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Anionic rearrangement of the germyl and silyl groups in [2-(trimethylgermyl)-2-(trimethylsilyl)ethyl]dimethylammonium *N*-methylide and related compounds

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Abstract

The reaction of [2,2-bis(trimethylsilyl)ethyl]- and [2,2-bis(trimethylgermyl)ethyl]-trimethylammonium iodides (**3a** and **3c**) with n-butyllithium gives *N*-[(trimethylsilyl)methyl]- and *N*-[(trimethylgermyl)methyl]dimethylamines (**5a** and **5b**), respectively. A mixture of **5a** and **5b** is obtained from the reaction of [2-(trimethylgermyl)-2-(trimethylsilyl)ethyl]trimethylammonium iodide (**3b**). Use of lithium diisopropylamide in place of n-butyllithium gives the corresponding 1,1-bis(trimethylelemento)ethylenes (**8a**, **8b**, and **8c**) as the main products.

Introduction

Organo-silicon and -germanium compounds usually have similar reactivities and undergo the same Peterson-type reactions [1–3]. However, in reactions of (trimethylgermyl)(trimethylsilyl)-substituted acetates [1], acetamides [2], and acetonitrile anions [3] with aldehydes, the germyl groups always remain in the reaction products. The silyl group rearranges preferentially to the oxygen-anion in the initial adduct, and is then converted to the trimethylsilyloxy group to give the final product (Scheme 1). This selectivity may be due to the higher affinity of silicon for oxygen than that of germanium. The order of these affinities is related to the bond dissociation energies of Si–O (100 kcal/mol) and Ge–O (85 kcal/mol) bonds.

Treatment of [2-(trimethylsilyl)ethyl]trimethylammonium iodide with n-butyllithium gives *N*-[(trimethylsilyl)methyl]dimethylamine, which is produced by [1,4]-anionic migration of the silyl group from carbon to the carbon in an *N*-methylide intermediate [4]. The dissociation energy of the Si–C bond (79 kcal/mol) is larger than that of the Ge–C bond (58 kcal/mol). When the silyl and germyl groups compete with each other in this type of reaction, the silyl group is transferred preferentially at the anionic site. Here we report the synthesis of [2-(trimethylgermyl)-2-(trimethylsilyl)ethyl]trimethylammonium iodide and related compounds

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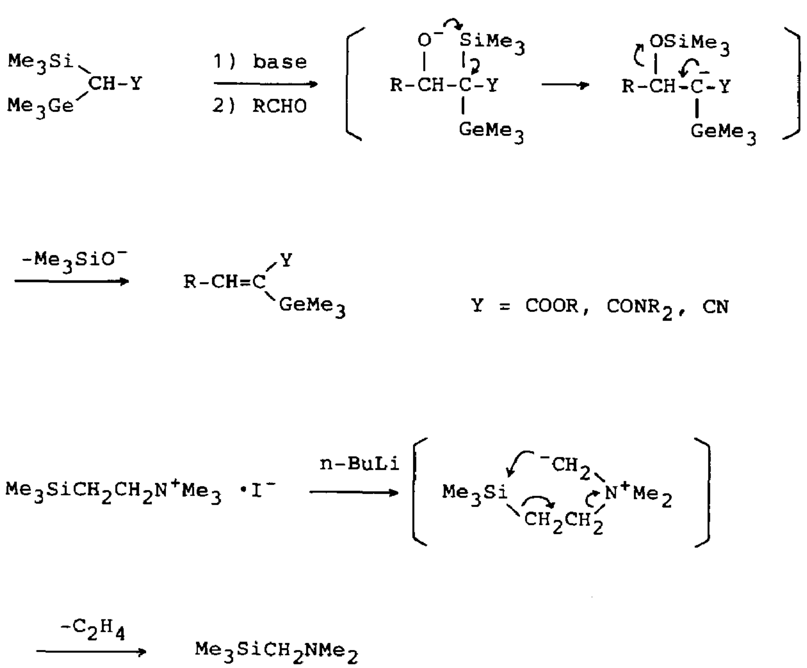

Scheme 1

and the behavior of the silyl and germyl groups during ylide formation.

Results and discussion

We have synthesized *N*,*N*-dimethyl-2,2-bis(trimethylsilyl)-, *N*,*N*-dimethyl-2-(trimethylgermyl)-2-(trimethylsilyl)-, and *N*,*N*-dimethyl-2,2-bis(trimethylgermyl)acetamides (**1a**, **1b**, and **1c**), respectively from *N*,*N*-dimethylacetamide [2]. They were converted into *N*-[2,2-bis(trimethylsilyl)ethyl]-, *N*-[2-(trimethylgermyl)-2-(trimethylsilyl)ethyl]-, and *N*-[2,2-bis(trimethylgermyl)ethyl]dimethylamines (**2a**, **2b**, and **2c**), respectively, by treatment with lithium aluminum hydride in ether *. These amines were quaternized with iodomethane.

Treatment of [2,2-bis(trimethylsilyl)ethyl]- and [2,2-bis(trimethylgermyl)ethyl]-trimethylammonium iodides (**3a** and **3c**) with n-butyllithium at −20 °C in a mixture of diethyl ether and hexamethylphosphoramide (HMPA) gave the expected products [(dimethylamino)methyl]trimethyl-silane (**5a**) and -germane (**5b**), respectively (entries 1 and 5 in Table 1). The germyl group is rearranged at the anionic site as is the silyl group. Similar treatment of [2-(trimethylgermyl)-2-(trimethylsilyl)ethyl]trimethylammonium iodide (**3b**) produced a mixture of **5a** and **5b** in a ratio of 28/72 (entry 3). The germyl group rearranges a little more easily than the silyl which is contrary to our prediction. Trimethylvinyl-silane (**6a**) and -germane (**6b**), which are the other expected reaction products to be formed by this rearrangement, could not be

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* This reduction required heating for a long time in ether to reach completion; however, in boiling tetrahydrofuran (THF) the reaction was accompanied by reductive cleavage of the Si–C and/or Ge–C bonds.

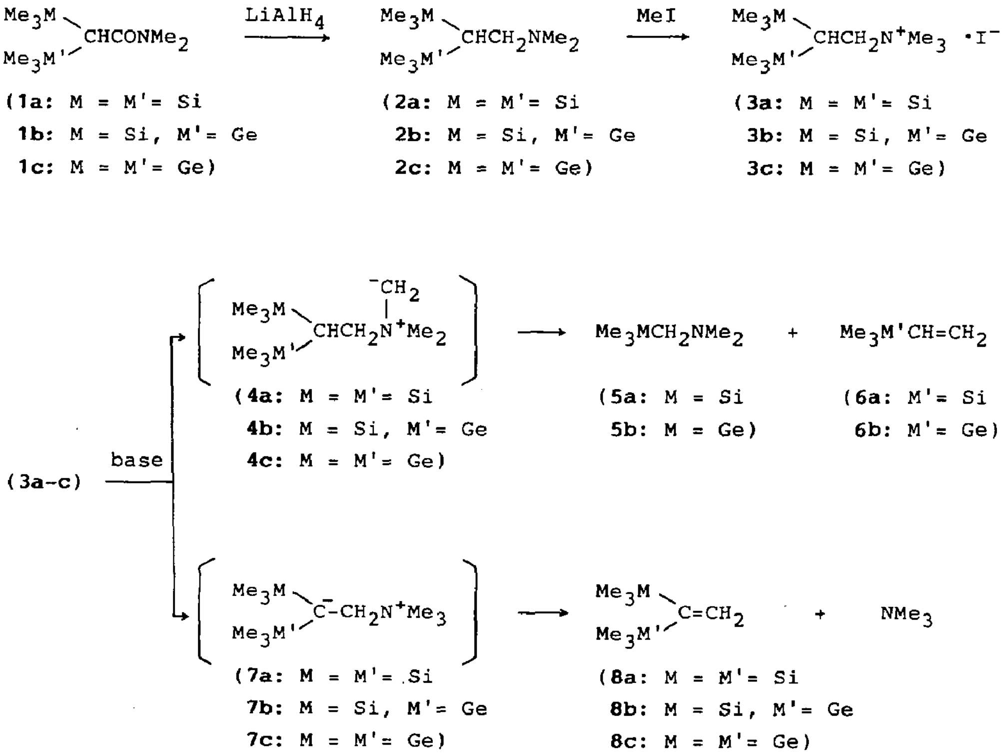
Table 1

Reaction of [2,2-bis(trimethylelemento)ethyl]trimethylammonium iodides (**3a**–**3c**) with base

Entry	Ammonium salts	Base	Products GLC yield, (%), (ratio)				
			5a	**5b**	**8a**	**8b**	**8c**
1	**3a**	n-BuLi	41 (82)		9 (18)		
2	**3a**	LDA	7 (9)		71 (91)		
3	**3b**	n-BuLi	18 (28)	47 (72)			
4	**3b**	LDA	11 (12)	20 (21)		64 (67)	
5	**3c**	n-BuLi		96 (100)			
6	**3c**	LDA		55 (57)			41 (43)

isolated because their boiling points are close to that of the solvent and GLC separation was insufficient.

When lithium diisopropylamide (LDA) was used in place of n-butyllithium, 1,1-bis(trimethylsilyl)ethylene (**8a**), 1-(trimethylgermyl)-1-(trimethylsilyl)ethylene (**8b**), or 1,1-bis(trimethylgermyl)ethylene (**8c**), was formed as the main product in each case. The ethylenes **8a**–**8c** are Hofmann-type elimination products that are formed via the intermediate **7a**–**7c** in Scheme 2. Interestingly n-butyllithium mainly attacks the α-hydrogen of **3** as a deprotonation reagent to give **4**, whereas LDA mainly attacks the β-hydrogen to give **7** with the carbanion being stabilized by the adjacent silyl and/or germyl groups.



Scheme 2

Experimental

All reactions were carried out under nitrogen. Diethyl ether and tetrahydrofuran (THF) were distilled from sodium benzophenone kethyl before use. HMPA was distilled under reduced pressure from sodium. ^1H NMR spectra were recorded on a JEOL JNM-PMX 60 or JNM-MH-100 spectrometer using Me_4Si as an internal standard. IR spectra were recorded on a JASCO IRA-2 spectrometer. Mass spectral data were obtained by using a JEOL JMS-DX 300 GC-MS system (70 eV, EI; 2-m, 5% Silicone SE-30 column). Gas chromatographic analyses were carried out on a Gasukuro Kogyo Model-370 chromatograph equipped with a TCD detector using a 2 m, 20% Silicone SE-30 or 10% Tergitol NP-35 column. All boiling points and melting points are uncorrected.

*N-[2,2-Bis(trimethylsilyl)ethyl]dimethylamine (**2a**)*

n-Butyllithium (10 w/v% in hexane, 94 ml, 145 mmol) was added dropwise to a solution of diisopropylamine (14.6 g, 145 mmol) in THF (150 ml) at 0 °C and the mixture was stirred for 0.5 h. The resulting LDA solution was cooled to −78 °C and a solution of *N,N*-dimethylacetamide (6.01 g, 69 mmol) in THF (60 ml) was added dropwise. After 1 h of stirring at −78 °C, a solution of chlorotrimethylsilane (15.8 g, 145 mmol) in THF (30 ml) was added with stirring for an additional 2 h. The reaction mixture was quenched with saturated aqueous NH_4Cl and the aqueous layer was extracted with ether.

The ethereal extract was dried ($MgSO_4$) and then mixed with $LiAlH_4$ (11.0 g, 290 mmol). The mixture was heated at reflux for 120 h, and then cooled in an ice bath. The reaction mixture was quenched with AcOEt (11 ml), 10% NaOH (11 ml), and water (33 ml). After the mixture had been filtered, the filter cake was washed with ether. The filtrate and washings were combined, washed with saturated aqueous NaCl, dried over $MgSO_4$, and concentrated. The residue was chromatographed on an aluminum oxide column (benzene/ether 10/1) to give **2a**: yield 2.70 g (18%); b.p. 69–70 °C (7 Torr); ^1H NMR ($CDCl_3$): δ 0.02 (18H, s, CH_3Ge), 0.43 (1H, t, J 9 Hz, CH), 2.18 (6H, s, NCH_3), 2.40 (2H, d, J 9 Hz, CH_2). Anal. Found: C, 55.13; H, 12.45; N, 6.25. $C_{10}H_{27}NSi_2$ calcd.: C, 55.22; H, 12.51; N, 6.44%.

*N-[2-(Trimethylgermyl)-2-(trimethylsilyl)ethyl]dimethylamine (**2b**) and N-[2,2-bis(trimethylgermyl)ethyl]dimethylamine (**2c**)*

A mixture of *N,N*-dimethyl-2-(trimethylgermyl)-2-(trimethylsilyl)acetamide (**1b**) or *N,N*-dimethyl-2,2-[bis(trimethylgermyl)]acetamide (**1c**) (43 mmol) and $LiAlH_4$ (3.27 g, 86 mmol) in ether (130 ml) was heated at reflux for 120 h. The mixture was cooled in an ice bath then quenched with AcOEt (3 ml), 10% NaOH (3 ml), and water (9 ml). The isolation of the products was similar to that described for **2a**.

2b: yield 7.55 g (67%); b.p. 88–89 °C (15 Torr); ^1H NMR ($CDCl_3$): δ 0.00 (9H, s, CH_3Si), 0.14 (9H, s, CH_3Ge), 0.44 (1H, t, J 9 Hz, CH), 2.08 (6H, s, NCH_3), 2.32 (2H, d, J 9 Hz, CH_2). Anal. Found: C, 45.58; H, 10.22; N, 5.22. $C_{10}H_{27}GeNSi$ calcd.: C, 45.84; H, 10.39; N, 5.35%.

2c: yield 10.71 g (84%); b.p. 81–83 °C (5 Torr); ^1H NMR ($CDCl_3$): δ 0.15 (18H, s, CH_3Ge), 0.70 (1H, t, J 9 Hz, CH), 2.11 (6H, s, NCH_3), 2.60 (2H, d, J 9 Hz, CH_2). Anal. Found: C, 38.88; H, 8.81; N, 4.42. $C_{10}H_{27}Ge_2N$ calcd.: C, 39.19; H, 8.88; N, 4.57%.

[2,2-Bis(trimethylsilyl)ethyl]trimethylammonium (3a), [2-(trimethylgermyl)-2-(trimethylsilyl)ethyl]trimethylammonium (3b), and [2,2-bis(trimethylgermyl)ethyl]trimethylammonium iodides (3c)

A mixture of **2a**, **2b**, or **2c** (3.8 mmol) and iodomethane (810 mg, 5.7 mmol) in acetone (10 ml) was heated at 40 °C for 2 h. The acetone was evaporated under reduced pressure. The products were purified by recrystallization.

3a: yield 1.27 g (93%); m.p. 178–179 °C (recrystallized from MeOH); ^{1}H NMR ($CDCl_3$): δ 0.22 (18H, s, CH_3Si), 0.42–0.71 (1H, m, CH), 3.43 (9H, s, NCH_3), 3.76 (2H, d, *J* 4 Hz, CH_2). Anal. Found: C, 36.70; H, 8.57; N, 3.86. $C_{11}H_{30}INSi_2$ calcd.: C, 36.76; H, 8.41; N, 3.90%.

3b: yield 1.46 g (95%); m.p. 168–169.5 °C (recrystallized from EtOH); ^{1}H NMR ($CDCl_3$): δ 0.21 (9H, s, CH_3Si), 0.37 (9H, s, CH_3Ge), 0.43–0.78 (1H, m, CH), 3.40 (9H, s, NCH_3), 3.63 (2H, d, *J* 5 Hz, CH_2). Anal. Found: C, 32.51; H, 7.21; N, 3.17. $C_{11}H_{30}GeINSi$ calcd.: C, 32.71; H, 7.49; N, 3.47%.

3c: yield 1.64 g (96%); m.p. 163–165 °C (recrystallized from EtOH/AcOEt); ^{1}H NMR ($CDCl_3$): δ 0.35 (18H, s, CH_3Ge), 0.75–0.96 (1H, m, CH), 3.47 (9H, s, NCH_3), 3.77 (2H, d, *J* 5 Hz, CH_2). Anal. Found: C, 29.20; H, 6.99; N, 3.01. $C_{11}H_{30}Ge_2IN$ calcd.: C, 29.46; H, 6.74; N, 3.12%.

Reaction of 3a, 3b, and 3c with n-BuLi

A solution of n-BuLi (1.5 ml, 2.4 mmol) was added dropwise at −20 °C to a solution of **3a**, **3b**, or **3c** (2 mmol) in a mixture of HMPA and ether (1/1, 10 ml). After 2 h of stirring at the same temperature, the reaction mixture was poured into chilled water (50 ml) and extracted with ether. The extract was analyzed by GLC and GC-MS on Silicone SE-30 columns. The structures of the products were confirmed by comparison with authentic samples of [(dimethylamino)methyl]trimethylsilane (**5a**) [5] and [(dimethylamino)methyl]trimethylgermane (**5b**). Their yields were determined on the basis of the integrated GLC value relative to an internal standard (trans-decaline). The results are listed in Table 1.

Reaction of 3a, 3b, and 3c with LDA

In a manner similar to that described above, a solution of LDA, prepared from n-BuLi (1.5 ml, 2.4 mmol), diisopropylamine (244 mg, 2.4 mmol) and ether (3 ml), was added to a solution of **3a**, **3b**, or **3c** (2 mmol) in a mixture of HMPA and ether (1/1, 10 ml). The ethereal extract after the aqueous work-up was washed with 5% HCl, water, and saturated aqueous NaCl. Then the mixture was dried ($MgSO_4$), concentrated, and distilled under reduced pressure to give 1,1-bis(trimethylsilyl)ethylene (**8a**), 1-(trimethylgermyl)-1-(trimethylsilyl)ethylene (**8b**), and 1,1-bis(trimethylgermyl)ethylene (**8c**).

8a: yield 217 mg (63%); b.p. 120 °C (133 Torr, Kugelrohr) [7].

8b: yield 260 mg (60%); b.p. 60 °C (12 Torr, Kugelrohr) [7].

8c: yield 162 mg (31%); b.p. 100 °C (68 Torr, Kugelrohr) [7].

GLC yields of the products were determined relative to internal standard (trans-decaline).

[(Dimethylamino)methyl]trimethylgermane (5b) [6]

Chlorotrimethylgermane (9.88 g, 50 mmol) was added to a mixture of finely cut lithium (1.39 g, 200 mmol), HMPA (35.84 g, 200 mmol) and THF (80 ml). The mixture was stirred for 8 h at room temperature. A solution of trimethylgermyllithium thus prepared was added dropwise to a solution of phenyl (dimethylamino)-methyl sulfide (8.36 g, 50 mmol) in THF (50 ml) at 6–10 ° C. After 15 h of stirring, the mixture was added to ice-water and extracted with ether. The ether layer was extracted with 10% HCl. The acid extract was neutralized and extracted with ether. The extract was dried, concentrated, and distilled to give **5b** (4.02 g, 46%); b.p. 123–124 ° C; ^{1}H NMR ($CDCl_3$): δ 0.21 (9H, s, CH_3Ge), 2.18 (2H, s, CH_2), 2.32 (6H, s, NCH_3).

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