $CH(CH_3)$), 1.86 (s, 3H, CH_3C=), 1.32 (d, 3H, $J = 7.5$).

$^{13}C\{^1H\}$ NMR ($CDCl_3$): *E*-**8** δ 133.0 ($(CH_3)(CH_2)C$=), 118.5 ($(CH_3)HC$=), 57.1 (CH_2O), 52.1 (CH_2N), 31.5 ($GeCH_2$), 17.8 (CH_3C=), 14.0 (CH_3CH=). *Z*-**8** δ 133.5 ($(CH_3)(CH_2)C$=), 117.6 ($(CH_3)HC$=), 57.3 (CH_2O), 52.2 (CH_2N), 24.1 ($GeCH_2$), 25.8 (CH_3C=), 13.9 (CH_3CH=). **9** δ 149.7 ($CH_3(GeCHMe)C$=), 108.4 (H_2C=), 57.3 (CH_2O), 52.5 (CH_2N), 36.8 ($GeCHMe$), 23.5 ($(CH_3)C$=), 15.9, ($GeCH(CH_3)$). Anal. Calc. for $C_{10}H_{21}GeNO_3$: C, 45.89; H, 7.35; N, 4.87. Found: C, 45.91; H, 7.29; N, 4.84%.

2.9. 2-Cyclohexen-1-yl germatrane (*10*)

In a 100 mL Schlenk flask under nitrogen, **5** (0.60 g, 2.3 mmol) was dissolved in toluene (15 mL). The flask was cooled to −78 °C whereupon ethanol (0.41 mL, 6.5 mmol) and triethylamine (0.96 mL, 6.8 mmol) were added. After warming to room temperature (40 min) the precipitate was filtered off and washed with further toluene (2×25 mL). The combined washings and filtrate were transferred to a 250 mL flask containing triethanolamine (0.34 g, 2.25 mmol). The flask was fitted with a reflux condenser and the mixture was heated to 90 °C for 6 h. The reaction was cooled and the volatiles removed. The white residue was washed with pentane (10 mL) and the residue after washing dissolved in methylene chloride (10 mL). The solution was filtered through a pad of silica which was subsequently washed with further methylene chloride (15 mL). The combined filtrate and washings were taken to dryness leaving white solid, **10**, melting at 158 °C. Yield: 0.50 g, 73%. ^{1}H NMR ($CDCl_3$): δ 5.88 (m, 1H, CH=), 5.66 (m, 1H, CH=), 3.75 (m, 6H, CH_2O), 2.79 (m, 6H, CH_2N), 2.12 (m, 1H, $GeCHH$), 2.09–1.83 (m, 5H, cyclohexyl), 1.49 (m, 1H, cyclohexyl). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 128.7, 126.0, 57.1, 52.3, 32.4, 25.2, 24.7, 22.6. Anal. Calc. for $C_{12}H_{21}NO_3Ge$: C, 48.10; H, 7.35; N, 4.85. Found: C, 48.10; H, 7.10; N, 4.65% (see Fig. 2).

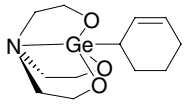


Fig. 2. Cyclohexenyl germatrane **10**.

2.10. General procedure for the palladium-catalyzed germatrane hydrogermylation of dienes

A 100 mL Schlenk flask equipped with a stirbar was charged with germatrane (1.0 mmol) and $Pd(PPh_3)_4$ (0.05 mmol). Toluene (10 mL) was added via syringe followed by the diene (4.0 mmol) and the resulting solution stirred at room temperature. After 12–60 h, the reaction mixture was filtered through a pad of Celite. The Celite was washed with CH_2Cl_2 (10 mL) and the combined filtrate and washings evaporated to dryness. In each case the residue contained the expected allylic germatrane and traces of triphenylphosphine oxide. Diene: 1,3-butadiene, product: *Z*-**7**, yield: 75%; isoprene, *Z*-**8**: 73%; 1,3-cyclohexadiene, **10**, 95%.

3. Results and discussion

While the transmetallation reactions between allylic trialkylstannanes and a range of main group Lewis acids have been investigated [7], to the best of our knowledge such reactions with germanium(IV) chloride have not. The likely products of these reactions are of interest to us because allylic germanium trichlorides are precursors to allylic germatranes, reagents with potential application in cross-coupling reactions. Although allylic germanium trihalides are available from the reaction of GeX_2·dioxane with allylic halides [8] we have examined the reactions of a number of allylic trialkylstannanes with germanium(IV) chloride in the hope that these reactions would prove more convenient.

The procedure used for the preparation of allylgermanium trichlorides was an adaptation of the method reported by Lutsenko for the preparation of halogermyl acetates from the corresponding esters of tributylstannyl acetic acid [9]. The two reagents were combined in a 1:1 ratio without solvent in a sealed flask and stirred for several hours either at room temperature or ca. 100 °C. Both allyl and methyl-substituted allyl germanium chlorides may be prepared in this manner. The products were isolated by distillation of the reaction mixture. Although stable enough to allow spectroscopic characterization, these compounds are extremely sensitive to hydrolysis and so were converted to the corresponding germatranes as quickly as was expedient. For the same reason, it was often not possible to obtain reproducible microanalytical data for these allylic germanium trichlorides.

The reaction of crotyl tributylstannane with germanium(IV) chloride did not yield crotyl germanium trichloride, which has been prepared previously by the reaction of methyl allene with trichlorogermane [10], but instead gave exclusively 3-buten-2-yl germanium trichloride. This result is in accord with the findings of Naruta who has previously explored the reaction

of crotyl tributylstannane with tin(IV) chloride [d]; however the reactions of the germanium analogue have a different temperature profile. In the tin case, the 3-buten-2-yl product is obtained initially in the transmetallation reaction when it is conducted at −50 °C, but this initial product rearranges to a mixture of crotyl tin trichloride products on warming to room temperature. In contrast, the conversion to the crotyl germanium trichloride requires prolonged heating at high temperature. Clearly the germanium trichloride analogue is more resistant to rearrangement. Even repeating the reaction at 110 °C gave a mixture of the crotyl and 3-buten-2-yl germanium trichlorides (**1**:**2** 55:45). Hence the initial transfer of the allylic group is γ-selective (Scheme 3) and subsequent rearrangement yields the crotyl derivative This S_E2' type behavior has been observed previously in the reaction of crotyl tributylstannane with several tin(IV) chloro compounds [7] and with phosphorus trihalides [b]. It should be noted that a significant amount (35%) of the less stable isomer, *Z*-**2**, is produced upon rearrangement in our reaction.

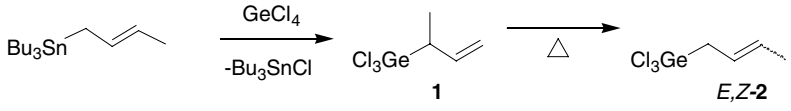
Introduction of more substituted allyl groups, such as those in *E*,*Z*-β-methylcrotyl tribuylstannane and 3-methyl-2-butenyl tributylstannane, does not interfere with formation of the allylic germanium trichlorides **3** and **4**. Compound **3** had been reported previously as a product formed in the high-temperature thermolysis of phenylgermanium trichloride in the presence of isoprene [11]. These reactions also appear to occur with a γ-selective initial transfer followed by some degree of subsequent rearrangement. Thus the ratio of isomers presently initially in the reagent *E*,*Z*-β-methylcrotyl tribuylstannane is not reflected in the product ratio of **3**, which is determined by kinetic preferences of the rearrangement of the initially formed **4** (Scheme 4).

We have emphasized allylic systems in which stereochemistry is an issue; nevertheless, the methodology also provides a straightforward route to other allylic germanium trichlorides. For example, the cyclic allylic compound 2-cyclohexen-1-yl tributylstannane [12] also reacts smoothly with germanium(IV) chloride to form the corresponding 2-cyclohexen-1-yl germanium trichloride.

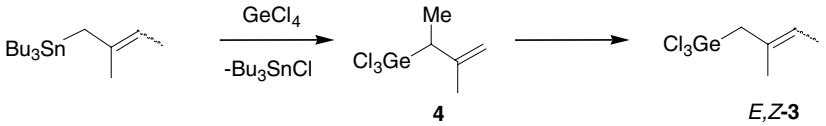
These allylic germanium trichlorides, **1**–**5** were converted to the corresponding allylic germatranes $N(CH_2CH_2O)_3Ge$(allyl) by the route outlined in Scheme 1. Prior conversion to the triethoxygermane, rather than direct reaction with triethanolamine, avoids potential difficulties resulting from protonation of the triethanolamine with HCl. The in situ reaction with ethanol and the subsequent transalkoxylation both proceed in high yield to give crystalline products.

Palladium-catalyzed hydrogermylation of terminal acetylenes by triphenyl germane, giving *E*-triphenylgermyl alkenes [13], and of isoprene by tri(2-furyl)germane [14] proceeds in both cases in good yield with marked stereochemical selectivity. We reasoned that allylic germatranes might also be prepared by the germatrane hydrogermylation of the corresponding dienes, Scheme 2. In this reaction, the hydrogermylation of butadiene gave *Z*-crotyl germatrane, *Z*-**7**, and a small quantity of the 1,2 addition product 3-buten-2-yl germatrane **6**. Similarly, isoprene is hydrogermylated to give *Z*-**8** as a single stereoisomer and **9** as a minor side-product (ca. 3%). The selectivity for the formation of the *Z*-product is consistent with the corresponding hydrostannylations which also show the same isomer selectivity [12]. Hydrogermylation of 1,3-cyclohexadiene gave the expected **10** in a slower reaction (60 h at room temperature).

The preparation of allylic germatranes by hydrogermylation of the corresponding diene is a very convenient route in comparison to many traditional multistep approaches to germatranes. One disadvantage of the reaction is that triphenylphosphine oxide is produced as a side-product that is somewhat troublesome to separate from the desired products [15]. Fortunately with our products, the contaminant could be removed by washing and the products could be prepared completely free of phosphine oxide by recrystallization.



Scheme 3. The γ-selectivity observed upon initial transfer from tin to germanium.



Scheme 4. The γ-selectivity upon initial transfer from tin to germanium provides a path for obtaining a different *E*:*Z* ratio in the product than existed in the tin reagent.

4. Conclusion

Allylic germatranes can be prepared either by the transmetallation of germanium(IV) chloride with the corresponding organostannanes followed by alcoholysis and reaction with triethanolamine or by the palladium-catalyzed germatrane hydrogermylation of the appropriate diene. The γ-selective initial transmetallation with crotyl tributylstannane can be an advantage for the preparation of pure 3-buten-2-yl germatrane. Subsequent rearrangement can provide the crotyl derivative with a relatively high *Z*-isomer component. If, however, only *Z*-crotyl germatrane is desired, the hydrogermylation route is preferred. Hydrogermylation also effectively provides a high isomeric purity (97%) of the *Z*-β-methylcrotyl germatrane. Consequently, the two routes provide complementary methods to conveniently provide isomeric allylic germatranes. Although crotyl germatrane could potentially be prepared via by the reaction of methyl allene with trichlorogermane [10], and subsequent treatment with triethanolamine, this would not provide a practical synthesis. Unfortunately, the reaction of methyl allene with trichlorogermane provides only 30% of the crotyl derivative along with 70% of isomeric vinyl derivatives [10], which would result in low yield and difficulties in separation.

The utility of allylic germatranes as reagents in carbon–carbon bond forming reactions is currently under investigation in this laboratory.

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References

[1] See for example C. Chuit, R.J.P. Corriu, C. Reye, J.C. Young, Chem. Rev. 93 (1993) 1371.
[2] (a) For leading references see P.G. Harrison, The Chemistry of Tin, Chapman Hall, New York, 1989;
(b) M. Pereyre, J.P. Quintal, A. Rahm, Tin in Organic Synthesis, Butterworth, London, 1987.
[3] (a) J.W. Faller, R.G. Kultyshev, J. Parr, Tetrahedron Lett. 44 (2003) 451;
(b) J.W. Faller, R.G. Kultyshev, Organometallics 21 (2002) 5911;
(c) J.W. Faller, R.G. Kultyshev, Organometallics 22 (2003) 199;
(d) M. Kosugi, T. Tanji, Y. Tanaka, A. Yoshida, K. Fugami, M. Kameyama, T. Magita, J. Organometal. Chem. 508 (1996) 255;
(e) C. Spino, N.J. Barriault, Org. Chem. 64 (1999) 5292;
(f) G. Gaultieri, S.J. Geib, D.P. Curran, J. Org. Chem. 68 (2003) 5013;
(g) T. Nakamura, H. Kinoshita, H. Shinokubo, K. Oshima, Org. Lett. 4 (2002) 3165;
(h) S. Patai, Z. Rappoport, The Chemistry of Organic Germanium, Tin and Lead Compounds, Wiley, Chichester, 1995.
[4] (a) T.K. Gar, N.Yu. Khromova, N.V. Sonina, V.S. Nikitin, M.V. Polyakova, V.F. Mironov, Zh. Obshch. Khim. 49 (1979) 1516;
(b) J.G. Verkade, Coord. Chem. Rev. 137 (1994) 233.
[5] D.D. Perrin, W.L.F. Armarego, The Purification of Laboratory Chemicals, third ed., Pergamon, Oxford, 1988.
[6] S. Weigand, R. Bruckner, Synthesis (1996) 475.
[7] (a) S. Le Serre, J.-C. Guillemin, Organometallics 16 (1997) 5844;
(b) S. Le Serre, J.-C. Guillemin, T. Karpati, L. Soos, L. Nyulaszi, T. Veszpremi, J. Org. Chem. 63 (1998) 59;
(c) J.-C. Guillemin, K. Malagu, Organometallics 18 (1999) 5259;
(d) Y. Naruta, Y. Nishigaichi, K. Maruyama, Tetrahedron 45 (1989) 1067;
(e) S.E. Denmark, S.T. Wilson, T.M. Willson, J. Am. Chem. Soc. 110 (1988) 984;
(f) A. Gambaro, P. Ganis, D. Marton, V. Peruzzo, G.J. Tagliavini, J. Organometal. Chem. 231 (1982) 307;
(g) A. Boaretto, D. Marton, G. Tagliavini, P.J. Ganis, J. Organometal. Chem. 321 (1987) 199;
(h) R.L. Marshall, D.J. Young, Tetrahedron Lett. 33 (1992) 2369.
[8] G.S. Zaitseva, S.S. Karlov, E.S. Alekseyeva, L.A. Aslanov, E.V. Avtomonov, J. Lorberth, Z. Naturforsch. Teil B. 52 (1997) 30.
[9] I.F. Lutsenko, Yu.I. Baukov, G.S. Burlachenko, J. Organometal. Chem. 6 (1966) 496.
[10] M. Massol, Y. Cabadi, J. Satge, Bull. Soc. Chim. Fr. 9 (1971) 3235.
[11] E.A. Chernyshev, N.G. Komalenkova, G.N. Yakovleva, V.G. Bykovchenko, N.N. Khromykh, V.N. Bochkarev, V.V. Shcherbinin, Russ. J. Gen. Chem. 69 (1999) 1406.
[12] (a) H. Miyake, K. Yamamura, Chem. Lett. (1992) 507;
(b) H. Miyake, K. Yamamura, Chem. Lett. (1992) 1099.
[13] Y. Ichinose, H. Oda, K. Oshima, Bull. Chem. Soc. Jpn. 60 (1987) 3468.
[14] H. Kinoshita, T. Nakamura, H. Kakiya, H. Shinokubo, S. Matsubara, K. Oshima, Org. Lett. 3 (2001) 2521.
[15] B.H. Lipshutz, P.A. Blomgren, Org. Lett. 3 (2001) 1869.