

A Facile High-Yield Synthesis and Purification of Tetrabutylammonium Tetrabutylborate

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The compound tetrabutylammonium tetrabutylborate has a long history of use in several areas of chemistry,¹ and particularly in studies of the thermodynamics of ion solvation.² Until very recently this compound was commercially available, albeit from a single source. Presently there are no commercial sources for tetrabutylammonium tetrabutylborate. Our search of the literature turned up only a single, low-yield (<10%) synthesis for the compound.³ In addition difficulties in its purification have been reported, and literature melting points for the pure compound range from 109.5 °C⁴ to 110.6–112.0 °C.³

We have prepared tetrabutylammonium tetrabutylborate in high yield by a modification and simplification of a procedure previously reported for related compounds.⁵ Lithium tetrabutylborate, made by reaction of *n*-butyllithium with tributylborane, was added to a solution of tetrabutylammonium bromide in water. After isolation of the precipitated product, recrystallization using various literature methods afforded material with correct NMR integrations. However, when this material was partitioned between aqueous and organic phases in preparation for thermodynamic studies, the aqueous phase was found to contain small amounts of a contaminating tetrabutylammonium salt, the anion of which gave no proton NMR signal. Repeated aqueous washings and recrystallizations failed to remove the contaminating material. TLC analysis on silica gel plates eluting with acetone/petroleum ether mixtures showed that the relatively nonpolar tetrabutylammonium tetrabutylborate eluted more rapidly than a fainter, contaminating compound which was significantly more polar. Accordingly, flash chromatography was used to afford tetrabutylammonium tetrabutylborate free of the contaminating material and which had a melting point after recrystallization of 112.5–113 °C. Multigram quantities of pure

tetrabutylammonium tetrabutylborate can easily and rapidly be obtained by this method.

Experimental Section

General Procedures. Reagents were obtained from commercial sources and used as received. Up to the point of combining the two water solutions, preparative steps were performed under a flow of anhydrous nitrogen, but without special equipment to ensure inert atmosphere or extraordinary measures to exclude water. NMR analysis was performed with a Bruker ARX400 in *d*₆-acetone solutions; shifts are reported in parts per million downfield from internal Me₄Si. Melting points were obtained using a Mel-Temp capillary melting point apparatus and are uncorrected. Combustion analysis was performed by Atlantic Microlab, Inc., Norcross, GA, and is reported as percentages.

Synthesis and Purification. Under nitrogen, 0.15 mol of tributylborane (Aldrich, 1.0 M diethyl ether solution) was introduced into a large Schlenk flask, and 0.15 mol of *n*-butyllithium (Aldrich, 2.5M solution in hexane, diluted to 1.0 M with additional hexane) was added dropwise over 1 h. The solution became warm, but no precipitate was formed. When the addition was complete, the solvent was removed under vacuum until the total volume was below 100 mL. This concentrated solution was placed in a –40 °C freezer until a solid formed. Sufficient hexane was added to this solid in order to form a slurry, and the wet product (lithium tetrabutylborate) was then warmed gently under vacuum as solvent was removed to near dryness. When the product had formed a thick slurry coating the walls of the flask, after drying for about 2 h, 150 mL of degassed water was added (distilled, deionized water was purged with nitrogen for 30 min). The product dissolved readily in the water, forming a cloudy solution. A separate aqueous solution of tetrabutylammonium bromide (Aldrich) was prepared under normal atmosphere (0.15 mol in 40 mL of water), and this was added all at once to the lithium tetrabutylborate. The addition produced an immediate and plentiful precipitate of the crude final product (tetrabutylammonium tetrabutylborate salt) which was then handled under normal atmosphere. The thick slurry which formed was shaken to ensure complete mixing, and the crude product was washed three times with 1 L of distilled water and dried under vacuum. The yield of crude, dry product was 65.0 g, 89.9%. Observance of yellow color in the dried product indicates inadequate water washing. The dried product was recrystallized from isopropyl ether using the method of Fuchs et al.³ The product was in the form of small, crystalline needles with a melting point of 110.5–111 °C. This product was purified by flash chromatography on silica gel (EM Scientific, 230–400 mesh), eluting with 30% acetone/petroleum ether. Separation of pure product from a tetrabutylammonium salt impurity was observed by TLC and confirmed by NMR analysis of fractions collected from the column. Fractions containing the product were combined for removal of solvent by rotary evaporation. The product was dried under vacuum and recrystallized from isopropyl ether, yielding colorless crystalline needles 0.5–2 cm long. These were dried under vacuum and had a melting point of 112.5–113 °C. Overall yield is 67%. ¹H NMR (acetone-*d*₆) δ –0.02 (m, 2H), 0.83 (t, *J* = 8.8 Hz, 3H), 0.99 (t, *J* = 8.8 Hz, 3H), 1.17 (m, 4H), 1.44 (m, 2H), 1.84 (m, 2H), 3.46 (m, 2H). Anal. Calcd for C₃₂H₇₂NB: C, 79.78; H, 15.06; N, 2.91. Found: C, 79.94; H, 15.11; N, 3.01.

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