Rapid Communication

CSIRO PUBLISHING

Aust. J. Chem. **2006**, *59*, 298–301

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Phosphonium-Based Ionic Liquids as Efficient Borane Carriers

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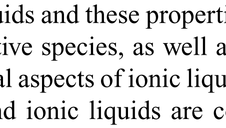
Phosphonium-based ionic liquids form new ionic liquids when treated with borane (BH_3), and these ionic liquids are useful for reduction reactions involving carbonyl compounds. Alane (AlH_3) reacts with the phosphonium cation, nevertheless the resulting solutions are capable of reducing esters to aldehydes. Phosphonium-based ionic liquids may serve as useful materials for reactive gas transport, and hence may serve as a fluid alternative to porous materials and may provide a convenient method of safely transporting boron hydrides for a variety of applications.

Manuscript received: 17 January 2006.
Final version: 27 April 2006.

Ionic liquids, and in particular imidazolium-based ionic liquids, have undergone extensive investigation for a myriad of applications over the last several years.[1–3] Studies examining quaternary phosphonium systems are much rarer, and this may reflect the fact that commercial supplies and convenient syntheses of these salts have only recently become available.[4,5] We have examined some of the chemistry of imidazolium ions and have shown that they are unsuitable for reactions involving active metals (i.e. Na or K)[6] or hydridic sources such as $[BH_4]^-$ and $[AlH_4]^-$.[7,8] The imidazolium ion is notoriously reactive at the C_2 hydrogen site,[9] and this reactivity can be a blessing[10] or a bane[11] depending on the reactions examined. Phosphonium-based ionic liquids, as shown in Fig. 1, are attractive since they are easily prepared, more robust, and thermally more stable than either quaternary ammonium or imidazolium salts.[4]

We have become interested in the materials aspects of ionic liquids and these properties include the ability to stabilize reactive species, as well as their fluid properties. More traditional aspects of ionic liquids include their solvent properties, and ionic liquids are considered to be among some of the 'greener' solvents.[1] The link between ionic liquids and green chemistry is largely due to their non-volatility, and yet they are still good solvents for many organic, inorganic, and metalloorganic compounds.[12,13] Perhaps of more importance are their non-flammability and their ability to act as a heat sink for strongly exothermic reactions.[14] Recently, we showed that phosphonium-based ionic liquids can support strong bases such as *N*-heterocyclic carbenes[6,15] and Grignard reagents,[16] and the stability of these basic compounds could be couched in kinetic arguments since access to the protic site of the phosphonium-based ionic liquids is difficult. Deprotonation of the phosphonium-based ionic liquid would lead to the formation of a phosphorane but this reaction was not observed. Hence, it seemed obvious that phosphonium-based ionic liquids would serve as an efficient carrier of hydriditic reagents, specifically borane (BH_3)[17] which is typically sold as an ethereal solution, most usually in tetrahydrofuran (THF). These solvents have the disadvantage of being flammable and volatile. Herein we report the synthesis of new phosphonium-based ionic liquid mixtures possessing borane hydride anions, and show their use in the reduction of aldehydes, ketones, and acid chlorides. We also show the reaction of AlH_3 with phosphonium-based ionic liquids leading to the decomposition of the phosphonium cation and the formation of a solution capable of reducing esters to aldehydes in good yields.



1 X = Cl
2 X = $C_9H_{19}CO_2$

Fig. 1. Selected phosphonium-based ionic liquids.

Commercially available phosphonium-based ionic liquids **1** and **2** were purified by washing the solvent with sodium bicarbonate solution and subsequent extraction with water and hexanes followed by drying by means of azeotropic distillation with toluene. Stable compounds, having the empirical formula $[R'_3RP][XBH_3]$, can be prepared either by passing gaseous B_2H_6 through the phosphonium-based ionic liquids[18,19] or by mixing one equivalent of $BH_3{\cdot}THF$ solution with the phosphonium-based ionic liquid followed by complete removal of the THF by exhaustive evacuation. These new ionic liquids are recyclable. After reduction and extraction of the products, the ionic liquids were purified by using the method described above, and these ionic liquids were

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reused for borane reduction of benzaldehyde to give 90% yield of benzyl alcohol.

Elemental analyses of the new ionic liquids are in accord with the expected values. Unambiguous assignment of the ^{1}H NMR signals in the new ionic liquid anion of **1**$\cdot$BH$_3$ and **2**$\cdot$BH$_3$ have not been made due to the complexity, overlap, and high intensity of the proton peaks in the phosphonium-based ionic liquids. The phosphonium-based ionic liquids **1**$\cdot$BH$_3$ and **2**$\cdot$BH$_3$ were also analyzed using ^{11}B NMR spectroscopy and these spectra generally exhibit broad resonances and interestingly a clear feature consistent with the presence of $[BH_4]^-$;[20] other peaks were not assigned. The IR spectra for the molecules exhibit peaks in the B–H stretching region (2000–2400 cm^{-1}). Specifically, the new phosphonium-based ionic liquid **1**$\cdot$BH$_3$ exhibits absorptions at 2037 (m), 2212 (m), and 2298 (s) cm^{-1} whereas **2**$\cdot$BH$_3$ exhibits peaks at 2139 (m), 2224 (m), and 2270 (s) cm^{-1}. The anion of **2** forms a new ionic liquid with BH$_3$ showing a shift in the carboxylate stretch in the IR spectrum. The solutions are dynamic, and we note that ligand exchange reactions occur for the anion $[BH_3Cl]^-$ to give a variety of boron hydride chlorides such as $[BH_2Cl_2]^-$ which further complicate the situation,[21] nevertheless reactivity studies using **1**$\cdot$BH$_3$ and **2**$\cdot$BH$_3$ with a known excess of benzaldehyde were also carried out and these showed that there are *three* hydrides available for reduction.

These new phosphonium-based ionic liquids, specifically **1**$\cdot$BH$_3$ and **2**$\cdot$BH$_3$, are air- and moisture-sensitive. Exposure of these compounds to moist air results in hydrolysis of the complex, giving a very large peak in the B–OH stretching region (3330 cm^{-1}) of the IR spectrum. These new ionic liquids are a convenient source of hydride for standard chemical reductions.[22,23] They are, in our experience, non-flammable, recyclable, and non-volatile, and represent a new class of odourless source of borane.[18] Moreover, these solutions may provide a new method of *hydride transport* using a flowing medium, possibly providing for a safer method of using boranes as an energy carrier.

We have used these new ionic liquids for classic reductions involving borane, namely the reduction of the carbonyl functionality. A series of reactions were performed by combining stoichiometric amounts (based on hydride) of the carbonyl compounds with the new **1**$\cdot$BH$_3$ or **2**$\cdot$BH$_3$ ionic liquids at room temperature. Yields were determined by gas chromatography–mass spectrometry analysis (GC-MS) of the extracts. The data are presented in Table 1. For comparison, the products were also extracted by Kulgelröhr distillation from the ionic liquids and the yields were comparable to those obtained in the GC-MS analyses of the extracts as well as to reactions performed in molecular solvents such as THF.[24]

Table 1. Reduction of carbonyl functionality

Phosphonium-based ionic liquid	Reaction	Yield [%]
1$\cdot$BH$_3$	Benzaldehyde → benzyl alcohol	94
2$\cdot$BH$_3$		95
1$\cdot$BH$_3$	Benzoyl chloride → benzyl alcohol	90
2$\cdot$BH$_3$		99
1$\cdot$BH$_3$	Benzophenone → benzhydrol	60
2$\cdot$BH$_3$		99
1$\cdot$BH$_3$	Cinnamaldehyde → cinnamyl alcohol	75
2$\cdot$BH$_3$		61
1$\cdot$10% BH$_3$	Benzaldehyde → benzyl alcohol	80
2$\cdot$10% BH$_3$		91

We note that phosphonium ions have been used as catalysts in several reaction types,[25,26] and phosphonium derivatives have been used historically for phase-transfer catalysis.[27,28] Of relevance to this report is that quarternary phosphonium cations activate carbonyl compounds.[29] In order to probe this interaction, we performed some simple experiments. A large degree of vapour pressure lowering was observed (namely, much less than predicted by Raoult's Law) when a known concentration of carbonyl or alcohol was added separately to phosphonium-based ionic liquid **1**. The deviation order is of ethanol > propionaldehyde > acetone, suggestive of the degree of association in solution.

We realize that there are two probable types of interaction between the solute (carbonyl compound) and the solvent (phosphonium centre), namely coordination through the quarternary cationic phosphonium site through $[P\cdots O]$ interactions or through hydrogen bonding to the hydrogen positioned α to the phosphonium cation. We performed some NMR titration experiments in order to probe the association between solute and solvent molecules. Addition of a carbonyl compound, such as benzaldehyde and propionaldehyde, to phosphonium-based ionic liquid **1** has little effect on the ^{31}P NMR spectra; however ^{1}H NMR studies indicate a *downfield* shift of the signal representing the proton α to the phosphorous with an increased concentration of the carbonyl compound. This observation suggests that the mode of association between solute and solvent likely involves a hydrogen bonding interaction. Finally, we note that the shortest cation anion contact in the simple phenoxide salt $[Ph_3PCH_3][2,6\text{-}Ph_2C_6H_3O]$ involves a novel $[C\text{–}H\cdots O]$ hydrogen bond.[30]

We have also looked at the reactivity of other reducing agents in phosphonium-based ionic liquids, namely NaBH$_4$, LiAlH$_4$, and AlH$_3$. NaBH$_4$ in phosphonium-based ionic liquid **1** reduces aldehydes, ketones, and acid chlorides to the anticipated products, but we suggest that there are few obvious advantages to using NaBH$_4$ in phosphonium-based ionic liquids over conventional solvents such as ethanol and isopropanol. On the other hand, LiAlH$_4$ and AlH$_3$, which are significantly more reactive than NaBH$_4$ and clearly incompatible with alcohols, react with **1** to give tetradecyl(dihexyl)phosphine and hexene and with **2** to give, after aqueous workup, tetradecyl(dihexyl)phosphine, hexane, and decanol as determined by GC-MS, NMR, and MS studies. Treatment of **2** with 10 mol-% of AlH$_3$ for 2 h under an inert atmosphere and at room temperature results in the generation of a new solution that shows 10–15% decomposition of the ionic liquid, as shown by the presence of hexene and phosphines in the solution,[31] consistent with decomposition via a Hoffman-type decomposition.[32] It should be noted that no further decomposition of the phosphonium ionic liquid with AlH_3 occurs and this was tested by leaving the new ionic liquid sitting for over one month. With the decomposition of the phosphonium-based ionic liquid, there is also the generation of a new aluminum hydride species. The resulting solution is capable of reducing aldehydes and ketones to alcohols (benzaldehyde 78%, 1-phenyl-ethanone 80%, benzophenone 82%) and esters to aldehydes (methyl benzoate 72%). Reactivity studies show the presence of two chemically reactive hydrides and the presence of the Al–H bond is confirmed by IR studies (1767, 1717 cm^{-1}). Treatment of the new phosphonium-based ionic liquid solution with water and subsequent analysis of the extracts clearly shows the presence of decanol, produced during reduction of the anion, decanoate. Unambiguous assignment of the structure of the aluminium-containing species has not been made.

This work is an important contribution since it demostrates a novel method for the delivery of a reactive and flammable gas using the novel materials properties of ionic liquids, and bodes well for the use of phosphonium-based ionic liquids to deliver reactive gases to reaction vessels. We have shown that phosphonium-based ionic liquids behave as potent borane carriers. The new ionic liquids are useful for the reduction of organic carbonyl containing molecules. The new solutions are stable under inert atmosphere for more than two months. Reduction of esters was possible in alane containing phosphonium-based ionic liquids but simultaneous decomposition of the ionic liquid was observed.

Experimental

NMR spectra were recorded on a Bruker AMX 400 MHz spectrometer in 5-mm Ø quartz tubes. ^1H and $^{13}C\{^1H\}$ chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS), $^{31}P\{^1H\}$ chemical shifts with respect to 85% phosphoric acid (0 ppm), and $^{11}B\{^1H\}$ with respect to $BF_3{\cdot}O(C_2H_5)_2$ (0 ppm). Infrared spectra were obtained using a Bomem MB spectrometer with the transmittance values reported in cm^{-1}. GC-MS was carried out on the extracts using gas chromatography electron ionization detector G 1800A GCD system.

1: δ_H (C_6D_6) 2.4–0.7 (various m). δ_P (C_6D_6) 33.3. ν_{max} (neat)/cm^{-1} 2956 (s), 2923 (s), 2856 (s), 1466 (s), 1416 (m), 1378 (s), 1300 (m), 1263 (m), 1216 (m), 1112 (m), 989 (m), 814 (m), 721 (s). (Calc. for $C_{32}H_{68}ClP$: C 74.0, H 13.2. Found: 74.3, H 13.0%.)

1·BH_3: δ_H (C_6D_6) 2.7–0.8 (various m). δ_P (C_6D_6) 33.5. δ_B (C_6D_6) 50 to −25 (v. br, sharp features at 18.6 & −12.0), −35.3 (quin, BH_4^-). ν_{max} (neat)/cm^{-1} 2956 (s), 2924 (s), 2855 (s), 2298 (s), 2212 (m), 2037 (m), 1465 (s), 1416 (s), 1378 (m), 1337 (s), 1261 (m), 1215 (m), 1166 (m), 1115 (s), 1071 (m), 814 (s), 721 (s) cm^{-1}. (Calc. for $C_{32}H_{71}BClP$: C 72.1, H 13.4. Found: C 72.4, H 13.6%.)

2: δ_H (C_6H_6) 2.8–0.8 (various m). δ_P (C_6D_6) 33.1. ν_{max} (neat)/cm^{-1} 2956 (s), 2925 (s), 2856 (s), 1579 (s, C=O), 1465 (m), 1377 (m), 1265 (m), 1110 (m), 812 (m), 722 (m).

2·BH_3: δ_H (C_6D_6) 2.6–0.8 (various m). δ_P (C_6D_6) 33.4. δ_B (C_6D_6) 50 to −25 ppm (v. br, sharp features at 18.1 & 2.1), −35.3 (quin, BH_4^-). ν_{max} (neat)/cm^{-1} 2956 (s), 2925 (s), 2855 (s), 2270 (s), 2224 (m), 2139 (m), 1661 (s, C=O of **2**·BH_3 complex), 1579 (m, C=O of uncomplexed **2**), 1466 (s), 1416 (s), 1378 (m), 1337 (s), 1297 (m), 1150 (m), 1111 (m), 1075 (m), 720 (m), 669 (s).

Acknowledgments

Financial support was provided by the Natural Sciences and Engineering Research Council of Canada (NSERC). We thank Cytec Canada Inc. for the generous donation of the phosphonium-based ionic liquids.

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