by evaporation under reduced pressure, and the residue was dried in vacuo. This yielded a sample of [2-methyl-2-[(diiodophenylstannyl)methyl]-1,3-propanediyl]bis[diiodophenylstannane] (**6**) that was sufficiently pure for immediate use in the following reaction: ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.47 (s, 3 H), 2.71 (s, 6 H), 7.4–7.7 (m, 15 H).

7-Methyl-1,3,5-triphenyl-1,3,5-tristanna-2,4,9-trithiatricyclo[3.3.1.1^{3,7}]decane (1-CH_3). A sample of [2-methyl-2-[(diiodophenylstannyl)methyl]-1,3-propanediyl]bis[diiodophenylstannane] (**6**) derived from [2-methyl-2-[(triphenylstannyl)methyl]-1,3-propanediyl]bis[triphenylstannane] (**5**; 80.3 mg, 0.0717 mmol) was treated with a solution of hexaphenyldistannathiane (317 mg, 0.433 mmol)[15] in dichloromethane (10 mL), and the mixture was stirred at 25 °C for 2 h. Solvent was then removed by evaporation under reduced pressure. Flash chromatography[27] of the residue (silica, hexane (60%)/dichloromethane (40%)) provided an analytically pure sample of 7-methyl-1,3,5-triphenyl-1,3,5-tristanna-2,4,9-trithiatricyclo[3.3.1.1^{3,7}]decane (**1**-CH_3; 45.9 mg, 0.0610 mmol, 85.1%) as a white solid: mp 240–243 °C; IR (KBr) 1480, 1430, 1070, 725, 695 cm^{-1}; ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 1.46 (s, average $^4J(^{117,119}Sn,^1H)$ = 26.1 Hz, 3 H), 1.79 (s, average $^2J(^{117,119}Sn,^1H)$ = 42.4 Hz, 6 H), 7.5 (m, 9 H), 7.7 (m, 6 H); ^{13}C NMR (100.62 MHz, 5% CD_2Cl_2 in CH_2Cl_2, gated proton decoupling) δ 34.5 (s, $^1J(^{117}Sn,^{13}C)$ = 381 Hz, $^1J(^{119}Sn,^{13}C)$ = 398 Hz), 45.2 (s, average $^3J(^{117,119}Sn,^{13}C)$ = 88.4 Hz), 45.8 (s, average $^2J(^{117,119}Sn,^{13}C)$ = 26.7 Hz), 128.9 (s), 130.2 (s), 134.7 (s), 139.5 (s); mass spectrum (FAB, 18-crown-6), *m/e* 756, 679, 265. Anal. Calcd for $C_{23}H_{24}S_3Sn_3$: C, 36.70; H, 3.22. Found: C, 36.85; H, 3.58.

Reaction of Hexaphenyldistannathiane and Tetramethylstannane with Iodine. A solution of hexaphenyldistannathiane (107 mg, 0.146 mmol)[15] and tetramethylstannane (25.8 mg, 0.144 mmol) in chloroform (15 mL) was treated with a solution of iodine (37.2 mg, 0.147 mmol) in chloroform (10 mL), and the mixture was stirred at 25 °C in the dark for 13 h. Volatiles were then removed by evaporation under reduced pressure, and the residue was extracted with acetonitrile. The insoluble fraction, a pale yellow solid, was further washed with ether, dried, and identified by its characteristic solubility and chromatographic properties as elemental sulfur (3.1 mg, 0.097 mmol, 66%). Concentration of the acetonitrile solution of the soluble fraction produced colorless crystals of iodotriphenylstannane (101 mg, 0.212 mmol, 72.6%): mp 119–120 °C (lit.[28] mp 121 °C).

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Registry No. 1-H, 87922-35-8; **1**-CH_3, 111769-98-3; **2**-H, 88212-59-3; **2**-CH_3, 111769-99-4; **3**, 96504-44-8; **4**, 111770-00-4; **5**, 111770-01-5; **6**, 111770-02-6; **7**, 111770-03-7; **12**, 639-58-7; bis(triphenyltin) sulfide, 77-80-5; tetramethylstannane, 594-27-4; iodotriphenylstannane, 894-09-7; bromotriphenylstannane, 962-89-0; 4-nitrobenzoyl chloride, 122-04-3; 4-nitroacetophenone, 100-19-6; 2-(hydroxymethyl)-2-methyl-1,3-propanediol, 77-85-0; triphenylstannane, 892-20-6.

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(28) Ingham, R. K.; Rosenberg, S. D.; Gilman, H. *Chem. Rev.* **1960**, *60*, 459–539.

Synthesis and Reactions of (Trimethylgermyl)acetates

Sumie Inoue, Yoshiro Sato,* and Tomoko Suzuki

Faculty of Pharmaceutical Sciences, Nagoya City University, Tanabe-dori, Mizuho-ku, Nagoya 467, Japan

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Base-assisted trimethylgermylation of ethyl acetate gave high yields of ethyl (trimethylgermyl)acetate (**2**), bis(trimethylgermyl)acetate (**5**), and tris(trimethylgermyl)acetate (**6**). The Peterson reaction of (trimethylgermyl)(trimethylsilyl)acetate (**4**), prepared from ethyl (trimethylsilyl)acetate (**1**), with aldehydes selectively yielded α-(trimethylgermyl)-α,β-unsaturated alkenoates (**15**). The addition of fluoride anion to **4** successfully induced selective desilylation. Some chemical properties of **6** were also examined.

Although the synthetic utility of α-trimethylsilyl esters has been amply demonstrated,[1,2] there is no direct method to prepare them from the corresponding esters. All reports to date on the direct trimethylsilylation of esters have shown that the predominant product is that due to O-silylation and not C-silylation.[1,3] One exception to this general observation is that of *tert*-butyl acetate, which can be attributed to a larger steric effect in the O-silylated material than in the C-silylated isomer.[4] However, the trimethylsilylation of *tert*-butyl (trimethylsilyl)acetate gave a mixture of both the C-silylated and O-silylated products.[5] Larson reported that methyldiphenylsilylation of esters favors the formation of the C-silylation product.[6] Previously we reported that the trimethylgermyl group tended to be introduced on the α-carbon rather than the carbonyl oxygen of ketones, whereas the trimethylsilyl group was usually introduced on the oxygen.[7] This paper describes

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(1) Before 1981, see: (a) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981. (b) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983.

(2) (a) Larson, G. L.; Hernandez, D. *Tetrahedron Lett.* **1982**, *23*, 1035. (b) Larson, G. L.; Kaifer, C. F.; Seda, R.; Torres, L. E.; Ramirez, J. R. *J. Org. Chem.* **1984**, *49*, 3385. (c) Larson, G. L.; L.-Cepero, I. M.; Torres, L. E. *Tetrahedron Lett.* **1984**, *25*, 1673. (d) Hernandez, D.; Larson, G. L. *J. Org. Chem.* **1984**, *49*, 4285. (e) Larson, G. L.; Hernandez, D.; Cepero, I. M. L.; Torres, L. E. *J. Org. Chem.* **1985**, *50*, 5260. (f) Sato, Y.; Takeuchi, S. *Synthesis*, **1983**, 734. (g) Zapata, A.; Ferrer, F. *Synth. Commun.* **1986**, *16*, 1611.

(3) Brownbridge, P. *Synthesis* **1983**, 1 and references cited therein.

(4) Rathke, M. W.; Sullivan, D. F. *Synth. Commun.* **1973**, *3*, 67.

(5) Hartzell, S. L.; Rathke, M. W. *Tetrahedron Lett.* **1976**, 2737.

(6) Larson, G. L.; Fuentes, L. M. *J. Am. Chem. Soc.* **1981**, *103*, 2418.

Table I. Reaction of the Germylacetate Anions with Aldehydes

entry	acetate			aldehyde	reactn conditns[a]	product		
		M	Y	R			% yield[b]	ratio[c] (*E*:*Z*)
1	**1**	Si	H	Ph	A	**14a**	84[d]	3–8:1
2	**2**	Ge	H	Ph	A	**14a**	65	>95:<5
3	**1**	Si	H	*n*-Oct	A	**14b**	81[d]	1:1
4	**2**	Ge	H	*n*-Oct	A	**14b**	57	95:5
5	**4**	Si	Me_3Ge	Ph	B	**15a**	49	>95:<5
6	**5**	Ge	Me_3Ge	Ph	B	**15a**	52	>95:<5
7	**4**	Si	Me_3Ge	*n*-Oct	B	**15b**	47	53:47
8	**5**	Ge	Me_3Ge	*n*-Oct	B	**15b**	43	72:28
9	**4**	Si	Me_3Ge	*n*-Bu(Et)CH	B	**15c**	43	69:31
10	**5**	Ge	Me_3Ge	*n*-Bu(Et)CH	B	**15c**	62	75:25

[a] Reaction conditions: A, −78 °C/1 h, −25 °C/1 h, and then 25 °C/1 h; B, −78 °C/1 h and then 0 °C/1 h. [b] Isolated yield. [c] Determined from the integrated values of GLC analyses. [d] Reference 10.

Table II. Ethyl 2-(Trimethylgermyl)-2-alkenoates (15a–c)

compd	bp, °C-(mmHg)[a]	IR, cm^{-1} (C=O)	^1H NMR ($CDCl_3$), δ		elemental anal. found (calcd)	
			Me_3Ge	—CH=	C	H
15a-*E*	95 (2)	1705	0.38	6.71 (s)	57.22 (57.41)	6.86 (6.88)
15b-*E*	140 (20)	1710	0.29	6.06 (t, *J* = 7 Hz)	58.19 (58.41)	9.91 (9.80)
15b-*Z*	140 (20)	1710	0.36	7.13 (t, *J* = 7 Hz)	58.39 (58.41)	9.72 (9.80)
15c-*E*	120 (12)	1710	0.27	5.74 (d, *J* = 9 Hz)	56.92 (57.20)	9.44 (9.60)
15c-*Z*	120 (12)	1710	0.35	6.90 (d, *J* = 11 Hz)	56.99 (57.20)	9.65 (9.60)

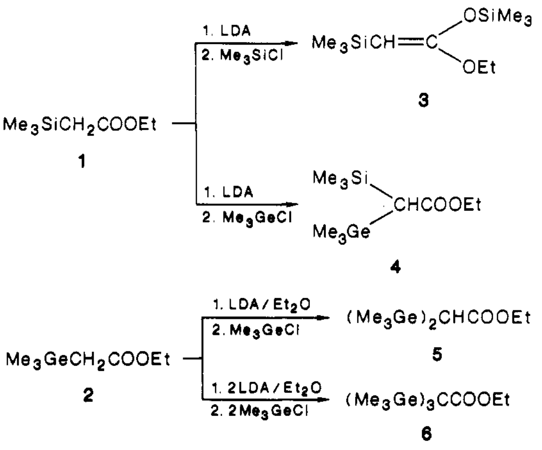
[a] Oven temperature of Kugelrohr distillation apparatus.

the synthesis of mono-, bis-, and tris(trimethylgermyl)acetates from ethyl acetate and the reactions of the related compounds.

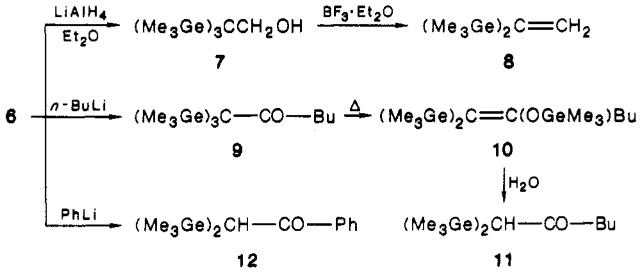
Results and Discussion

Ethyl (trimethylgermyl)acetate (**2**) was conveniently obtained in high yield by trimethylgermylation of ethyl acetate with the aid of lithium diisopropylamide (LDA), even though it had been previously prepared by the Reformatskii reaction of ethyl bromoacetate with chlorotrimethylgermane.[8] Trimethylgermylation of lithium salts of ethyl (trimethylsilyl)acetate (**1**) and **2** gave high yields of ethyl (trimethylgermyl)(trimethylsilyl)acetate (**4**) and ethyl bis(trimethylgermyl)acetate (**5**), respectively, whereas trimethylsilylation of **1** afforded only *O*-ethyl *O*-trimethylsilyl ketene acetal (**3**) (Scheme I). The use of excess amounts of LDA and chlorotrimethylgermane with **2** gave ethyl tris(trimethylgermyl)acetate (**6**) in a high yield. We previously showed that the trimethylgermylation of (trimethylgermyl)acetonitrile in the presence of 2 equiv of a base formed stable crystals of tris(trimethylgermyl)acetonitrile.[9] Compound **6** is also in the form of stable crystals and can be kept without detectable decomposition at room temperature.

Scheme I



Scheme II



Some reactivities of **6** were examined (Scheme II). The lithium aluminum hydride reduction gave a 78% yield of 2,2,2-tris(trimethylgermyl)ethanol (**7**) in ether, and the treatment with *n*-butyllithium at room temperature afforded an 86% yield of 1,1,1-tris(trimethylgermyl)-2-hexanone (**9**). Thus, the tris(trimethylgermyl)methyl group was not affected by the reduction or alkyllithium. Both tris(trimethylgermyl)-substituted compounds **7** and **9** were also stable in a moist atmosphere, and the former could be easily purified by distillation. However, the distillate of the latter at 100 °C (3 mmHg) was contaminated with 1,1-bis(trimethylgermyl)-2-hexanone (**11**), which was presumed to be the hydrolyzed form of the thermal rearrangement product, 1,1-bis(trimethylgermyl)-2-(trimethylgermoxy)-1-hexene (**10**). The isomerization from **9** to **10** was accelerated in the presence of silica gel in an ether solution.

When **7** was treated with boron trifluoride etherate, an 83% yield of 1,1-bis(trimethylgermyl)ethylene (**8**) was obtained with hydroxytrimethylgermane being generated as a byproduct. Treatment of **6** with phenyllithium gave only a small amount of α,α-bis(trimethylgermyl)acetophenone (**12**), although there was no reaction with either *n*-butylmagnesium bromide or phenylmagnesium bromide.

It is well-known that lithio(trimethylsilyl)acetates react with aldehydes to give α,β-unsaturated acid esters (**14**)[10,11]

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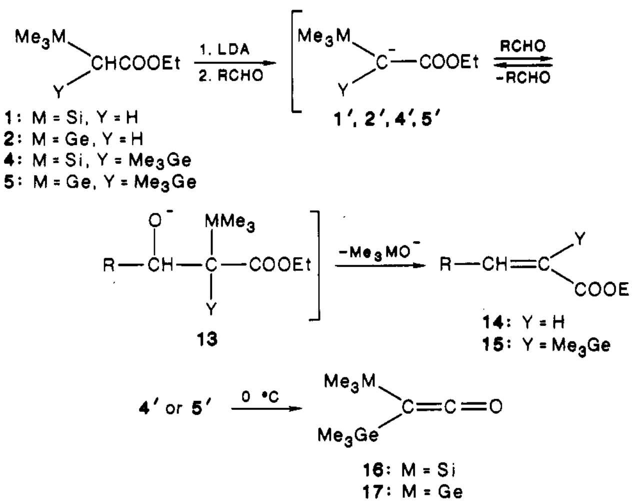
(7) Inoue, S.; Sato, Y. *Organometallics* **1987**, *6*, 2568.

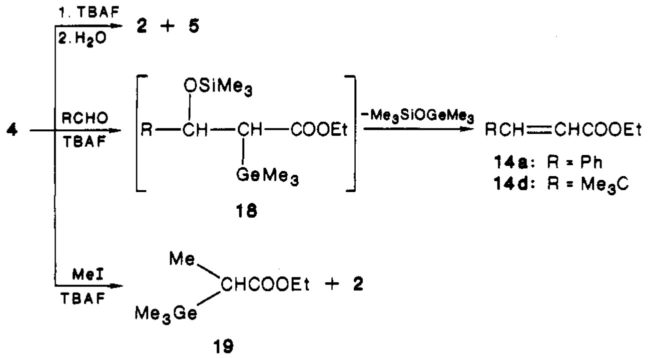
(8) Krumpolc, M.; Chvalovsky, V. *Synth. Inorg. Met.-Org. Chem.* **1971**, *1*, 51.

(9) Inoue, S.; Sato, Y. *Organometallics* **1986**, *5*, 1197.

Scheme III



Scheme IV



and that α-(trimethylsilyl)-α,β-unsaturated esters are obtained from lithio[bis(trimethylsilyl)]acetate (Peterson reaction).[2f,5] A similar reaction using the germyl analogue **2**, **4**, or **5** with some aldehydes was carried out (Scheme III), and the results are summarized in Tables I and II. The results of entries 2 and 4 are comparable with previously reported data (entries 1, 3).

The yields of ethyl α,β-unsaturated alkenoates **14a,b** from **2** were somewhat lower than those from **1** although the stereoselectivities were higher (entires 1–4 in Table I). The reaction of the aldehydes with the anion of **4** or **5** gave the same product, ethyl α-(trimethylgermyl)-α,β-unsaturated alkenoates (**15a–c**), respectively (entries 5–10). We previously revealed that the reaction of the (trimethylgermyl)(trimethylsilyl)acetonitrile anion with aldehydes formed α-(trimethylgermyl)-α,β-unsaturated alkenenitriles as the sole reaction product.[9] Thus, the trimethylsiloxy group is selectively eliminated from the Peterson-type reaction intermediate (e.g., **13**, M = Si, Y = Me_3Ge, in Scheme III) in the reaction of trimethylgermyl, trimethylsilyl-substituted carbanion with carbonyl compounds.

The yields of **15a–c** were unexpectedly low with 34–56% of used **4** or **5** remaining at the end of the reaction (entries 5–10). When the temperature of the reaction mixture rose to room temperature after the addition of the aldehyde, (trimethylgermyl)(trimethylsilyl)ketene (**16**) or bis(trimethylgermyl)ketene (**17**) was notably produced. A high yield of either **16** or **17** was isolated from the solution of **4′** or **5′** after being at 0 °C for 1 h. There may be an equilibrium between the acetate anion (**4′** or **5′**) and the adduct (**13**) which makes it difficult to complete the reaction. The analogous formation of bis(trimethylsilyl)ketene from *tert*-butyl lithiobis(trimethylsilyl)acetate has been reported by Rathke.[12]

The fluoride ion induced reaction of organosilicon compounds is an important synthetic method. Degermylation also occurs quickly by the addition of fluoride ion, e.g. α-(trimethylgermyl)acetophenone was degermylated at −78 °C.[7] However, selective desilylation of silyl, germyl-substituted compounds may be possible because there is a considerable difference between the bond dissociation energies of Si–F (143 kcal/mol^{-1}) and Ge–F (113 kcal/mol^{-1}) bonds.

The addition of tetra-*n*-butylammonium fluoride (TBAF) followed by water to **4** gave a mixture of **2** and **5** (Scheme IV). It has been reported that the trimethylgermyl group of (trimethylgermyl)acetonitrile rearranges quickly to give bis(trimethylgermyl)acetonitrile in the presence of a base.[13] The formation of **5** may also result from the intermolecular anionic rearrangement of the trimethylgermyl group to the (trimethylgermyl)acetate anion produced by the desilylation of **4**. In the presence of non-enolizable aldehydes such as benzaldehyde and trimethylacetaldehyde, the corresponding ethyl α,β-unsaturated carboxylates (**14a,d**) were obtained. (Trimethylsilyl)acetic acid ester with the non-enolizable aldehydes gave the Reformatskii-type products under a similar reaction condition.[14] The formation of **14** may proceed via the intermediate **18** with the elimination of trimethyl(trimethylsiloxy)germane. Small amounts of ethyl 2-(trimethylgermyl)propionate (**19**) were isolated from the desilylation of **4** in the presence of methyl iodide.

Experimental Section

All reactions were carried out under a nitrogen atmosphere. Diethyl ether and tetrahydrofuran were dried by distillation from sodium benzophenone ketyl prior to use. ^1H NMR spectra were recorded on a JEOL JNM-PMX 60 spectrometer using Me_4Si as internal standard. IR spectra were recorded on a JASCO IRA-2 spectrometer. All melting points and boiling points are uncorrected. *n*-Butyllithium, 15% in hexane, was purchased from Merck & Co., Inc, Schuchardt.

Ethyl (Trimethylgermyl)acetate (2). A. A solution of *n*-BuLi in hexane (21 mL, 33 mmol) was added to a solution of diisopropylamine (3.33 g, 33 mmol) in ether (15 mL) at 0 °C with continuous stirring for 0.5 h. The resulting LDA solution was cooled at −78 °C, and a solution of ethyl acetate (2.64 g, 30 mmol) in ether (15 mL) was added dropwise. After 1 h, a solution of chlorotrimethylgermane (5.05 g, 33 mmol) in ether (15 mL) was added with additional stirring for 1 h. Saturated aqueous NH_4Cl was added to the mixture. The organic layer was separated, and the aqueous layer was extracted with ether. The combined extracts were dried over anhydrous $MgSO_4$, concentrated, and distilled under reduced pressure to give **2** (4.80 g, 78%): bp 76–78 °C (30 mmHg) [lit.[8] bp 83–84 °C (37 mmHg)]; IR (film) 1720 (CO), 830, 610, 580 cm^{-1} (Me_3Ge); ^1H NMR ($CDCl_3$) δ 0.26 (9 H, s, Me_3Ge), 1.26 (3 H, t, J = 8 Hz, CH_3), 1.96 (2 H, s, CH_2CO), 4.20 (2 H, q, J = 8 Hz, CH_2).

B. A solution of ethyl bromoacetate (43.25 g, 259 mmol) in benzene (25 mL) was added to a mixture of chlorotrimethylgermane (30.83 g, 201 mmol), activated granular zinc (26.28 g, 402 mmol), benzene (50 mL), and THF (80 mL). After 20 h of stirring at 30 °C, saturated aqueous NH_4Cl was added to the

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(10) Shimoji, K.; Taguchi, H.; Oshima, K.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* **1974**, *96*, 1620.

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

(12) Sullivan, D. F.; Woodbury, R. P.; Rathke, M. W. *J. Org. Chem.* **1977**, *42*, 2038.

(13) Kanemoto, N.; Inoue, S.; Sato, Y. *Synth. Commun.* **1987**, *17*, 1273.

(14) Nakamura, E.; Shimizu, M.; Kuwajima, I. *Tetrahedron Lett.* **1976**, 1699.

mixture. The organic layer was separated, and the aqueous layer was extracted with benzene. The combined extracts were dried ($MgSO_4$), concentrated, and distilled to give **2** (29.41 g, 71%) (lit.[8] 47%).

Ethyl (Trimethylgermyl)(trimethylsilyl)acetate (4). To a solution of LDA, prepared from diisopropylamine (3.09 g, 30.5 mmol) and *n*-BuLi (20 mL, 31.2 mmol) in ether (15 mL), was added dropwise a solution of ethyl (trimethylsilyl)acetate (4.83 g, 30.2 mmol) in ether (10 mL) at −78 °C. After 1 h of stirring, a solution of chlorotrimethylgermane (5.82 g, 37.9 mmol) in ether (5 mL) was added with additional stirring for 3.5 h at the same temperature. After the addition of a saturated aqueous NH_4Cl solution, the organic layer was separated and the aqueous layer was extracted with benzene. The combined extracts were washed with water and saturated aqueous NaCl, dried over anhydrous $MgSO_4$, and concentrated. Distillation of the residual oil gave **4** (6.59 g, 79%): bp 101–105 °C (15 mmHg); IR (film) 1690 (CO), 1250, 820, 600 cm^{-1} (Me_3Si and Me_3Ge); ^1H NMR ($CDCl_3$) δ 0.13 (9 H, s, Me_3Si), 0.29 (9 H, s, Me_3Ge), 1.23 (3 H, t, J = 8 Hz, CH_3), 1.59 (1 H, s, CH), 4.13 (2 H, q, J = 8 Hz, CH_2). Anal. Calcd for $C_{10}H_{24}GeO_2Si$: C, 43.35; H, 8.75. Found: C, 43.42; H, 8.73.

Ethyl Bis(trimethylgermyl)acetate (5). In a manner similar to that described for **4**, diisopropylamine (3.09 g, 30.6 mmol), *n*-BuLi (19.5 mL, 30.5 mmol), **2** (6.14 g, 30 mmol), and chlorotrimethylgermane (5.05 g, 33 mmol) were allowed to react and worked up to give **5** (8.92 g, 93%): bp 121–122 °C (28 mmHg); IR (film) 1695 (CO), 820, 595, 565 cm^{-1} (Me_3Ge); ^1H NMR ($CDCl_3$) δ 0.25 (18 H, s, Me_3Ge), 1.22 (3 H, t, J = 6.5 Hz, CH_3), 1.60 (1 H, s, CH), 4.05 (2 H, q, J = 6.5 Hz, CH_2). Anal. Calcd for $C_{10}H_{24}Ge_2O_2$: C, 37.36; H, 7.52. Found: C, 37.30; H, 7.47.

Ethyl Tris(trimethylgermyl)acetate (6). A solution of **2** (6.16 g, 30 mmol) in THF (8 mL) was added dropwise at −78 °C to a LDA solution, prepared from diisopropylamine (12.04 g, 119 mmol) and *n*-BuLi (77 mL, 120 mmol) in THF (40 mL). After 1 h of stirring, a solution of chlorotrimethylgermane (18.48 g, 120 mmol) in THF (18 mL) was added dropwise with additional stirring for 4 h at the same temperature. Saturated aqueous NH_4Cl was added to the mixture, and it was extracted with benzene. The organic layer was washed with water and saturated aqueous NaCl, dried over $MgSO_4$, and concentrated. Distillation of the residue gave **6** (10.78 g, 82%): bp 140–150 °C (20 mmHg); mp 160–171 °C; IR (Nujol) 1675 (CO), 820, 595, 565 cm^{-1} (Me_3Ge); ^1H NMR ($CDCl_3$) δ 0.30 (27 H, s, Me_3Ge), 1.23 (3 H, t, J = 7 Hz, CH_3), 4.10 (2 H, q, J = 7 Hz, CH_2). Anal. Calcd for $C_{13}H_{32}Ge_3O_2$: C, 35.64; H, 7.36. Found: C, 35.75; H, 7.25.

2,2,2-Tris(trimethylgermyl)ethanol (7). A mixture of **6** (2.21 g, 5 mmol) and $LiAlH_4$ (387 mg, 10 mmol) in ether (30 mL) was heated at reflux for 8 h. The reaction mixture was cooled in an ice bath and worked up by the addition of ethyl acetate (0.5 mL), 10% NaOH (0.5 mL), and water (1.5 mL). The mixture was filtered, and the filter cake was washed with ether. The filtrate and washings were combined and washed with saturated aqueous NaCl, dried over $MgSO_4$, and concentrated. Distillation of the residue gave **7** (1.55 g, 78%): bp 120–130 °C (10 mmHg, oven temperature of a Kugelrohr distillation apparatus); mp 181–185 °C; IR (Nujol) 3450 (OH), 810, 580, 560 cm^{-1} (Me_3Ge); ^1H NMR ($CDCl_3$) δ 0.28 (27 H, s, Me_3Ge), 2.68 (2 H, s, CH_2), 4.06 (1 H, s, OH). Anal. Calcd for $C_{11}H_{30}GeO$: C, 33.35; H, 7.63. Found: C, 33.06; H, 7.53.

1,1-Bis(trimethylgermyl)ethylene (8). A solution of boron trifluoride etherate (188 mg, 1.3 mmol) in dichloromethane (3 mL) was added dropwise to a solution of **7** (396 mg, 1.0 mmol) in dichloromethane at 0 °C. After 1 h of stirring, saturated aqueous NH_4Cl was added and the mixture was extracted with ether. The ethereal extract was washed with water, saturated aqueous NaCl, dried over $MgSO_4$, and concentrated under reduced pressure to give **8** (216 mg, 83%): bp 70 °C (77 mmHg, Kugelrohr); IR (film) 1230, 950, 815, 590, 560 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.22 (18 H, s, Me_3Ge), 6.13 (2 H, s, CH_2). Anal. Calcd for $C_8H_{20}Ge_2$: C, 36.76; H, 7.71. Found: C, 36.49; H, 7.56.

1,1,1-Tris(trimethylgermyl)-2-hexanone (9). To a solution of **6** (448 mg, 1.1 mmol) in ether (5 mL) was added dropwise *n*-BuLi (2.1 mL, 3.3 mmol) at room temperature with continuous stirring for 1 h. The mixture was cooled in an ice bath, and saturated aqueous NH_4Cl was added. The ethereal extract of the reaction mixture was washed with water and saturated aqueous NaCl and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave 470 mg of the crude oil that was chromatographed on a silica gel column (hexane/ethyl acetate, 80:1) to give **9** (388 mg, 86%): IR (film) 1640 (CO), 820, 660, 570 cm^{-1} (Me_3Ge); ^1H NMR ($CDCl_3$) δ 0.36 (27 H, s, Me_3Ge), 0.86 (3 H, t, J = 8 Hz, CH_3), 1.12–1.71 (4 H, m, CH_2CH_2), 2.33 (2 H, t, J = 8 Hz, CH_2CO). Anal. Calcd for $C_{15}H_{36}Ge_3O$: C, 40.02; H, 8.06. Found: C, 40.20; H, 8.05.

1,1-Bis(trimethylgermyl)-2-hexanone (11). Distillation of **9** (260 mg, 0.78 mmol) in a Kugelrohr distillation apparatus at 100 °C under 3 mmHg gave 235 mg of a mixture of **9** and **11** (GLC ratio, 83:17). The ratio of **9** to **11** was changed to 17:83 after being stirred with silica gel (1 g) in ether (5 mL) for 1 day at room temperature. The silica gel was filtered off, and the filtrate was distilled to give 186 mg of **11**: bp 115 °C (9 mmHg, Kugelrohr); IR (film) 1665 (CO), 820, 600, 570 cm^{-1} (Me_3Ge); ^1H NMR ($CDCl_3$) δ 0.25 (18 H, s, Me_3Ge), 0.90 (3 H, t, J = 6 Hz, CH_3), 1.14–1.66 (4 H, m, CH_2CH_2), 2.18 (1 H, s, CHCO), 2.31 (2 H, t, J = 7.4 Hz, CH_2CO). Anal. Calcd for $C_{12}H_{28}Ge_2O$: C, 43.21; H, 8.46. Found: C, 43.07; H, 8.34.

***α,α*-Bis(trimethylgermyl)acetophenone (12).** A solution of phenyllithium in cyclohexane/diethyl ether (7:3) (2.0 M, 3 mL, 6 mmol) was added dropwise to a solution of **6** (438 mg, 1.0 mmol) in ether (5 mL) at room temperature with continuous stirring for 1 h. The reaction mixture was worked up in a manner similar to that described for **9**. Chromatography of the crude oil (555 mg) on a silica gel column (hexane/ether, 40:1) gave **6** (310 mg, 71%) and **12** (36 mg, 10%): bp 130 °C (3 mmHg, Kugelrohr); IR (film) 1635 (CO), 820, 600, 565 cm^{-1} (Me_3Ge); ^1H NMR ($CDCl_3$) 0.27 (18 H, s, Me_3Ge), 3.10 (1 H, s, CH), 7.20–7.61 and 7.78–8.05 (each 3 H and 2 H, m, ArH). Anal. Calcd for $C_{14}H_{24}Ge_2O$: C, 48.95; H, 7.04. Found: C, 48.95; H, 7.06.

Ethyl 2-Alkenoate (14) and Ethyl 2-(Trimethylgermyl)-2-alkenoate (15) (General Procedure). A solution of 2.4 mmol of **2**, **4**, or **5** in THF (3 mL) was added dropwise at −78 °C to a solution of LDA, prepared from *n*-BuLi (1.5 mL, 2.4 mmol) and diisopropylamine (243 mg, 2.4 mmol) in THF (4 mL). After 1 h of stirring, a solution of an aldehyde (2 mmol) in THF (3 mL) was added dropwise, and stirring was continued at −78 °C for 1 h, −25 °C for 1 h, and 25 °C for 1 h (entries 1–4 in Table I) or −78 °C for 1 h and 0 °C for 1 h (entries 5–10). Saturated aqueous NH_4Cl was added to the reaction mixture. The ethereal extract of the mixture was washed with water and saturated aqueous NaCl, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was distilled (entries 5, 6) or chromatographed on a silica gel column (hexane/ether) (entries 2, 4, 7–10) to give **14–*E*** and **14–*Z*** or **15–*E*** and **15–*Z***.

The *E*,*Z* assignment of two geometrical isomers of **15** was performed, according to the reported method, by the comparison of the chemical shifts of olefinic protons and trimethylgermyl groups in their ^1H NMR spectra and the retention times of GLC.[9,15] The characteristic data of **15–*E*,*Z*** are summarized in Table II.

(Trimethylgermyl)(trimethylsilyl)ketene (16). A solution of **4** (554 mg, 2 mmol) in ether (3 mL) was added dropwise at 0 °C to a solution of LDA, prepared from *n*-BuLi (1.3 mL, 2 mmol) and diisopropylamine (202 mg, 2 mmol) in ether (4 mL). After 1 h of stirring at 0 °C, saturated aqueous NH_4Cl was added. The ethereal extract of the mixture was washed with water and saturated aqueous NaCl and dried over $MgSO_4$. Evaporation of the solvent gave crude **16** (391 mg, 85%). Kugelrohr distillation of the crude product gave 295 mg (64%) of the pure product: bp 75 °C (21 mmHg) [lit.[16] bp 60 °C (12 mmHg)]; ^1H NMR ($CDCl_3$) δ 0.18 (9 H, s, Me_3Si), 0.38 (9 H, s, Me_3Ge).

Bis(trimethylgermyl)ketene (17). In a manner similar to that described for **16**, **5** (772 mg, 2.4 mmol), *n*-BuLi (1.5 mL, 2.4 mmol), and diisopropylamine (243 mg, 2.4 mmol) were treated to give crude 17 (609 mg, 92%). Distillation of the crude product gave 505 mg (76%) of pure product: bp 80 °C (12 mmHg) [lit.[17]

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(15) Chan, T. H.; Mychajlowskii, W.; Amouroux, R. *Tetrahedron Lett.* **1977**, 1605.

(16) Efimova, I. V.; Kazankova, M. A.; Lutsenko, I. F. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1985**, *55*, 1465.

(17) Ponomarev, S. V.; Erman, N. B.; Lebedev, S. A.; Pechurina, S. Ya.; Lutsenko, I. F. *Zh. Obshch. Khim.* **1971**, *41*, 127.

bp 80–81 °C (20 mmHg)]; ^{1}H NMR ($CDCl_3$) δ 0.39 (s) (lit.[17] δ 0.29).

Desilylation of 4 with Tetra-*n*-butylammonium Fluoride (TBAF). To a solution of 4 (554 mg, 2.0 mmol) in THF (10 mL) was added dropwise a solution of TBAF (0.2 M in THF, dried over molecular sieves 4A, 10 mL, 2.0 mmol) at −78 °C. After 5 s, the reaction mixture was mixed with chilled ether (50 mL). The mixture was washed with 5% HCl, water, and saturated aqueous NaCl. Concentration of the organic layer on a rotary evaporator, after drying over anhydrous $MgSO_4$, gave 342 mg of a mixture of **2** (74%) and **5** (6%). Identification of the products was accomplished by the comparison with authentic samples on GLC and NMR. Yield of each compound was calculated from the mole ratio based on the proton ratios in ^{1}H NMR of the mixture.

Ethyl Cinnamate (14a). To a mixture of benzaldehyde (212 mg, 2.0 mmol) and TBAF (0.2 M in THF, 5 mL, 1.0 mmol) was added dropwise a solution of 4 (277 mg, 1.0 mmol) in THF (3 mL) at 0 °C. After 1 h of stirring, the reaction mixture was mixed with ether (50 mL). The mixture was washed with saturated aqueous NaCl, dried over $MgSO_4$, concentrated, and distilled to give 102 mg (58%) of **14a**.

Ethyl 4,4-Dimethyl-2-pentenoate (14d).[18] To a solution of 4 (554 mg, 2.0 mmol) and trimethylacetaldehyde (345 mg, 4.0 mmol) in THF (5 mL) was added dropwise TBAF (0.2 M in THF, 2 mL, 0.4 mmol) at −78 °C with continuous stirring for 1 h. After the addition of ether (50 mL), the mixture was washed with saturated aqueous NaCl, dried over $MgSO_4$, and concentrated under reduced pressure. Silica gel column chromatography (hexane/ether) of the residue gave **14d** (188 mg, 60%).

Ethyl 2-(Trimethylgermyl)propionate (19). To a solution of 4 (554 mg, 2.0 mmol) and methyl iodide (568 mg, 4.0 mmol) in THF (5 mL) was added dropwise TBAF (0.2 M in THF, 5 mL, 1.0 mmol) at −78 °C with continuous stirring for 1 h. After the addition of ether (50 mL), precipitated tetra-*n*-butylammonium iodide was filtered. The filtrate was washed with saturated aqueous NaCl, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographed on a silica gel column (hexane/ether, 40:1) to give **2** (181 mg, 45%) and **19** (55 mg, 13%): bp 65 °C (13 mmHg, Kugelrohr); IR (film) 1715 (CO), 830, 610, 575 cm^{-1} (Me_3Ge); ^{1}H NMR ($CDCl_3$) δ 0.22 (9 H, s, Me_3Ge), 1.20 (3 H, d, J = 6.4 Hz, CH_3CH), 1.23 (3 H, t, J = 7.2 Hz, CH_3), 2.16 (1 H, q, J = 6.4 Hz, CH), 4.10 (2 H, q, J = 7.2 Hz, CH_2). Anal. Calcd for $C_8H_{18}GeO_2$: C, 43.91; H, 8.29. Found: C, 43.70; H, 8.18.

Registry No. **1**, 4071-88-9; **2**, 32583-34-9; **4**, 111999-58-7; **5**, 111999-59-8; **6**, 111999-60-1; **7**, 111999-61-2; **8**, 7428-06-0; **9**, 111999-62-3; **11**, 27394-64-5; **12**, 38860-13-8; (*E*)-**14a**, 4192-77-2; (*Z*)-**14a**, 4610-69-9; (*E*)-**14b**, 51577-37-8; (*Z*)-**14b**, 51577-38-9; **14d**, 87995-20-8; (*E*)-**15a**, 111999-64-5; (*Z*)-**15a**, 111999-65-6; (*E*)-**15b**, 111999-66-7; (*Z*)-**15b**, 111999-67-8; (*E*)-**15c**, 111999-68-9; (*Z*)-**15c**, 111999-69-0; **16**, 38860-05-8; **17**, 32329-69-4; **19**, 111999-63-4; ethyl acetate, 141-78-6; ethyl bromoacetate, 105-36-2; benzaldehyde, 100-52-7; trimethylacetaldehyde, 630-19-3; nonanal, 124-19-6; 2-ethylhexanal, 123-05-7.

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(18) Marmor, R. S. *J. Org. Chem.* 1972, *37*, 2901.

Lanthanoid–Olefin Complex Formation: A Matrix-Isolation Ultraviolet–Visible and Infrared Study of the Direct Synthesis of $(C_2H_4)_nEu$ Using Europium Atoms[†]

Mark P. Andrews* and Andrea L. Wayda*

AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974

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$Eu(C_2H_4)_n$ complexes have been synthesized at 12 K by codepositing Eu atoms with ethylene, neat or doped in Ar or Xe. UV–visible absorption spectroscopy of the highest stoichiometry product revealed a broad, intense visible transition centered at 537 nm. The complex is unstable above 50 K, consistent with the absence of any evidence for reaction in 77 K metal vapor reactions. Optical spectroscopy of the products formed in dilute matrices indicated the formation of a lower stoichiometry $Eu–C_2H_4$ complex. This was confirmed by infrared studies of absorptions in the coupled ν(C═C)/δ(CH_2) region. Under high dilution conditions, a matrix split 1198/1182 cm^{-1} doublet is assigned to a monoethylene europium π complex. Matrix-annealing experiments combined with Eu/C_2H_4 reactions in C_2H_4/rare-gas matrices of increasing C_2H_4 concentration trace the conversion of $Eu(C_2H_4)$ to the highest stoichiometry species absorbing at 1233 cm^{-1}. In general, the $Eu(C_2H_4)_n$ IR spectra are similar to those of matrix-isolated group VIII (8–10) and IB (11) ethylene π complexes. The optical spectra of the odd-electron lanthanoid–olefin molecules, however, most closely resemble those of the coinage metals. The latter show intense visible metal-to-ligand charge-transfer transitions. Similarly, the green absorption of the europium olefin complexes may be associated with excitations of the Eu f electrons into the olefin. The comparatively low thermal stability of the Eu and group IB (11) olefin complexes is rationalized with the Dewar–Chatt–Duncanson bonding description. Molecular orbital calculations indicate that a model C_{2v} $Eu(C_2H_4)$ species is only weakly bonded by donation from a europium f orbital into the π^* system of ethylene, with little "forward" donation from the olefin σ or π orbitals.

Introduction

Although common in organotransition-metal chemistry, isolable, formally zerovalent complexes are extremely rare in organolanthanoid chemistry.[1] This dichotomy in chemical stability is undoubtedly linked to several factors, chief among them being (1) the electropositive character of the lanthanoid metals which favors di- and trivalent oxidation states of these metals and (2) the relative inability of the corelike lanthanoid metal valence electrons

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[†] In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13-18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

(1) The first well-characterized examples of formally zerovalent, thermally stable, isolable species of these metals, the lanthanoid diazadiene complexes, have only recently been reported. See Cloke, F. G. N.; de Lemas, H. C.; Sameh, A. A. *J. Chem. Soc., Chem. Commun.* 1986, 1344.

0276-7333/88/2307-0743$01.50/0