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A novel synthesis of (*Z*)-2-(1-trimethylgermyl-1-alkenyl)-1,3,2-dioxaborinanes and their conversion into carboxylic acids

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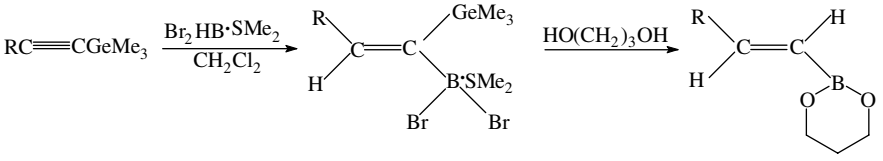
Abstract—A novel procedure for preparing heterocyclic compounds such as (*Z*)-2-(1-trimethylgermyl-1-alkenyl)-1,3,2-dioxaborinanes based on 1-trimethylgermyl-1-alkynes is described. 1-Trimethylgermyl-1-alkynes easily obtainable by deprotonation of 1-alkynes with *n*-butyllithium followed by treatment with trimethylgermanium chloride, are readily hydroborated in *n*-pentane in the presence of boron trichloride in hexane at 0 °C for 3 h. The resulting supernatant clear solution was separated from boron trichloride–methyl sulfide complex. It was then reacted with 1,3-propane diol at 0 °C for 0.5 h. The resulting representative (*Z*)-2-(1-trimethylgermyl-1-alkenyl)-1,3,2-dioxaborinanes were isolated in good yields (65–86%) and in high stereochemical purities (>98%) as evidenced by NMR spectral data. The carbon skeletons present in these intermediates were confirmed by alkaline hydrogen peroxide oxidation to the corresponding carboxylic acids.

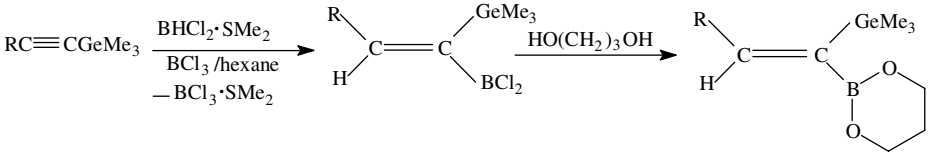
1. Introduction

The syntheses of stereodefined alkenyl *gem*-dimetallic[1–6] compounds are well documented in the literature. We wanted to undertake a stereospecific synthesis of an alkenyl *gem*-dimetallic compound such as the preparation of (*Z*)-2-(1-trimethylgermyl-1-alkenyl)-1,3,2-dioxaborinane via the hydroboration of 1-trimethylgermyl-1-alkyne with dibromoborane–methyl sulfide complex followed by the reaction with 1,3-propane diol. To our surprise, we obtained degermylated product (Eq. 1). Presumably, the hydrogen bromide generated caused the degermylated product.

Consequently, we explored a different procedure to prepare (*Z*)-2-(1-trimethylgermyl-1-alkenyl)-1,3,2-dioxaborinanes involving the hydroboration of 1-trimethylgermyl-1-alkynes with dichloroborane–methyl sulfide[7,8] complex in the presence of stoichiometric amount of boron trichloride in hexane followed by the reaction with 1,3-propane diol[9] (Eq. 2). We herein report the results of our investigation.



(1)



(2)

Keyword: Carboxylic acid.
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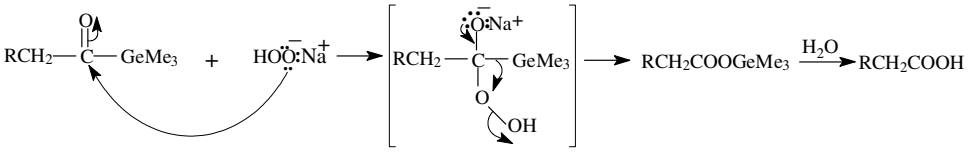
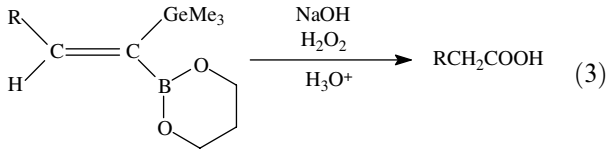


Scheme 1.

2. Results and discussions

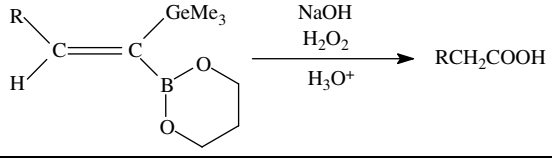
In a typical experiment,[10] 1-trimethylgermyl-1-hexyne was prepared by the deprotonation of 1-hexyne with *n*-butyllithium at −78 °C followed by treatment with trimethylgermanium bromide. It was then hydroborated with dichloroborane–methyl sulfide complex in the presence of stoichiometric amount of boron trichloride at 0 °C for 3 h. The product was isolated in 78% yield and characterized as (*Z*)-2-(1-trimethylgermyl-1-hexenyl)-1,3,2-dioxaborinane by NMR spectral data. Using the above procedure representative (*Z*)-2-(1-trimethylgermyl-1-alkenyl)-1,3,2-dioxaborinanes (Eq. 2) were prepared (see Table 1). The carbon skeletons present in these intermediates were confirmed by oxidation with alkaline hydrogen peroxide followed by acidification of the corresponding carboxylic acids[11] (Eq. 3, Table 1).



(3)

Most probably, the initial oxidation must have produced acylgermanes as intermediates. The conversion of these to the substituted acetic acids can be envisioned to involve nucleophilic addition of hydroperoxy anion to acylgermane followed by a rearrangement of germanium to oxygen and loss of hydroxide (Scheme 1). A similar mechanism has been proposed in the case of acylsilanes[12–14] undergoing oxidation to the carboxylic acids with alkaline hydrogen peroxide.

Table 1. The synthesis of (*Z*)-2-(1-trimethylgermyl-1-alkenyl)-1,3,2-dioxaborinanes and their conversion into carboxylic acids



No.	R =	Carboxylic acid	Yield[a] (%)
1	*n*-C_4H_9	*n*-C_4H_9	78
2	*n*-C_5H_{11}	*n*-C_5H_{11}	75
3	*n*-C_6H_{13}	*n*-C_6H_{13}	86
4	–$C(CH_3)_3$	–$C(CH_3)_3$	68
5	–$(CH_2)_3Cl$	–$(CH_2)_3Cl$	70
6	–Ph	–Ph	65

[a] All of the reactions were carried out on a 10 mmol scale. The yields are isolated yields of carboxylic acids based on the (*Z*)-2-(1-trimethylgermyl-1-alkenyl)-1,3,2-dioxaborinanes. The spectral data (^{1}H NMR and ^{13}C NMR) were consistent with the proposed carboxylic acids.

3. Conclusions

In summation, we have developed a novel method to prepare the (*Z*)-2-(1-trimethylgermyl-1-alkenyl)-1,3,2-dioxaborinanes for the first time based on 1-trimethylgermyl-1-alkynes in good yields. The carbon skeletons present in these heterocyclic compounds were confirmed by converting them into the corresponding carboxylic acids. We are currently exploring the synthetic versatility of these promising stereodefined alkenyl *gem*-dimetallic intermediates by converting them into a variety of products.

Acknowledgements

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10. The preparation of (*Z*)-2-(1-trimethylgermyl-1-hexenyl)-1,3,2-dioxaborinane is representative: In an oven dried 100 mL side-arm round bottom flask equipped with a septum inlet were placed 10 mL of *n*-pentane and 1-trimethylgermyl-1-hexyne (10 mmol, 1.99 g) under nitrogen atmosphere. The solution was cooled to 0 °C and the dichloroborane–methyl sulfide complex (10 mmol, 1.45 g) was added dropwise followed by a solution of boron trichloride in hexane (10 mmol, 10 mL, 1 M solution in hexane). The resulting mixture was stirred for 3 h at 0 °C followed by 1 h at room temperature. The supernatant solution was transferred to another 100 mL round bottom flask and the solution 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 hydrocarbon layer containing the desired product was separated and the solvent was removed to provide the (*Z*)-2-(1-trimethylgermyl-1-hexenyl)-1,3,2-dioxaborinane in 78% (2.20 g) yield. The ^{1}H

NMR and ^{13}C NMR spectral data indicated that the compound isolated is a crude product, which was not purified further. The ^{13}C NMR spectrum revealed a peak at δ 157.42 ppm characteristic of an olefinic carbon atom. The quaternary alkenyl carbon was not indicated in ^{13}C NMR spectrum. Had it been a mixture of *E*- and *Z*-isomers, we would have observed two peaks in the olefinic region of the ^{13}C NMR spectrum. Since the hydroboration is a *syn*-addition, we concluded that the double bond present in the compound has *Z*-configuration.

11. The preparation of *n*-hexanoic acid from the (*Z*)-2-(1-trimethylgermyl-1-hexenyl)-1,3,2-dioxaborinane is representative: To a solution of (*Z*)-2-(1-trimethylgermyl-1-hexenyl)-1,3,2-dioxaborinane (10 mmol, 2.85 g) in tetrahydrofuran (10 mL) was added 5 mL of methanol. It was then cooled to 0 °C and sodium hydroxide (3 M, 5 mL) was added followed by 30% hydrogen peroxide slowly (25 mmol, 2.5 mL). The reaction mixture was allowed to attain room temperature and the stirring was continued for 4 h at room temperature. An additional 5 mL of 3 M sodium hydroxide was added. The reaction mixture was washed twice with ether (2×30 mL). Acidification of the aqueous phase was performed with concentrated hydrochloric acid. It was then extracted with ether (2×30 mL) followed by the removal of ether provided *n*-hexanoic acid in 78% (0.90 g) isolated yield. The compound was characterized by IR, ^1H NMR, and ^{13}C NMR spectral data. IR (neat): <2926 and 1718 cm^{-1}; ^1H NMR ($CDCl_3$/without TMS): δ 0.8 (3H, m), 1.28–1.57 (6H, m), 2.30 (2H, m), and 11.75 (1H, s) ppm; ^{13}C NMR ($CDCl_3$/without TMS): δ 13.79, 22.31, 24.37, 31.24, 34.11, and 180.74 ppm.
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