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REACTION OF TRIORGANO(TRIORGANOGERMYL)SILANES WITH ALKALI-METAL ALLYL AICOHOLATES

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Reaction of the lithium alcoholates of 1-vinylcyclohexanol (**2a**), (±)-linalool (**2b**), and 1-octen-3-ol (**2c**) with (dimethylphenylgermyl)trimethylsilane (**3a**) gave selectively the corresponding allyldimethylphenylgermane derivatives (**5a,c,e**). Similar treatment with dimethylphenyl(trimethylgermyl)silane (**3b**) gave mixtures of the allyltrimethylgermanes (**5b,d,f**) and allyldimethylphenylsilanes (**7b,d,f**), whereas use of the potassium alcoholates afforded selectively **5b,d,f**.

Hexaorganodisilanes silylate hydrazine[1] and α-cyclopropylbenzyl alcohol[2] under alkaline conditions. Hwu et al. reported that heating at 80 °C of lithium allyl alcoholates with hexamethyldisilane gave allylsilane derivatives in hexamethylphosphoric triamide (HMPA).[3] This reaction proceeds from the initial attack of the alkoxy anions to one silyl group in the Si-Si bond followed by the counterattack[4] of the other silyl group to the vinyl carbon.

When triorgano(triorganogermyl)silanes are similarly treated with the allyl alcoholates, the attack of the oxy-anions may selectively occur to the silyl groups

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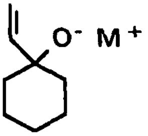
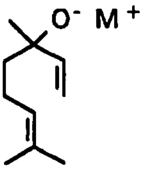
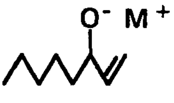
Table. Reaction of Alkali-Metal Allyl Alcoholates (2) with $Me_3SiGeMe_2Ph$ (3a) or $PhMe_2SiGeMe_3$ (3b)

Entry	Allyl alcoholate (2)	M^+	Conditions: 3 / Solvent[b]	Isolated yield (%): 5 (*E/Z*)[c]	Isolated yield (%): 7 (*E/Z*)[c]	Ratio[a] 5:7
1	 **2a**	Li^+	3a / E-H	5a, 69	7a, [d]	97:3
2		Li^+	3b / E-H	5b, 18	7b, 32	36:64
3		K^+	3b / E-H	5b, 50	7b, 0	>99:<1
4		Li^+	3b / T-H	5b, 27	7b, 12	69:31
5		K^+	3b / T-H	5b, 38	7b, 0	>99:<1
6		Cs^+	3b / T-H	5b, 36	7b, 0	>99:<1
7	 **2b**	Li^+	3a / E-H	5c, 60 (7:3)	7c, [d]	98:2
8		Li^+	3b / E-H	5d, 13 (4:1)	7d, 32 (4:1)	29:71
9		Li^+	3b / T-H	5d, 26 (5:2)	7d, 12 (3:1)	68:32
10		K^+	3b / T-H	5d, 29 (5:2)	7d, 0	>99:<1
11	 **2c**	Li^+	3a / E-T	5e, 57 (9:1)	7e, [d]	94:6
12		Li^+	3b / T-H	5f, 6 ([e])	7f, 18 ([e])	25:75
13		Na^+	3b / T-H	5f, 11 ([e])	7f, 0	>99:<1
14		K^+	3b / T-H	5f, 22 ([e])	7f, 0	>99:<1

[a] Determined from the integrated values of GLC analysis of the reaction mixture. [b] E-H: mixture of Et_2O/HMPA = 1:1, T-H: THF/HMPA = 1:1. [c] Estimated by GLC analysis. The major isomer was temporarily assigned as *E*. [d] Not isolated. [e] Not determined.

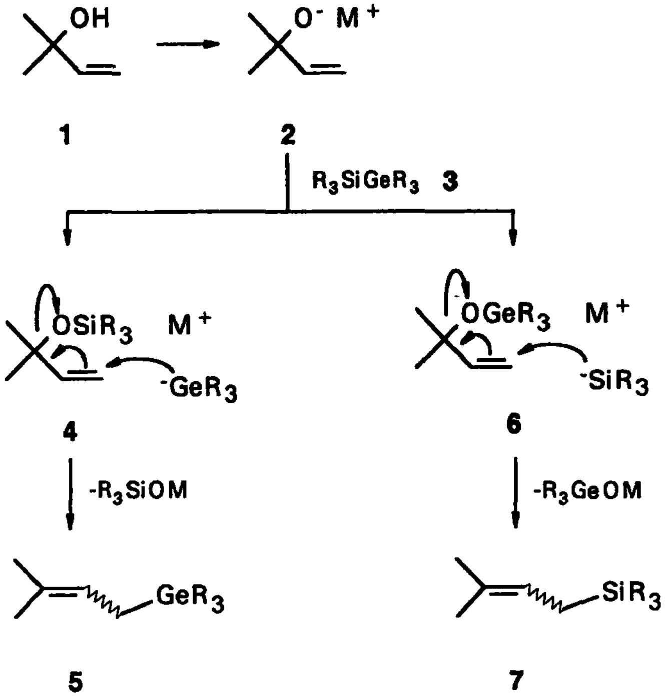


FIG 1

and the following counterattack of the germyl anions then may give allyl germanes, because silicon has higher affinity with oxygen than germamium, and germanium tends to link with carbon rather than oxygen.[5-7] We now report the reaction of some alkali-metal allyl alcoholates (**2**) with triorgano(triorganogermyl)silanes (**3**).

Reaction of (dimethylphenylgermyl)trimethylsilane (**3a**) with the lithium alcoholates of 1-vinylcyclohexanol (**2a**), (±)-linalool (**2b**), and 1-octen-3-ol (**2c**) gave selectively the expected allyldimethylphenylgermane derivatives (**5a,c,e**) in a mixed solvent of ether and HMPA (1:1) at room temperature (entries 1, 7, and 11 in Table). However, similar treatments with dimethylphenyl(trimethyl-

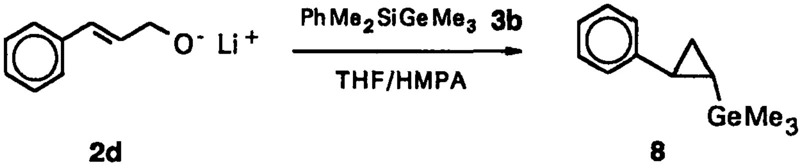


FIG 2

germyl)silane (**3b**) afforded mixtures of the allyltrimethylgermanes (**5b,d**) and allyldimethylphenylsilanes derivatives (**7b,d**) (entries 2 and 8). Although change of the solvent to a mixture of THF and HMPA (1:1) resulted in some improvement in the ratio of **5** to **7**, the total yields were decreased (entries 4, 9, and 12).

In the reactions of **2a-c** with **3b**, the initial attack of the oxy-anions occurred competitively on the dimethylphenylsilyl and trimethylgermyl groups to give **4** or **6**, and the following counterattacks of the trimethylgermyl and dimethylphenylsilyl anions afforded respective **5** and **7** (Fig 1). Selective formation of **5** was observed when the cation of **2** was potassium or cesium (entries 3, 5, 6, 10, and 14). Sodium also exhibited selectivity, but yield was poor (entry 13). It is interesting that the significant change of the ratio of **5** to **7** resulted from changing the cations of **2**.

The reaction of **3b** with the lithium alcoholates of (*E*)-2-decen-1-ol and 2-cyclohexenol gave no corresponding allylgermanes. Lithium (*E*)-cinnamyl alcoholate (**2d**) afforded *trans*-1-trimethylgermyl-2-phenylcyclopropane (**8**, 39%).

Experimental Section

All reactions were carried out under an Ar or N_2 atmosphere. Diethyl ether and THF was distilled from sodium benzophenone ketyl prior to use. HMPA was distilled under reduced pressure from sodium. ^{1}H NMR spectra were recorded at 60, 100, or 400 MHz. Gas chromatographic analyses were carried out on a 1-m, 20% silicone SE-30 column. All boiling points were the oven temperature of Büchi Kugelrohr distillation apparatus and were uncorrected.

Reaction of Alkali-Metal Allyl Alcoholates (2a-d) with (Dimethylphenylgermyl)trimethylsilane (3a) or Dimethylphenyl(trimethylgermyl)silane (3b). General Procedure. (A) A solution of *n*-BuLi in hexane (1.58 M, 1.4 mL, 2.2 mmol) was added to a solution of 1-vinylcyclohexanol (**1a**), (±)-linalool (**1b**), 1-octen-3-ol (**1c**), or (*E*)-cinnamyl alcohol (**1d**) (2 mmol) in Et_2O or THF (8 mL) at 0 °C, and the mixture was stirred for 0.5 h. Then a solution of **3** (660 mg, 2.6 mmol) in HMPA (8 mL) was added with additional stirring for 24 h at room temperature. Water (30 mL) was added and the mixture was extracted with Et_2O (3 × 20 mL). The ethereal extract was washed with H_2O, dried ($MgSO_4$), and concentrated. The residue was chromatographed on a silica gel column (hexane) to give the allylgermane **5** and/or allylsilane derivatives **7**. The results are listed in the Table.

(B) KH (35% in mineral oil, 280 mg) or NaH (65% in mineral oil, 80 mg) was placed in a 20-mL flask and washed with Et_2O (2 × 8 mL), dried under reduced pressure, and the flask was flushed with N_2. A solution of **1a-d** (2 mmol) in Et_2O or THF (8 mL) was added with additional stirring for 0.5 h. Then a solution of **3** (2.6 mmol) in HMPA (8 mL) was added and treated in a manner similar to that described in (A).

(C) A solution of **1a** (246 mg, 2 mmol) in THF (8 mL) was added to Cs (ca. 800 mg), placed in a 20-mL flask and the mixture was stirred overnight at room temperature. A solution of **3b** (660 mg, 2.6 mmol) in HMPA (8 mL) was added and treated in a manner similar to that described in (A).

(2-Cyclohexylideneethyl)dimethylphenylgermane (5a): bp 125 °C (2 mmHg); ^1H NMR ($CDCl_3$) δ 0.38 (s, 6 H), 1.35-1.56 (m, 6 H), 1.80 (d, 2 H, J = 8.7 Hz), 2.02-2.08 (m, 4 H), 5.16 (t, 1 H, J = 8.7 Hz), 7.31-7.39 (m, 3 H), 7.43-7.49

(m, 2 H); IR (film): 1430, 1095, 815 cm^{-1}. Anal. Calcd for $C_{16}H_{24}Ge$: C, 66.51; H, 8.37. Found: C, 66.66; H, 8.36.

(2-Cyclohexylideneethyl)trimethylgermane (5b): bp 90 °C (14 mmHg); ^1H NMR ($CDCl_3$) δ 0.12 (s, 9 H), 1.20-2.53 (m, 12 H), 5.55 (t, 1 H, J = 9 Hz); IR (film) 1450, 1240, 825 cm^{-1}. Anal. Calcd for $C_{11}H_{22}Ge$: C, 58.23; H, 9.77. Found: C, 58.19; H, 10.12.

(2-Cyclohexylideneethyl)dimethylphenylsilane[8] **(7b)**: ^1H NMR ($CDCl_3$) δ 0.27 (s, 6 H), 1.12-2.50 (m, 12 H), 5.50 (t, 1 H, J = 9 Hz), 7.97 (m, 5 H).

1-Dimethylphenylgermyl-3,7-dimethyl-2,6-octadiene (5c): bp 105 °C (4 mmHg, a mixture of *E* and *Z*); IR (film) 1430, 1095, 825 cm^{-1}. Anal. Calcd for $C_{18}H_{28}Ge$: C, 68.20; H, 8.90. Found: C, 68.27; H, 9.08. **(*E*)-5c**: ^1H NMR ($CDCl_3$) δ 0.36 (s, 6H), 1.50 (bs, 3 H), 1.60 (bs, 3 H), 1.67 (bs, 3 H), 1.79 (bd, 2 H, J = 8.7 Hz), 1.94-2.08 (m, 4 H), 5.05-5.12 (m, 1 H), 5.17-5.27 (m, 1 H), 7.30-7.36 (m, 3 H), 7.44-7.47 (m, 2 H).

1-Trimethylgermyl-3,7-dimethyl-2,6-octadiene (5d): bp 130 °C (11 mmHg, a mixture of *E* and *Z*); IR (film) 1450, 1240, 820 cm^{-1}. Anal. Calcd for $C_{13}H_{26}Ge$: C, 61.24; H, 10.28. Found: C, 61.43; H, 10.63. **(*E*)-5d**: ^1H NMR ($CDCl_3$) δ 0.11 (s, 9 H), 1.55 (bd, 2 H, J = 8.8 Hz), 1.55 (bs, 3 H), 1.60 (bs, 3 H), 1.67 (bs, 3 H), 1.98-2.10 (m, 4 H), 5.09 (t, 1 H, J = 6.8 Hz), 5.22 (t, 1 H, J = 8.8 Hz).

(*E*)-1-Dimethylphenylsilyl-3,7-dimethyl-2,6-octadiene[9] **(7d)**: ^1H NMR ($CDCl_3$) δ 0.25 (s, 6 H), 1.48 (bs, 3 H), 1.60 (bs, 3 H), 1.68 (bs, 3 H), 1.63 (d, 2 H, J = 8.4 Hz), 1.94-2.10 (m, 4 H), 5.08 (m, 1 H), 5.17 (t, 1 H, J = 8.4 Hz), 7.34 (m, 3 H), 7.51 (m, 2 H).

Dimethylphenylgermyl-2-octene (5e): bp 135 °C (5 mmHg, a mixture of *E* and *Z*); IR (film) 1430, 1095, 800 cm^{-1}. Anal. Calcd for $C_{16}H_{26}Ge$: C, 66.05; H, 9.01. Found: C, 65.83; H, 8.,96. **(*E*)-5e**: ^1H NMR ($CDCl_3$) δ 0.37 (s, 6 H), 0.88 (t, 3 H, J = 7.0 Hz), 1.21-1.34 (m, 6 H), 1.79 (d, 2 H, J = 7.9 Hz), 1.95

(m, 2 H), 5.28 (dt, 1 H, J = 15.0, 6.8 Hz), 5.41 (dt, 1 H, J = 15.0, 7.9 Hz), 7.29-7.36 (m, 3 H), 7.42-7.48 (m, 2 H).

1-Trimethylgermyl-2-octene (5f): bp 120 °C (55 mmHg, a mixture of *E* and *Z*); IR (film) 1470, 1240, 825 cm^{-1}. Anal. Calcd for $C_{11}H_{24}Ge$: C, 57.72, H, 10.57. Found: C, 57.58; H, 10.84. (*E*)-**5f**: ^1H NMR ($CDCl_3$) δ 0.11 (s, 9 H), 0.88 (t, 3 H, J = 7.0 Hz), 1.21-1.36 (m, 6 H), 1.54 (d, 2 H, J = 8.1 Hz), 1.96 (dt, 2 H, J = 6.8, 6.5 Hz), 5.24 (dt, 1 H, J = 15.0, 6.8 Hz), 5.40 (dt 1 H, J = 15.0, 8.1 Hz).

1-Dimethylphenylsilyl-2-octene (7f): bp 120 °C (55 mmHg, a mixture of *E* and *Z*); IR (film) 1470, 1240, 1140, 820 cm^{-1}. Anal. Calcd for $C_{16}H_{26}Si$: C, 77.97; H, 10.63. Found: C, 77.52, H, 10.94. (*E*)-**7f**: ^1H NMR ($CDCl_3$) δ 0.26 (s, 6 H), 0.88 (bt, 3 H, J = 7.0 Hz), 1.10-2.20 (m, 10 H), 5.17-5.40 (m, 2 H), 7.20-7.60 (m, 5 H).

***trans*-1-Phenyl-2-(trimethylgermyl)cyclopropane (8)**: bp 110 °C (7 mmHg); ^1H NMR ($CDCl_3$) δ 0.13 (s, 9 H), 0.31 (ddd, 1 H, J = 10.1, 7.5, 6.0 Hz), 0.87 (ddd, 1 H, J = 7.6, 7.5, 4.3 Hz), 0.98 (ddd, 1 H, J = 10.1, 4.5, 4.3 Hz), 1.74 (ddd, 1 H, J = 7.6, 6.0, 4.5 Hz), 7.15 (m, 1 H); IR (film) 1610, 1500, 1460, 1240, 825 cm^{-1}. Anal. Calcd for $C_{12}H_{18}Ge$: C, 61.37, H, 7.72. Found: C, 61.37; H, 8.00.

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