

A simple synthesis of B-2-(1-trimethylgermyl-1-alkyl)-1,3,2-dioxaborinanes. Isolation and selective oxidation to 1-trimethylgermyl-1-alkanols

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Abstract—(Z)-1-Trimethylgermyl-1-alkenes easily prepared by the hydroboration of the corresponding 1-trimethylgermyl-1-alkynes followed by protonolysis with acetic acid, readily react with dichloroborane–dioxane complex in dichloromethane for 6 h. The resulting solution is then treated with 1,3-propane diol in dichloromethane at 0 °C for half an hour to provide the corresponding *gem*-dimetalloalkanes containing boron and germanium. These α -trimethylgermylalkylboronate esters are purified by vacuum distillation in high yields (72–82%) and the structures of these novel intermediates are further confirmed by selective oxidation with alkaline hydrogen peroxide to provide the corresponding alcohols containing α -trimethylgermyl group in very good yields (74–84%).

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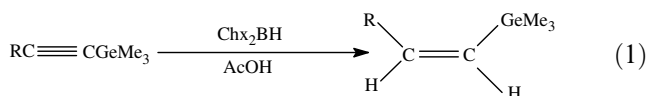
1. Introduction

Hydroboration of 1-trimethylgermyl-1-alkynes with dicyclohexylborane¹ was recently reported in the literature. The protonolysis of the resulting boron intermediates with acetic acid² provided the corresponding (Z)-1-trimethylgermyl-1-alkenes in high stereochemical purities. Different *gem*-dimetalloalkanes containing aluminum and zirconium,³ zinc and zirconium,⁴ zinc and magnesium,⁵ zinc and lithium,⁵ zinc and boron,⁶ copper and boron,⁶ boron and lithium,⁷ and boron and zirconium⁸ have been reported in the literature. Pelter and co-workers have reported an example of *gem*-dimetalloalkane containing boron and silicon.⁹ Literature search revealed that no truly general simple synthetic procedures were available to prepare *gem*-dimetalloalkanes containing boron and germanium. Consequently, we undertook a methodology involving (Z)-1-trimethylgermyl-1-alkenes via the hydroboration–alcoholysis sequence to achieve the synthesis of *gem*-dimetalloalkanes containing boron and germanium. In this report, we reveal the results of our investigation.

2. Results and discussion

We reacted terminal alkynes with *n*-butyllithium at –78 °C for 1 h followed by treatment with trimethylgermanium bromide at –78 °C for 1 h and allowed the reaction mixture to stir overnight. The resulting 1-trimethylgermyl-1-alkynes were isolated and kept in refrigerator under nitrogen atmosphere for further use. They were characterized by 300 MHz NMR spectral data.

The hydroboration of 1-trimethylgermyl-1-alkynes with dicyclohexylborane¹⁰ (freshly prepared by mixing cyclohexene with borane–methyl sulfide complex) in tetrahydrofuran proceeded cleanly at 0 °C, for 3 h followed by stirring for 1 h at room temperature. The resulting clear solution was treated with acetic acid and the stirring continued for 6 h at room temperature. The solvents were removed and replaced by *n*-pentane. Monoethanolamine¹¹ was added to remove the boron by-product. Representative (Z)-1-trimethylgermyl-1-alkenes (Table 1) were prepared (Eq. 1) and characterized by 300 MHz NMR data.



Keyword: Trimethylgermyl.

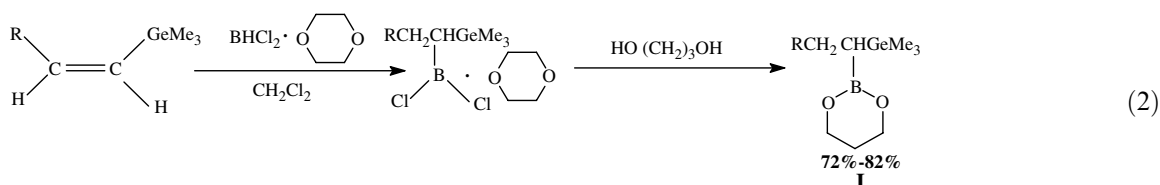
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Table 1. Synthesis of 1-trimethylgermyl-1-alkenes

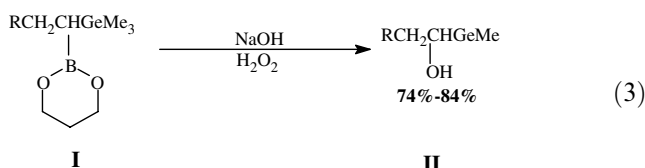
No.	R = (Eq. 1)	Yield ^a (%)
1	<i>n</i> -C ₄ H ₉	84
2	<i>n</i> -C ₅ H ₁₁	80
3	<i>n</i> -C ₆ H ₁₃	86
4	–(CH ₂) ₃ Cl	78
5	–C(CH ₃) ₃	76
6	–CH ₂ CH ₂ CH(CH ₃) ₂	79

^a All of the reactions were carried out on a 50 mmol scale. The compounds were purified by chromatography over alumina followed by vacuum distillation.

The (*Z*)-1-trimethylsilyl-1-alkenes thus prepared were subjected to hydroboration with dichloroborane–dioxane complex¹² in dichloromethane at room temperature for 6 h. The resulting solution was reacted with 1,3-propane diol in dichloromethane at 0 °C for half an hour. The supernatant solution was removed by double-ended needle technique and the solvents were pumped off and the resulting liquids were purified by high vacuum distillation. The representative selection of *gem*-dimetalloalkanes was prepared¹³ (Table 2, Eq. 2) using the above procedure.



These novel *gem*-dimetalloalkanes containing boron and germanium were reacted with alkaline hydrogen peroxide at room temperature for 4 h and the resulting alcohols¹³ containing α -trimethylgermyl group (Eq. 3, Table 3) were purified by column chromatography over alumina.

**Table 2.** The synthesis of *gem*-dimetalloalkanes containing boron and germanium

No.	R = (Eq. 2)	Yield ^a (%)
1	<i>n</i> -C ₄ H ₉	80
2	<i>n</i> -C ₅ H ₁₁	82
3	<i>n</i> -C ₆ H ₁₃	80
4	–(CH ₂) ₃ Cl	72
5	–C(CH ₃) ₃	74
6	–CH ₂ CH ₂ CH(CH ₃) ₂	76

^a All of the reactions were carried out on a 10 mmol scale. The compounds were purified by vacuum distillation. The carbon skeletons present in these compounds were confirmed by selective oxidation to alcohols containing α -trimethylgermyl group (Eq. 3).

Table 3. The synthesis of α -trimethylgermyl-1-alkanols

No.	R = (Eq. 3)	Yield ^a (%)
1	<i>n</i> -C ₄ H ₉	84
2	<i>n</i> -C ₅ H ₁₁	82
3	<i>n</i> -C ₆ H ₁₃	84
4	–(CH ₂) ₃ Cl	76
5	–C(CH ₃) ₃	80
6	–CH ₂ CH ₂ CH(CH ₃) ₂	74

^a All of the reactions were carried out on a 10 mmol scale. The compounds were purified by column chromatography over alumina.

3. Conclusions

In summation, we have developed for the first time a simple, and efficient conversion of 1-trimethylgermyl-1-alkynes into the corresponding *gem*-dimetalloalkanes containing boron and germanium in high yields. These *gem*-dimetalloalkanes were isolated and characterized using 300 MHz NMR spectral data for the first time. The carbon skeletons present in these intermediates are further confirmed by selective oxidation studies with alkaline hydrogen peroxide to provide the corresponding alcohols containing α -trimethylgermyl group. We

are presently utilizing these valuable compounds for further synthetic transformations.

Acknowledgements

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References and notes

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13. The preparation of B-2-(1-trimethylgermyl-1-hexyl)-1,3,2-dioxaborinane and 1-trimethylgermyl-1-hexanol is representative: In an oven dried 100 mL side-arm round bottom flask equipped with a septum inlet was placed (Z)-1-trimethylgermyl-1-hexene (10 mmol, 2.0 g) under nitrogen atmosphere. It was cooled to 0 °C and the dichloroborane–dioxane complex (3 M solution, 10 mmol, 3.3 mL) in methylene chloride was added dropwise. The resulting mixture was stirred for 1 h at 0 °C followed by 6 h at room temperature. The reaction mixture was cooled to 0 °C. To this cooled solution was added 1,3-propane diol (10 mmol, 0.76 g) dropwise and the resulting reaction mixture was stirred at 0 °C for 0.5 h. The methylene chloride layer containing the desired product was separated and the solvent was removed to provide the B-2-(1-tri-

methylgermyl-1-hexyl)-1,3,2-dioxaborinane in 80% (2.29 g) yield. The NMR spectral data indicated that the compound was the desired product. PMR (CDCl₃/without TMS): δ –0.03 (9H, s), 0.74–1.77 (14H, m), and 3.86 (4H, m), CMR (CDCl₃/without TMS): δ –1.25, 13.95, 14.03, 22.58, 25.40, 27.26, 27.43, 31.59, and 61.68 ppm. To a solution of B-2-(1-trimethylgermyl-1-hexyl)-1,3,2-dioxaborinane (10 mmol, 2.86 g) in tetrahydrofuran 10 mL) was added at 0 °C the sodium hydroxide (3 M, 5 mL) followed by 30% hydrogen peroxide slowly (25 mmol, 2.5 mL). The reaction mixture was allowed to come to room temperature and the stirring was continued for 4 h at room temperature. The compound was then extracted with ether (2 \times 25 mL) and the ether layer was washed with water (2 \times 10 mL). It was then dried over anhydrous sodium sulfate. The removal of the solvent followed by chromatography over alumina provided 1-trimethylgermyl-1-hexanol in 84% (1.83 g) isolated yield. The compound was characterized by NMR spectral data. The compound was characterized by spectral data. IR (neat): ν 3380 cm^{–1}, PMR (CDCl₃/without TMS): δ 0.20 (9H, s), 0.87 (3H, m), 1.23–1.90 (9H, m), and 03.74 (1H, s) ppm; CMR (CDCl₃/without TMS): δ –2.54, 14.12, 2.41, 25.24, 25.81, 34.14, and 65.85 ppm.