Syntheses and Properties of Molten Tetraalkylammonium Tetraalkylborides

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Eight tetraalkylammonium tetraalkyborides have been prepared on a large scale from the corresponding tetraalkylammonium bromides and lithium tetraalkylborides. All melt at <50°, are miscible with most organic materials, and are sufficiently stable to heat, light, oxygen, and water to permit their use as solvents. Their completely filled valence shells of electrons prevent acid–base interactions with each other or with solutes, but their ionic character gives them polarities comparable to many polar organic solvents.

Most investigations of molten salts have concentrated on the thermodynamic, electrochemical, and spectroscopic properties and synthetic uses of inorganic materials.[1] Although the high temperature and ionic nature of fused inorganic salts limit their use as solvents for organic compounds, some organic reactions have been carried out in fused alkali hydroxides, bromides, chlorides, acetates, and thiocyanates.[2,3] Molten tetraalkylammonium salts have shown more promise than fused salts of metals as solvents for organic compounds because of their lower melting points and polarities.[3] Particularly notable are the aromatic substitutions and oxidations in tetraalkylammonium nitrates,[3,4] homogeneous catalysis of olefin hydrogenation and carbonylation in tetraalkylammonium trichlorogermanates and trichlorostannates,[5] solvolysis of *tert*-butyl chloride and electrochemical reductions in tetra-*n*-hexylammonium benzoate hemihydrate,[6] and electrochemical reduction of benzalaniline in tetraethylammonium *p*-toluenesulfonate.[7]

Relative to tetraalkylammonium salts little is known about tetraalkylborides.[8] Isolated reports of lithium and sodium tetraalkylborides[9] preceded the first tetraalkylammonium tetraalkylborides.[10] Damico[10a] found that some tetramethylammonium tetraalkylborides have low melting points (<25 to 112°) and are moderately stable in air. Tetramethylammonium tetra-*n*-butylboride is completely stable in water at pH 10 and 35° for 16 hr but hydrolyzes readily in 20% acetic acid at 60°.[10a] Lithium tetraalkylborides behave similarly in aqueous acid and base but decompose in air.[10a] However, sodium tetraethylboride is reported to be stable in air.[9a] Lithium tetraalkylborides react as hydride donors with alkylating agents.[9e,11] More recent reports of lithium and tetraalkylammonium tetraalkylborides have confirmed the earlier observations of their properties.[12]

The results of Damico[10a] suggested to us that tetraalkylammonium tetraalkylborides which are fluid at or near room temperature might be suitable solvents for organic compounds. As solvents they would possess unique properties. They are ionic, yet less polar than other molten salts because of their alkyl groups; they cannot interact with solutes or with each other as Lewis acids or bases; and they permit only electrostatic, ion dipole, ion-induced dipole, and dispersion forces. Potential obstacles to their use as solvents might be their instability in acids, possible instability in air, thermal decomposition, and other unforseen chemical reactions of tetraalkylboride ions. Tetraalkylammonium ions in general are stable to all but very strong bases at <100°.[13] In this paper we describe an efficient method for preparation of molten tetraalkylammonium tetraalkylborides for use as solvents.

Results and Discussion

The key to obtaining low-melting tetraalkylammonium tetraalkylborides is the attachment of at least one relatively long alkyl chain to either nitrogen or boron; every such compound we have prepared has melted at <50°. Our general synthetic approach, illustrated in eq 1–3 with $N_{2226}B_{2226}$,[14] is the same one

$$(C_2H_5)_3N + n\text{-}C_6H_{13}Br \longrightarrow N_{2226}Br \qquad (1)$$

$$(C_2H_5)_3B + n\text{-}C_6H_{13}Li \xrightarrow{\text{hexane}} LiB_{2226} \qquad (2)$$

$$N_{2226}Br + LiB_{2226} \xrightarrow{H_2O} N_{2226}B_{2226} + LiBr \qquad (3)$$

used previously.[10] Detailed methods for preparation of eight different salts which are molten at ≤50° appear in the Experimental Section.

By design our molten tetraalkylammonium tetraalkylborides are highly resistant to crystallization. They usually form glasses when cooled to −78°.

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(14) Subscripts refer to the number of carbon atoms in the *n*-alkyl groups.

Instead of purifying the final products we have carried out the syntheses by techniques that exclude the most likely impurities. A variety of tests suggest that they are sufficiently pure for many uses as solvents. They exhibit only end absorption in the ultraviolet. They have correct peak areas and contain no noticeable impurities by pmr spectroscopy. They give reasonable elemental analyses. A limited number of samples tested for lithium and halogens contained ≤ 0.02 ppm lithium and ≤ 0.1 ppm halogen. The most sensitive test of their purity found by us is absorption of visible light. After exposure to air for days to months our tetraalkylammonium tetraalkylborides develop a yellow color due to an absorption maximum at *ca.* 365 nm (in ethanol). These pale yellow samples have pmr and ir spectra and microanalyses indistinguishable from those of the original colorless samples. After extended autoxidation, however, the molten salts become darker and less viscous, and in their ir spectra new peaks appear at 2410 (B–H stretch) and 1565 cm^{-1}, and the strong sharp peak at 1095 cm^{-1} (B–C stretch of tetraalkylboride) disappears.[10a,15] Also new broad peaks appear in their pmr spectra at δ 5–6.

The rate at which tetraalkylammonium tetraalkylborides decompose in air varies greatly from one preparation to the next. Preparations carried out in an inert atmosphere with argon-purged solvents give samples which require months for discoloration in air, but slight exposure to air during preparation at the lithium tetraalkylboride stage leads to molten salts which discolor in air in just a few hours. We suspect that tetraalkylammonium tetraalkylborides of higher purity than we have yet obtained would be indefinitely stable in air, and that the decompositions observed by us are initiated by a trace impurity of some peroxy boron compound. Trialkylboranes autoxidize extremely fast *via* a radical chain sequence in which one propagation step is addition of molecular oxygen to the boron atom,[16] but we see no reason why tetravalent boron should react rapidly with oxygen. The decomposition of tetraalkylborides most likely begins by loss of a hydrogen atom from the α or β carbon. Unless the lithium ion plays a role in their decomposition, lithium tetraalkylborides should be as stable in the presence of oxygen as their tetraalkylammonium counterparts. However, we have confirmed Damico's[10a] observation that the lithium tetraalkylborides decompose readily in air. Perhaps most or all of the impurities responsible for initiating decomposition are removed during conversion of the lithium to the tetraalkylammonium tetraalkylborides.

Tetraalkylammonium tetraalkylborides are remarkably stable to light and heat. A sample of $N_{2222}B_{4448}$ in a Pyrex tube showed no visible change after standing for 6 months in direct contact with a 20-W fluorescent lamp. Samples of $N_{1116}B_{1116}$, $N_{2226}B_{2226}$, $N_{3333}B_{3336}$, and $N_{4446}B_{4446}$ in sealed tubes showed no change in their color or pmr spectra after 60 min at 200°.

Our tetraalkylammonium tetraalkylborides are not appreciably soluble in water or aliphatic hydrocarbons, but they are miscible in all proportions with many organic solvents ranging in polarity from benzene to methanol. $N_{2226}B_{2226}$ can be stirred and poured readily at room temperature, but the others are substantially more viscous. $N_{2226}B_{2226}$ is too viscous for high-resolution pmr spectra at 25° but not at 50°, while $N_{4446}B_{4446}$ requires heating to *ca.* 90° to give pmr spectra that do not suffer from viscosity broadening. The densities of three molten tetraalkylammonium tetraalkylborides studied by Grindley and Lind[12c] lie in the range of 0.77–0.80 g/ml at 90–160°, and the density of $N_{2226}B_{2226}$ varies from 0.836 g/ml at 22° to 0.819 g/ml at 65°.

In conclusion, molten tetraalkylammonium tetraalkylborides are suitable for use as solvents which are chemically different from any solvents ever used before. Some are sufficiently low melting and nonpolar to permit organic molten salt chemistry at room temperature. All are reasonably stable to heat, light, oxygen, and water and are miscible with a wide variety of organic materials. In subsequent papers we plan to report uses of these new molten salt solvents.

Experimental Section[17]

General.—Melting points were obtained with a calibrated Du Pont Model 900 thermal analyzer. Pmr spectra were obtained with Varian A-60A, A-56/60, and HA-100 instruments. Uv-visible spectra were obtained with a Cary 14 spectrophotometer. Ir spectra were obtained with Perkin-Elmer Model 137 and 237B instruments. The Vacuum Atmospheres Corp. drybox was argon filled and fitted with a dry train described earlier.[18] Microanalyses were performed by J. Nemeth and associates.

Materials.—Hexane and pentane were washed with concentrated sulfuric acid, dried over potassium hydroxide, and distilled from calcium hydride. All other solvents were reagent grade and were used as obtained. Triethylamine, tri-*n*-propylamine, and tri-*n*-butylamine were washed with acetic anhydride and distilled from barium oxide. Tetraethylammonium bromide and tetra-*n*-propylammonium bromide were recrystallized twice from chloroform–diethyl ether. Tetra-*n*-butylammonium iodide was recrystallized twice from methanol–water. 1-Bromohexane, 1-chlorohexane, and 1-chlorooctane were freshly distilled from calcium hydride. Triethylborane and tri-*n*-butylborane (both from Callery Chemical Co.) were distilled shortly before use under argon at 760 and 2 Torr, respectively. Tri-*n*-propylborane was prepared by reaction of *n*-propylmagnesium bromide with boron trifluoride etherate[19] and was vacuum distilled. *Caution: All of these trialkylboranes burn spontaneously in air.* All other reagents were obtained commercially and used without further purification.

Trimethyl-*n*-hexylammonium Bromide.—A mixture of 0.50 mol of 1-bromohexane, 100 ml of petroleum ether (bp 30–60°), and excess trimethylamine was held in a flask equipped with a Dry Ice condenser at 25° by day and at −10° by night for 10 days. Periodic additions used a total of 2.5 mol of trimethylamine. The resulting white solid was recrystallized from acetone to give 0.295 mol of $N_{1116}Br$, mp 186° (lit.[20] mp 186°).

Triethyl-*n*-hexylammonium Bromide.—A mixture of 0.50 mol of 1-bromohexane, 0.50 mol of triethylamine, and 75 ml of acetonitrile was refluxed for 24 hr. Removal of solvent under vacuum left a pale pink solid which was recrystallized from acetone–ethyl acetate to give 0.464 mol of white $N_{2226}Br$, mp 108° (lit.[21] mp 103.0–104.0°).

Tri-*n*-butyl-*n*-hexylammonium Bromide.—A mixture of 0.50 mol of 1-bromohexane, 0.50 mol of tri-*n*-butylamine, and 100 ml

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[17] All new compounds had satisfactory elemental analyses for C, H, and N except when specifically noted. The microanalytical data are compiled in a supplement to this paper prepared for the microfilm edition. See paragraph at end of paper regarding supplementary material.

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of ethyl acetate was refluxed for 86.5 hr. Removal of solvent under vacuum left a colorless oil which deposited white crystals after 2 months of storage at −20°. Three recrystallizations from chloroform–ether gave 0.245 mol of $N_{4446}Br$, mp 52°, which did not change with further recrystallization. However, microanalyses for C, H, and N failed to conform to calculated values.

***n*-Hexyllithium in Hexane.**—Small segments of lithium wire (30.5 g, 4.40 g-atoms) were washed with hexane under argon and placed with 100 ml of hexane in an argon-filled flask fitted with mechanical stirrer and addition funnel. A solution of 1.26 mol of 1-chlorohexane in 250 ml of hexane was added with stirring over 3 hr at −10°. The mixture was allowed to warm to room temperature, stirred overnight, and transferred to the drybox, where it was filtered into 250-ml bottles for storage. Titration with 2-butanol in xylene and 1,10-phenanthroline as indicator[22] gave a carbon-bound lithium concentration of 1.05 *M* and a yield of 38%.

***n*-Octyllithium in Hexane.**—Lithium dispersion (1.48 g-atoms) was washed with benzene and hexane in an argon atmosphere. To the stirred dispersion 0.60 mol of 1-chlorooctane in 250 ml of hexane was added over 2 hr at room temperature. The solution was filtered and stored under argon. It was 0.61 *M* in carbon-bound lithium (25% yield) by a double titration analysis.[23] The method used for *n*-hexyllithium would probably also give a better yield of *n*-octyllithium.

General Method for Molten Salts. Triethyl-*n*-hexylammonium Triethyl-*n*-hexylboride.—All glassware was dried at 120° for at least 12 hr. All solvents were purged with a vigorous flow of argon through a gas dispersion tube for at least 30 min immediately before use. All operations were carried out in an argon atmosphere either in the laboratory or in the drybox.

In a 2000-ml flask was placed 0.45 mol of *n*-hexyllithium in hexane, and a solution of 0.46 mol of triethylborane in 300 ml of hexane was added with stirring over 60 min at room temperature. After the triethylborane addition another 800 ml of hexane was added in several portions to prevent caking of the thick solid. The resulting suspension of LiB_{2226} was transferred to the drybox and washed with six 350-ml portions of hexane. The solid LiB_{2226} was removed from the drybox, dissolved in 300 ml of water, and washed with two 100-ml portions of hexane. A solution of 0.47 mol of $N_{2226}Br$ in 120 ml of water was added to the aqueous LiB_{2226} solution and mixed thoroughly. Two phases separated. The heavier aqueous phase was removed, and the lighter molten salt phase was washed with six 150-ml portions of water. The molten salt was dried at 10^{-5} Torr and 25° for 12 hr. Yield was 138.6 g of colorless liquid salt.

In some preparations washing of the lithium tetraalkylboride was performed in 250-ml centrifuge bottles by repeated cycles of centrifugation, removal of supernatant hexane solution, and agitation with fresh hexane. In some preparations the wet molten salt was filtered in acetone, benzene, or methanol solution.

Numerous preparations of impure molten salts early in this investigation taught us to (1) avoid contact of stopcock grease with molten salt, (2) carry out all operations under argon, (3) purge all solvents with argon to minimize any possible contact of intermediate solids and solutions with oxygen, and (4) avoid rubber serum caps and molecular sieves, which hasten discoloration of molten salts.

By this general method the following tetraalkylammonium tetraalkylborides were prepared in yields of 75–87%:[17] $N_{2222}B_{4446}$, liquid; $N_{2222}B_{4448}$, liquid; $N_{2226}B_{2226}$, liquid; $N_{2226}B_{4448}$, liquid; $N_{3333}B_{3336}$, liquid; $N_{3333}B_{4446}$, mp 14°; $N_{4446}B_{4446}$, mp 27°. Those designated as liquid formed glasses on cooling to −78° but never crystallized. All had pmr multiplets in acetonitrile at δ 2.8–3.4 (NCH_3 and NCH_2), −0.5 to 0.2 (BCH_3 and BCH_2), and 0.5–1.6 (all other CH_2 and CH_3 groups) which had correct relative areas for the assigned structures. All had ir absorption as neat films at 2930–2950, 2870–2910, 2760–2770, 1455–1480, 1070–1095, 1000–1010, and 780–785 cm^{-1}. These spectral properties are similar to those reported earlier[10a,12b] for lithium and tetraalkylammonium tetraalkylborides.

Trimethyl-*n*-hexylammonium Trimethyl-*n*-hexylboride.—The following preparation of trimethylborane is modified from the method of Brown.[19] A solution of methylmagnesium bromide was prepared from 1.00 g-atom of magnesium turnings and excess methyl bromide in 200 ml of di-*n*-butyl ether. The flask containing the methylmagnesium bromide was connected with flexible tubing to a second flask containing 0.100 mol of *n*-hexyllithium in hexane. The second flask was fitted with a Dry Ice condenser, mechanical stirrer, and Dry Ice jacket. A solution of 0.40 mol of boron trifluoride in 85 g of di-*n*-butyl ether was added over 40 min to the methylmagnesium bromide solution. The resulting trimethylborane was swept with a stream of argon into the −78° *n*-hexyllithium solution through a tube fixed below the liquid surface. After 60 min the slurry of LiB_{1116} in hexane was warmed to room temperature and converted by the general method to $N_{1116}B_{1116}$, mp 46°, 46% yield based on *n*-hexyllithium. Filtration of the $N_{1116}B_{1116}$ was carried out in methanol, and the methanol was removed at 5 Torr prior to drying under high vacuum. $N_{1116}B_{1116}$ is very hygroscopic; it did not give an acceptable microanalysis.

Lithium Content of Molten Salts.—A mixture of 0.5091 g of $N_{2222}B_{4448}$ was heated with 1.80 g of concentrated sulfuric acid and after cooling was diluted to 10.00 ml with water. Comparison to standard lithium chloride solutions by flame photometry[24] indicated that the $N_{2222}B_{4448}$ contained 4.4 × 10^{-5} *M* lithium. Similar analyses of $N_{2222}B_{4446}$ and $N_{2226}B_{2226}$ samples showed that they contained <4 × 10^{-5} *M* lithium.

Halogen Content of Molten Salts.—A sample of 0.9197 g of $N_{2226}B_{2226}$ and 6.208 g of a 50:50 (w/w) mixture of sodium and potassium hydroxide pellets were melted together in a nickel crucible and heated vigorously for 5 min. The flux was cooled, dissolved in water, acidified with 12 *M* nitric acid, and diluted to 50.0 ml. The halide content relative to standard sodium bromide solutions was determined by a standard mercuric thiocyanate–ferric ammonium sulfate spectrophotometric method[25] using as a blank a sample prepared from the same weight of sodium and potassium hydroxides but no $N_{2226}B_{2226}$. Halogen contents of molten salts determined by this method were $N_{2226}B_{2226}$, 1.42 × 10^{-4} *M*; $N_{3333}B_{4446}$, 9.3 × 10^{-4} *M*; and $N_{4446}B_{4446}$, 8.88 × 10^{-3} *M*. Note that the sodium–potassium hydroxide digestion results in detection of covalently bound halogen in addition to halide ions in the molten salts.

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Registry No.—$N_{2222}B_{4446}$, 41724-43-0; $N_{2222}B_{4448}$, 41724-44-1; $N_{2226}B_{2226}$, 41724-45-2; $N_{2226}B_{4448}$, 41724-46-3; $N_{3333}B_{3336}$, 41724-47-4; $N_{3333}B_{4446}$, 41724-48-5; $N_{4446}B_{4446}$, 41724-49-6; $N_{1116}B_{1116}$, 41724-50-9; $N_{1116}Br$, 2650-53-5; $N_{2226}Br$, 13028-71-2; $N_{2222}Br$, 71-91-0; $N_{3333}Br$, 1941-30-6; $N_{4446}Br$, 37026-90-7; triethylborane, 97-94-9; tri-*n*-butylborane, 122-56-5; tri-*n*-propylborane, 1116-61-6; trimethylborane, 593-90-8; 1-bromohexane, 111-25-1; trimethylamine, 75-50-3; triethylamine, 121-44-8; tri-*n*-butylamine, 102-82-9; *n*-hexyllithium, 21369-64-2; 1-chlorohexane, 544-10-5; *n*-octyllithium, 3314-49-6; 1-chlorooctane, 111-85-3.

Supplementary Material Available.—Microanalytical data will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20 × reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-73-3916.

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