# Reactivities of Triethylgermylborate in Methanol

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The reactivity of lithium (triethylgermyl)triphenylborate, prepared from unsolvated triethylgermyllithium and triphenylborane, with organic substrates in methanol was investigated. The germylborates reacted with organic halides and acyl halides to give the corresponding germyl-substituted compounds. From the reaction with carbonyl compounds, esters, carboxylic acid, alkenes, and alkynes, germylborates were completely recovered.

The group 14 element–alkali metal species as nucleophiles have been extensively studied in organic and organometallic syntheses, e.g., the introduction of group 14 elements into organic halides, metal halides, carbonyl compounds, etc.[1–3]

Very recently, our group reported the first successful isolation of lithium (triethylgermyl)triphenylborate (**1**), prepared from unsolvated triethylgermyllithium[4] and triphenylborane [5,6]

$$Et_3GeLi + Ph_3B \xrightarrow[\text{r.t., 24 h}]{\text{benzene/hexane}} \underset{\mathbf{1}}{[Et_3GeBPh_3]Li} \qquad (1)$$

The polymeric structure of germylborate **1** in the solid state was destroyed by addition of MeOH to give a dimeric structure of **1** with coordination of MeOH to the lithium atoms, $\{[Et_3GeBPh_3][Li(MeOH)]\}_2$ (**2**). The molecular structures of **1** and **2** were confirmed by X-ray diffraction analysis. We report herein some reactions of **2** with organic substrates in MeOH.

At first, the stability of the MeOH-coordinated germylborate **2** was examined in excess of degassed MeOH and $H_2O$. The germylborate **2** was very stable in excess degassed MeOH and $H_2O$ at room temperature for 1–4 days, and was completely recovered unreacted. The germylborate **2** did not change in degassed MeOH even at 50 °C for 10 h. The stability of **2** is may be explained by its planar four-membered ring composed of two lithium and two oxygen atoms.[5]

The displacement of halides and other groups from organic substrates by metalate anions represents one of the most important routes for the formation of metal–carbon $\sigma$ bonds. The reactions of **2** with simple alkyl halides and aromatic halides (RX) in MeOH solvent were carried out at room temperature for 4 days. Hydrolysis of the reaction mixture led to triethylgermyl-substituted products as major products together with some unidentified byproducts. All products were identified by comparing their NMR, GC–MS spectra, and retention times on GC with those of authentic samples. The results are summarized in Table 1.

$$\mathbf{2} + RX \xrightarrow[\text{r.t}]{\text{MeOH}} R\text{-}GeEt_3 + \text{other products} \qquad (2)$$

The yields of the products increased in the order of RCl < RBr < RI for the octyl halides and phenyl halides shown in Table 1. This order is consistent with the recognized reactivities of triethylgermyl–alkali metals in HMPA and the bond strength of the carbon–halogen bond.[7] The rest of **2** remained unreacted. The reaction of **2** with benzyl bromide afforded mainly benzyltriethylgermane in low yield. Several unidentified byproducts were also detected by GC–MS spectra.

No formation of coupling products derived by elecetron-transfer in the reactions of **2** with organic halides were detceted by GC.

**Table 1**. Reactions of **2** with organic halides in MeOH

| RX | Conditions | Products, Yields/%[a] |
|---|---|---|
| $C_8H_{17}Cl$ | r.t., 4 d | $C_8H_{17}GeEt_3$ (17) |
| $C_8H_{17}Br$ | r.t., 4 d | $C_8H_{17}GeEt_3$ (31) |
| $C_8H_{17}I$ | r.t., 4 d | $C_8H_{17}GeEt_3$ (98) |
| PhCl | r.t., 4 d | $PhGeEt_3$ (9) |
| PhBr | r.t., 4 d | $PhGeEt_3$ (38) |
| PhI | r.t., 4 d | $PhGeEt_3$ (90) |
| $PhCH_2Br$ | r.t., 4 d | $PhCH_2GeEt_3$ (40) |

[a] Yields were determined by GC and NMR.

With acyl chlorides, the germylborate **2** in MeOH at room temperature for 2 days gave the corresponding triethylgermyl ketones as the sole product in high yields.[8]

$$\mathbf{2} + RCOCl \xrightarrow[\text{r.t}]{\text{MeOH}} RCOGeEt_3 \qquad (3)$$

The results of the reactions of **2** with various acyl chlorides (RCOCl) in MeOH are summarized in Table 2.

**Table 2**. Reactions of **2** with acyl chlorides (RCOCl) in MeOH

| RCOCl | Conditions | Products, Yields/%[a] |
|---|---|---|
| t-BuCOCl | r.t., 2 d | $t\text{-}BuCOGeEt_3$ (> 95) |
| $C_6H_5COCl$ | r.t., 2 d | $C_6H_5COGeEt_3$ (> 95) |
| $p\text{-}MeC_6H_4COCl$ | r.t., 2 d | $p\text{-}MeC_6H_4COGeEt_3$ (> 95) |
| $p\text{-}MeOC_6H_4COCl$ | r.t., 2 d | $p\text{-}MeOC_6H_4COGeEt_3$ (>95) |

[a] Yields were determined by NMR.

The MeOH-coordinated germylborate **2** smoothly reacted with trimethylacetyl chloride and aroyl chlorides in MeOH to give the corresponding germylketones, respectively, in high yields shown in Table 2. These germylketones are commonly yellow, which were purified by rapid column chromatographic separation (silica gel, hexane/ether) and were identified by NMR and GC–MS spectra.

Representative methods of preparation of acylgermanes hitherto reported are (a) germylation of an acyl anion equivalent based on dithiane compounds followed by hydrolysis,[9,10] (b) germylation of metalated enol ethers,[11] (c) direct carbonylation by germyl–lithiums,[12] (d) Pd-catalyzed germylation of acyl halides,[13] (e) germylation of acyl chlorides by germylcuprates,[14–16] (f) hydrolysis of $\alpha$-chloro ethers.[17] However, these reactions involve strongly reducing conditions, oxidation procedures, or severe reaction conditions. The germylborate **2** is a very useful reagent of germylation of acyl halides in MeOH solvent.

The reactions of the MeOH-coordinated germylborate as nucleophiles with carbonyl compounds, esters, carboxylic acid and carbon–carbon multiple bonds were also examined. The reaction of MeOH-coordinated germylborate **2** with 3-pentanone in MeOH did not occur at 50 °C for 6 h, and remained unreacted. To the MeOH solution of **2** was added benzophenone under similar reaction conditions. The color of the solution turned to yellow, but the germylborate **2** was mostly recovered. The observed color may arise from a charge-transfer interaction of the σ HOMO of germylborate and the LUMO of carbony compound.

$$\mathbf{2} + \mathrm{R_2CO} \;\not\xrightarrow[50\ ^{\circ}\mathrm{C}]{\mathrm{MeOH}}\; \text{no reaction} \qquad (4)$$

The reaction of **2** with acetic acid in MeOH did not proceed at room temperature for 4 days and recovered unreacted. With methyl acetate the germylborate **2** in MeOH under similar reaction conditions did not change.

The germylborate **2** in MeOH proved to be unreactive toward carbon–carbon multiple bonds. With 2,3-dimethyl-2-butene and 6-dodecyne under similar reaction conditions, the germylborate **2** recovered unreacted from the MeOH solutions. These results observed in MeOH are in marked contrast to those in the reactions of triethylgermyllithium with carbonyl compounds, esters, alkenes, and alkynes in HMPA.[2] It is well known that the germyllithium in HMPA reacts with carbonyl compounds, esters, alkenes, and alkynes to give the corresponding germyl-substituted products.[1]

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