

THE REACTION OF TETRAMETHYLSILANE WITH BORON TRIBROMIDE

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Abstract. The reaction of tetramethylsilane with boron tribromide in deuteriochloroform in ambient temperature or at 40°C led to bromotrimethylsilane (3) and to dibromomethylborane (4). Identity of products was confirmed by NMR spectroscopy. Analogical reaction carried out in 1,3-dichloropropane allowed to separate products of the reaction and to obtain them in 68% and 59% yields respectively.

Key words: Tetramethylsilane, boron tribromide, bromine replacement, dibromomethylborane

Tetramethylsilane is known as a stable compound and for this reason this reagent is commonly used as an internal reference in NMR spectroscopy. However, there are some examples of its reaction catalysed by aluminium chloride^{1,2} to give chlorotrimethylsilane.

The analogue of tetramethylsilane – tetramethylstannane reacts more easily with halogenating agents. Some papers have been published, which described various aspects of its reaction with boron tribromide, which gave dibromomethylborane.³⁻⁵ Aryltrimethylstannanes were claimed to react with boron trichloride to yield dichloromethylborane.^{6,7} The synthesis of dibromomethylborane from silyl compound was reported only once from boron tribromide and tris-(trimethylsilyl)amine.⁸

To our best knowledge, there are no examples for the reaction between tetramethylsilane and boron trihalide. Literature reports some successful attempts of the reaction between aryltrimethylsilanes^{9,10} or vinyltrialkylsilanes¹¹ and boron trihalides to give aryl- or vinylhaloboranes respectively.

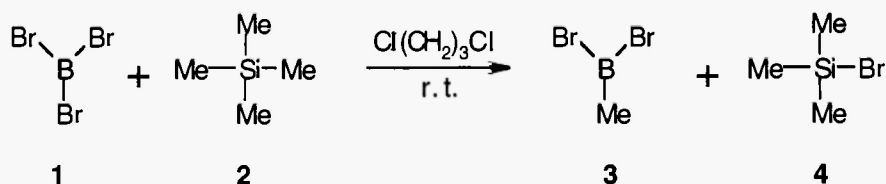
In this paper, we would like to report the first example of the reaction between tetramethylsilane and boron tribromide providing bromotrimethylsilane (4) and dibromomethylborane (3) in fair yields. The reaction is a possible new method for synthesis of dibromomethylborane.

The reaction between tetramethylsilane (1) and boron tribromide (2) was carried out directly in the NMR tube in deuteriochloroform at room temperature for several days. After a one day of storage, NMR analysis showed the formation of two new compounds and, after 5 days, the reaction was complete. ¹H NMR signals appeared at δ_H=0.58 and -2.8 ppm, ¹³C NMR - at δ_C=4.13 and (-0.62) ppm. ¹¹B NMR and ²⁹Si NMR gave resonances at δ_B=62.95 ppm and at δ_{Si}=27.2 ppm respectively.

These data allowed to characterize products formed. According to Ralph and Landucci¹² as well as to an NMR data compilation¹⁴, bromotrimethylsilane 3 gives ¹H NMR signal at δ_H=0.58 ppm, ²⁹Si NMR signal at δ_{Si}=26.5 ppm, ¹³C NMR shift value is quoted^{11,13} to occur at δ_C=4.6 ppm.

Our NMR measurements of post-reaction mixture showed δ_H=0.58 ppm, δ_{Si}=27.2 ppm and δ_C=4.13 ppm, so values so close to published observations that they show undoubtedly that one of two products is bromotrimethylsilane 3.

The second compound, which in our opinion is dibromomethylborane 4, gave a ¹H NMR signal at δ_H= -2.9 ppm, ¹³C NMR signal at δ_C= -0.62 ppm and a ¹¹B NMR resonance occurred at δ_B= 62.95 ppm.



Scheme 1

A compilation¹⁵ as well as Nöth *et al*⁴ quoted a ¹¹B NMR chemical shift δ_B= 62.5 ppm, which fits perfectly with our observation. Some disagreement with literature data appeared in the case of the ¹H NMR resonance, which according to Nöth⁴ appears at δ_H= -1.42 ppm in CCl₄. Our measurements were performed in

deuteriochloroform and this might be a reason for the difference observed. As for ^{13}C NMR, we found no data in the literature for carbon chemical shift of dibromomethylborane.

When the reaction was carried out at 40°C, it was completed within 36 hours. Products were separated by fractional distillation, but as boiling points of deuteriochloroform (bp=60.9°C)¹⁶ and dibromomethylborane (bp=58-60°C)⁸ are very close, we obtained a mixture of these two compounds. Bromotrimethylsilane was isolated as the last fraction boiling at 79-81°C (lit¹⁶=79°C).

When the reaction was carried out in 1,3-dichloropropane, the separation of the products was much easier as the solvent boil at higher temperature. Dibromomethylborane was isolated by fractional distillation, collected at 59-61°C in 53% yield. Bromotrimethylsilane was isolated as above in 68% yield.

Yields are maybe not satisfactory, but the reaction provides useful reagents starting from cheap starting materials.

Experimental section

Deuteriochloroform (Merck), tetramethylsilane (Fluka) and boron tribromide (Aldrich) were used as received. 1,3-Dichloropropane was routinely distilled and dried prior to use. All NMR spectra were recorded on a Bruker 300 AC spectrometer.

Reaction between tetramethylsilane (1) and boron tribromide (2) in deuteriochloroform

Tetramethylsilane (89 mg, 1 mmol) was dissolved in deuteriochloroform (3 mL) and then boron tribromide (25 mg, 1 mmol) was added. The reaction was stored for 5 days at room temperature or heated at 40°C for 36 hrs. The progress of the reaction was monitored by ^1H and ^{11}B NMR spectroscopy. The mixture was separated by distillation, first fraction was collected at 59-61°C. It was the solution of dibromomethylborane 4 and deuteriochloroform.

Reaction between tetramethylsilane (1) and boron tribromide (2) in 1,3-dichloropropane

Tetramethylsilane (89 mg, 1 mmol) was dissolved in 1,3-dichloropropane (3 mL) and then boron tribromide (25 mg, 1 mmol) was added. The mixture was stirred under nitrogen for 5 days. Then, the mixture was separated by fractional distillation. The first fraction was collected at 59-61°C and identified as dibromomethylborane 4. The second fraction, bromotrimethylsilane 3, was collected at 79-81°C.

Bromotrimethylsilane 3

Yield 68%. Bp. 79-81°C, lit¹⁶ 79°C, n_D^{20} =1.4235, lit¹⁶ 1.4240.

^1H NMR (300 MHz, CDCl_3): δ 0.52 (CH_3). ^{13}C NMR (75 MHz, CDCl_3): δ 4.13 (CH_3). ^{29}Si NMR (59 MHz, CDCl_3): δ 27.3.

Dibromomethylborane 4.

Yield 59%. Bp. 59-61°C, lit⁸ 58-60°C. ^1H NMR (300 MHz, CDCl_3): δ -2.9 (CH_3). ^{13}C NMR (75 MHz, CDCl_3): δ -0.62 (CH_3). ^{11}B NMR (96 MHz, CDCl_3): δ 62.95.

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