Synthesis of Chiral Carbohydrate Ionic Liquids

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Abstract: Chiral room temperature ionic liquids, containing a carbohydrate moiety linked at the anomeric centre to an *N*-methylimidazolium group have been synthesised. The ionic liquids were prepared in a concise manner and provided ready access to both the D- and L-arabino enantiomers. The same strategy enabled the preparation of D-ribofuranose and D-xylofuranose analogues, in excellent yields.

Keywords: synthesis, chiral ionic liquid, carbohydrate, *N*-methylimidazolium

There has been a major research effort in the area of ionic liquids during the last twenty years; with the first example of a Friedel–Crafts acylation being reported in 1986.[1] Since then the development and use of room temperature ionic liquids (RTIL) has emerged as one of the fascinating technologies in science because of their physiochemical properties and specific applications in bioorganic research. The last decade has seen a substantial growth in the use of RTIL as environmentally benign[2] and useful solvents in diverse applications such as organic synthesis, chemical catalysis, biocatalysis, separation technology, analytical chemistry.[3] A feature that adds to the attractiveness of the use of RTIL in organic synthesis is the ease of their separation and recyclability in addition to their immeasurably low vapor pressure, high stability, range of viscosities, moderate solvation of organic compounds, as well as adjustable miscibility and polarity.[4]

Typical RTIL are composed of a large organic cation and a weakly coordinating inorganic anion.[5] The cations being typically imidazolium, pyridinium, pyrrolidinium, quaternary ammonium, or phosphonium ions while the anions include Cl^-, Br^-, ClO_4^-, AlX_4^-, BF_4^-, PF_6^-, $CF_3SO_3^-$, $(CF_3SO_3)_2N^-$ or $(CN)_2N^-$. Changing the counterions often results in significant modifications in the properties of RTIL such as miscibility with organic solvents and/or water, polarity, viscosity, and density. For example, anions such as Cl^- or Br^- impart hydrophilic characteristics while fluorinated anions such as $[PF_6]^-$ or $[BF_4]^-$ impart hydrophobic properties depending on the nature of the associated cation.[3a] Employing the appropriate cation and anion, RTIL with desired physicochemical properties or specific functions can be achieved.[6]

The development of chiral RTIL has received increasing attention over the last few years with the aim of providing novel chiral solvents. A number of chiral RTIL have been designed and prepared with the specific goal of influencing the outcomes of asymmetric reactions.[7] However, this has been realized in a small number of cases and there are only a few chiral ionic liquids that have found use in synthesis.[8] The majority of the existing chiral RTIL are based on the modification of the various cations, namely, pyridinium,[9] oxazolium,[10] thiazolium,[11] and ammonium[12] and imidazolium species. More recently, a number of groups have reported RTIL where the imidazolium cation has been modified to incorporate the chirality.[13] The chiral RTIL based on the imidazole ring system can be regarded as derivatives of imidazole **1–6** (Figure 1) having counterions commonly found in achiral ionic liquids.

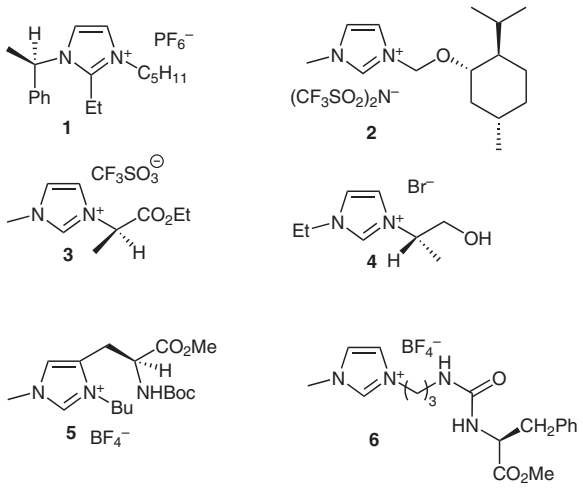
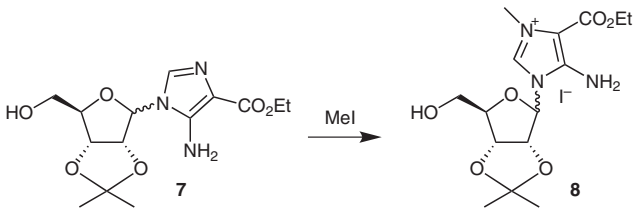


Figure 1

Nucleotides having a C-1 imidazolium ring occur widely and they tend to be highly crystalline structures. For example, a number of syntheses of these compounds proceed via the intermediacy of crystalline cationic structures[14] (Scheme 1).



Scheme 1

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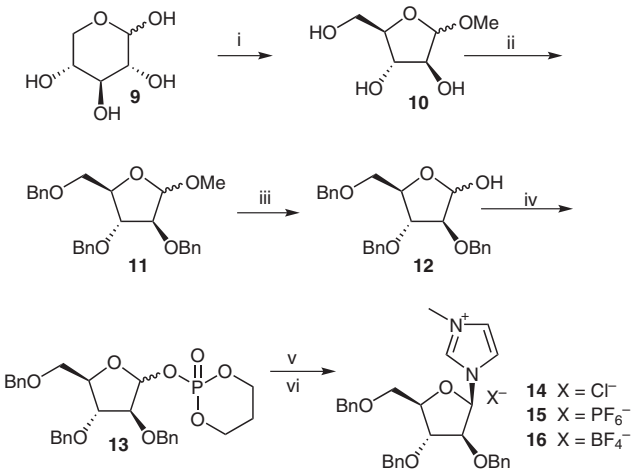
With these thoughts, we considered the preparation of chiral ionic liquids based on carbohydrates as these are rich sources of stereochemistry and chirality and as a consequence have been utilised widely as chiral building blocks. We reasoned that the incorporation of the imidazole nucleus at the anomeric center of monosaccharides along with the judicious choice of protecting groups would provide access to a new generation of imidazolium-based carbohydrate chiral ionic liquids.

For our initial approach towards the synthesis of these carbohydrate ionic liquids we chose to study the chemistry of arabinofuranosides based on the fact that both the D- and L-enantiomers of arabinose are commercially available and would thus provide an entry to both enantiomeric series.

2,3,5-Tri-*O*-benzyl-α,β-D-arabinofuranoside **12** was prepared in three steps from D-arabinose[15] (Scheme 2). Subsequent treatment with propane-1,3-diyldioxyphosphoryl chloride gave the arabinoside **13** consisting predominately of the α-anomer.[16]

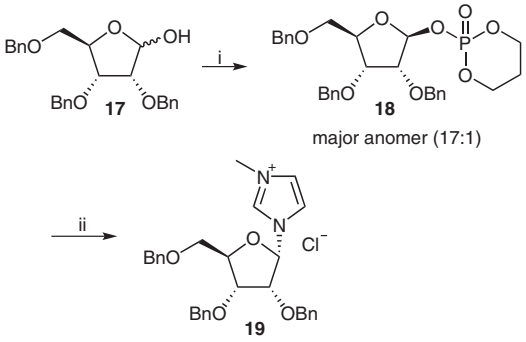


Scheme 2 *Reagents and conditions*: (i) MeOH, PTSA·H_2O, 40 °C, 20 h (98%); (ii), NaH, DMF, 0 °C, 30 min, Bu_4NI, BnBr, r.t., 4 h (95%); (iii) MeCN–H_2O–TFA (4:3:1), reflux, 12 h (81%); (iv) propane-1,3-diyldioxyphosphoryl chloride, CH_2Cl_2, Me*N*Im, 0 °C, (72%); (v) Me*N*Im·HCl, TMSOTf (cat.), CH_2Cl_2, –78 °C, (58%); (vi) NH_4PF_6 (98%) or NH_4BF_4 (98%).

We next investigated the displacement reaction of phosphate **13** with *N*-methylimidazole as the nucleophile. In the first instance we were able to obtain the desired ionic liquid **14** in 15–20% yields using a catalytic amount of trimethylsilyl triflate (TMSOTf), an excess of *N*-methylimidazole and potassium chloride. However, reaction of the crude phosphate **13** with 1.5 equivalents of *N*-methylimidazole hydrochloride and catalytic TMSOTf gratifyingly led to ionic liquid **14** in 58% yield after chromatography,[17,18] furthermore, we were able to conduct this reaction on a 5 g scale with a similar result. The outcome of this reaction was somewhat unexpected in that we only obtained the β-anomer, on the basis of its ^{13}C NMR spectrum in which the anomeric carbon was found to resonate at δ = 87.3 ppm. In the ^1H NMR the anomeric proton appeared at δ = 6.46 ppm with a coupling constant of 5.8 Hz suggestive of a *cis* relationship to the H-2 proton of the arabinofuranoside. Further support for the assignment as being β was obtained from COSY, HMQC, and HMBC experiments. The TGA analysis showed that the ionic liquid was stable up to 180 °C, demonstrating its robustness. Following this we proceeded to exchange the counterion to PF_6^- and BF_4^- by treatment with ammonium hexafluorophosphate and ammonium tetrafluoroborate, respectively. These two counterions afforded ionic liquids **15** and **16** at room temperature, which were immiscible with water, soluble in chloroform, dichloromethane, methanol, and acetonitrile. In the ^1H NMR spectrum of ionic liquid **15** the anomeric proton experienced an upfield shift to δ = 6.05 ppm while the ^{31}P NMR spectrum showed a septet at δ = –142.9 with a coupling constant of 712.7 Hz.

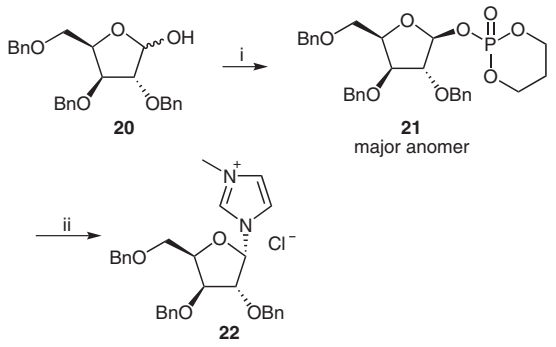
In order to confirm that the chloride ion had been exchanged successfully with PF_6^- we conducted a ^{31}P NMR experiment where we had introduced an equimolar amount of triphenyl phosphite as an internal standard and integrated the observed phosphorus resonances. This resulted in a 1:1 ratio for observed signals for the two components. Similar chemistry using the L-enantiomer of arabinose gave the corresponding ionic liquid.

We subsequently turned our attention to the synthesis of RTIL based on D-ribofuranose (Scheme 3). This proceeded uneventfully and gave the corresponding ionic liquid **19** in good yield. The anomeric proton was found to resonate at δ = 6.25 ppm with a coupling constant of 5.8 Hz suggestive of a *cis* relationship to the H-2 proton of the ribofuranose ring while the C-2 imidazole proton was observed at δ = 9.28 ppm. The inversion of stereochemistry at the anomeric centre resulting in formation of the *cis*-isomer may occur as a result of an S_N2 displacement of the propane-1,3-diyl phosphate group. The chloride counterion was exchanged to PF_6^- using the same protocols that had been applied to the arabinosides.



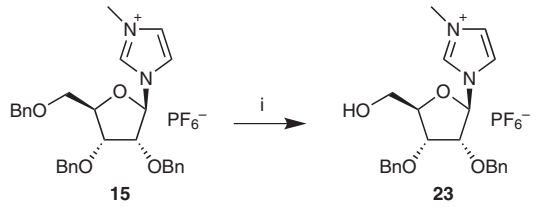
Scheme 3 *Reagents and conditions*: (i) propane-1,3-diylphosphorylchloride, CH_2Cl_2, Me*N*Im, 0 °C, (68%); (ii) Me*N*Im·HCl, TMSOTf (cat.), CH_2Cl_2, –78 °C, (46%).

Similarly, synthesis of RTIL based on D-xylofuranose gave the corresponding ionic liquid **22** in good yield (Scheme 4). The anomeric proton was found to resonate at δ = 6.30 ppm with a coupling constant of 3.7 Hz while the C-2 imidazole proton was observed at δ = 9.26 ppm.



Scheme 4 *Reagents and conditions*: (i) propane-1,3-diylphosphorylchloride, CH_2Cl_2, Me*N*Im, 0 °C, (70%); (ii) Me*N*Im·HCl, TMSOTf (cat.), CH_2Cl_2, –78 °C, (52%).

In order to ascertain if any hydrolysis of the D-arabino series of RTIL **14** had occurred, we rerecorded its ^{1}H NMR spectrum after six months storage at room temperature. The NMR data for the synthesised RTIL after six months of storage at room temperature was exactly comparable to the data obtained for the newly synthesised ionic liquids. This experiment established that there were no resonances due to the formation of the of the hydrolysis product **12**. The possible formation of α-,β-2,3,5-tri-*O*-benzyl-arabinofuranosyl chlorides was excluded on the basis that the resonances for the anomeric protons for these compounds occur δ = 6.17 and 6.21 ppm,[19] and these signals were not observed in our experiments. Furthermore, the stability of these ionic liquids was supported by their recovery after reactions conducted with organozinc reagents, catalytic hydrogenation, and Grignard reactions. To investigate the chemical stability of the ionic liquid we undertook a series of reaction employing methylmagnesium chloride with benzaldehyde and aryl-substituted benzaldehydes using THF as the solvent along with one equivalent of the ionic liquid **15** as co-solvent. These reactions afforded the corresponding alcohol in chemical yields >95% and were complete in 5–10 minutes at –78 °C. Disappointingly no enantiomeric excess for the alcohols was observed. In order to establish the stability of the heterocyclic ring towards hydrogenolysis, we examined the transfer hydrogenation of **15** using palladium hydroxide as the catalyst and this resulted in the formation of the primary alcohol **23** in 85% yield, where the primary benzyl protecting group had been removed selectively (Scheme 5).



Scheme 5 *Reagents and conditions*: (i) $Pd(OH)_2$, cyclohexene, EtOH, reflux, 7d.

In summary, we have prepared stable chiral ionic liquids based on sugar furanose frameworks in an efficient process. We envisage that these new chiral RTIL will be useful as new chiral solvents in addition to serve as catalysts for a range of asymmetric reactions that are being investigated in our laboratories.

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(17) **Selected Data**
Compound **14** (X = Cl): $[\alpha]_D^{28}$ +28 (*c* 1.1, $CHCl_3$). IR (film): ν_{max} = 3429, 3143, 3064, 3032, 2923, 2870, 1634, 1578, 1556, 1454, 1364, 1264, 1157, 1090, 1030, 748, 701, 638 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.60 (3 H, s), 3.62 (1 H, dd, *J* = 2.8, 10.9 Hz), 3.82 (1 H, dd, *J* = 3.0, 10.9 Hz), 4.13 (1 H, m), 4.23 (1 H, t, *J* = 6.8 Hz), 4.41 (1 H, d, *J* = 11.1 Hz), 4.48 (1 H, d, *J* = 11.1 Hz), 4.53 (1 H, d, *J* = 11.9 Hz), 4.64 (2 H, d, *J* = 6.3Hz), 4.57 (1 H, m), 4.69 (1 H, d, *J* = 11.9 Hz), 6.46 (1 H, d, *J* = 5.8 Hz), 7.22–7.40 (16 H, m), 7.73 (1 H, m), 9.40 (1 H, s) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.0, 68.0, 72.5, 73.5, 78.2, 81.0, 82.6, 87.3, 121.5, 122.5, 128.1, 127.9, 128.1, 128.2, 128.3, 128.5, 128.6, 135.5, 136.4, 137.1, 137.2 ppm. ESI-MS: *m/z* calcd $C_{30}H_{33}N_2O_4$: 485.2435; found: 485.2423. Glass-transition temperature: 18 °C.
Compound **15** (X = PF_6^-): $[\alpha]_D^{28}$ +14 (*c* 1.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 3.41 (3 H, s), 3.57 (1 H, dd, *J* = 3.2, 10.9 Hz), 3.75 (1 H, dd, *J* = 3.3, 10.8 Hz), 4.09 (1 H, m), 4.17 (1 H, t, *J* = 6.7 Hz), 4.37 (1 H, d, *J* = 10.8 Hz), 4.43–4.50 (5 H, m), 4.62 (1 H, d, *J* = 11.8 Hz), 6.05 (1 H, d, *J* = 5.6 Hz), 7.05 (1 H, t, *J* = 1.7 Hz), 7.15–7.36 (15 H, m), 7.39 (1 H, t, *J* = 1.7 Hz), 8.56 (1 H, br s) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.9, 68.2, 73.3, 73.4, 73.5, 78.6, 81.3, 82.3, 87.4, 121.3, 122.7, 127.7, 127.9, 128.0, 128.1, 128.2, 128.3, 128.5, 128.6, 134.9, 136.2, 137.1, 137.2 ppm. ^{31}P NMR (160 Hz, $CDCl_3$): δ = –142.9 (sept., *J* = 712.7 Hz) ppm. Glass-transition temperature –23 °C.
Compound **16**: $[\alpha]_D^{28}$ +9.5 (*c* 1.05, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 3.48 (3 H, s, NCH_3), 3.59 (1 H, dd, *J* = 3.2, 10.9 Hz), 3.76 (1 H, dd, *J* = 3.2, 10.9 Hz, H-5, H-5′), 4.09 (1 H, m, H-4), 4.18 (1 H, t, *J* = 6.4 Hz, H-3), 4.38 (1 H, d, *J* = 11.0 Hz), 4.45 (1 H, d, *J* = 11.0 Hz), 4.46–4.53 (4 H, H-2), 4.61 (1 H, d, *J* = 11.8 Hz), 6.22 (1 H, d, *J* = 5.5 Hz), 7.16–7.36 (16 H), 7.53 (1 H, t, *J* = 1.7 Hz,), 8.75 (1 H, br s) ppm. ^{13}C (100 MHz, $CDCl_3$): 35.7, 67.9, 72.2, 73.1, 75.0, 78.3, 80.9, 82.1, 87.1, 121.1, 122.1, 127.4–128.4, 134.9, 136.3, 137.0, 137.1 ppm. ^{19}F (376.5 MHz, $CDCl_3$): –151.0 ppm. Glass-transition temperature –36 °C.
Compound **19**: $[\alpha]_D^{28}$ +22.3 (*c* 1.3, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 3.46 (1 H, dd, *J* = 3.2, 10.6 Hz), 3.52 (1 H, dd, *J* = 3.5, 10.6 Hz), 3.77 (3 H, s), 4.01 (1 H, dd, *J* = 1.8, 5.1 Hz), 4.41–4.62 (8 H, m), 6.25 (1 H, d, *J* = 5.8 Hz), 7.19–7.36 (16 H, m), 7.54 (1 H, s), 9.28 (1 H, s) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.0, 69.7, 72.5, 73.3, 73.4, 76.4, 76.9, 77.3, 78.1, 84.7, 87.9, 121.6, 122.1, 127.6, 127.8, 127.9, 128.0, 128.1, 128.3, 128.4, 136.5, 136.8, 137.3 ppm. Glass-transition temperature 16 °C.
Compound **22**: ^1H NMR (400 MHz, $CDCl_3$): δ = 3.67–3.76 (2 H, m), 3.93 (3 H, s), 4.05 (1 H, m), 4.22 (1 H, t, *J* = 5.3 Hz), 4.35–4.46 (3 H, m), 4.51 (1 H, d, *J* = 11.9 Hz), 4.59 (1 H, d, *J* = 11.9 Hz), 4.62–4.69 (2 H, m), 6.30 (1 H, d, *J* = 3.7 Hz), 7.08 (1 H, br s), 7.11–7.36 (15 H, m), 7.39 (1 H, br s), 9.26 (1 H, br s) ppm. ^{13}C (100 MHz, $CDCl_3$): δ = 36.3, 68.7, 72.5, 73.3, 75.0, 75.3, 78.0, 82.1, 85.0, 121.1, 122.1, 127.7, 128.5, 135.1, 137.3, 137.7, 137.8, 137.9 ppm.
Compound **23**: ^1H NMR (400 MHz, $CDCl_3$): δ = 3.42 (3 H, s), 3.63 (1 H, dd, *J* = 2.1, 11.0 Hz), 3.89 (1 H, dd, *J* = 2.5, 11.0 Hz), 4.12 (1 H, m), 4.20 (1 H, t, *J* = 7.7 Hz), 4.38 (1 H, d, *J* = 10.5 Hz), 4.47 (1 H, d, *J* = 10.5 Hz), 4.60 (1 H, d, *J* = 11.9 Hz), 4.75 (1 H, dd, *J* = 5.8, 7.2 Hz), 4.85 (1 H, d, *J* = 11.9 Hz), 6.02 (1 H, d, *J* = 5.7 Hz), 7.06 (1 H, br s), 7.23–7.39 (10 H, m), 7.69 (1 H, br s), 8.96 (1 H, br s) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.1, 68.0, 72.6, 73.5, 78.1, 80.9, 82.6, 87.3, 121.6, 122.4, 127.7, 128.5, 135.8, 136.5, 137.2, 137.3.
(18) **General Procedure**
The 2,3,5-tri-*O*-benzylsugar (1 mmol) was dissolved in dry CH_2Cl_2 (10 mL) and cooled to 0 °C under Ar atmosphere. Propane-1,3-diyldioxyphosphoryl chloride (2 mmol) was added, followed by 1-methylimidazole (2.5 mmol). The mixture was allowed to warm up to r.t. and stirred overnight (16 h). The reaction was then quenched with sat. $NaHCO_3$ (10 mL) and the organic layer washed with H_2O (2 × 10 mL) and dried (Na_2SO_4). The solvent was then removed in vacuo to give the crude sugar phosphate, which was re-dissolved in dry CH_2Cl_2 (10 mL) under an Ar atmosphere and cooled to –78 °C. trimethylsilyl triflate (cat.) was added and the mixture stirred for 2 min. 1-Methylimidazole hydrochloride (2 mmol) was then added. The reaction mixture was allowed to warm up to r.t. and stirred until TLC ($CHCl_3$–MeOH, 80:20) showed the reaction had gone to completion (4 h). The mixture was then diluted with CH_2Cl_2 (10 mL) and washed with sat. aq $NaHCO_3$ (2 × 20 mL) and H_2O (2 × 20 mL). The organic layer was dried (Na_2SO_4) and concentrated in vacuo to give a crude product, that was further purified by column chromatography ($CHCl_3$–MeOH, 80:20).
Silver nitrate test for ionic liquids with anions other than chloride, derived via metathesis: The ionic liquid (1 mg) is dissolved in MeOH–deionized H_2O (1:1; 1 mL). The resulting solution is tested with 0.1 M $AgNO_3$ (2 drops). No precipitation was observed in BF_4 and PF_6 ionic liquids.
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