Green Chemistry

PAPER

View Article Online
View Journal | View Issue

Cite this: *Green Chem.*, 2014, **16**, 1489

Electrochemical pinacol coupling of aromatic carbonyl compounds in a [BMIM][BF_4]–H_2O mixture†

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Received 12th August 2013,
Accepted 5th December 2013

DOI: 10.1039/c3gc41641k

www.rsc.org/greenchem

The electrochemical pinacol coupling reactions of aromatic carbonyl compounds were carried out using an 80% [BMIM][BF_4]–H_2O mixture as the electrolytic medium. The corresponding diols were obtained in good to excellent yields with moderate diastereoselectivity. The stereoselectivity can be explained using the strongly-bound ion-pairs formed between the imidazolium cation and the radical anions of the carbonyl compounds. The ionic liquid replaces both organic solvents and supporting electrolytes generally used in the electrosynthetic method. The electrolytic medium can be recycled and successfully reused at least in five consecutive reactions.

Introduction

Electrosynthesis is an economical and environmentally benign technology that possesses enormous potential for the development of eco-friendly transformations.[1–3] Electrons are considered as redox reactants and are one of the cheapest reagents in chemistry. The reducing or oxidizing power in electrolysis is controlled by voltage applied to the electrochemical cells. The method prevents the use of dangerous and polluting external chemical oxidants or reductants (*e.g.* PCC, OsO_4, $LiAlH_4$ and NaH) and minimizes the waste formation of these reactions, making the process environmentally friendly and economically feasible. An electrosynthetic reaction typically requires two electrodes (anode and cathode) that can also be considered as heterogeneous catalysts and they are in contact with a solution that contains an electrolyte. These electrodes can simply be physically removed at the end of the reaction without using external reagents. In addition, most electrosynthetic reactions take place at room temperature, reducing the energy consumption. The diverse and frequently complex chemistry has been elucidated to date using electrochemical conditions.[4–8] However, the electrosynthesis suffers from the frequent requirement for organic solvents and expensive supporting electrolytes to carry out reactions and the difficulty in separating the product from the complex electrolytic media.

Room temperature ionic liquids (RTILs), which are completely composed of ions, can replace the volatile organic solvents and supporting electrolytes frequently used in electrosynthesis increasing its experimental appeal. RTILs display many advantages over common organic solvents, such as nonvolatilities, immiscibilities with many organic solvents, and good solvating properties for both inorganic and organic compounds. RTILs can be easily recovered and reused in order to eliminate pollution risks and reduce costs. They have played an increasingly important role in chemical synthesis and many organic, organometallic and biocatalyzed reactions have been investigated in ionic liquids in recent years.[9–13] RTILs generally exhibit a wide electrochemical potential window, which is a highly desirable property for applying them as solvents in electrosynthesis.[14] Being composed entirely of ions, RTILs are supposed to be among the most concentrated electrolytic fluids with many charge carriers per unit volume. When these charge carriers are mobile, very high conductivities are possible. The application of RTILs in electrosynthesis has been receiving more and more attention in recent years. Among the recent reports, electrochemically promoted nucleophilic aromatic substitution,[15] carboxylation,[16] the Henry reaction,[17] epoxidation of alkenes,[18] and reductive coupling[19] have been performed in RTILs. Notwithstanding the unique advantages of RTILs, some distinct ionic liquid properties such as high viscosity and low ion conductivity can be considered as electrochemically disadvantageous.[20] Armed with this information, we investigated the possibility of using RTILs as a user- and eco-friendly electrolytic medium for one of the reductive coupling reactions: the pinacol coupling of carbonyl compounds.

Pinacol coupling is one of the most important and widely studied carbon–carbon bond forming reactions in organic chemistry. The popularity of this reaction stems from its intrinsic ability to furnish 1,2-diols which can serve as a

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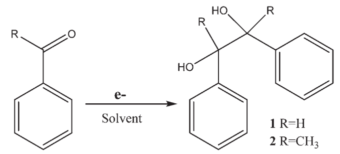
† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3gc41641k

structural motif in total synthesis and as chiral ligands or auxiliaries.[21,22] Pinacol coupling has been playing an important role in the synthesis of pharmacologically important agents such as taxol, cotylenol, and HIV-I protease.[23,24] The reaction also enables controlling both diastereoselectivity and enantioselectivity in a single step and remains a challenging target for organic chemists. Various low-valent metal reducing agents have been used to promote the pinacol coupling reaction.[25–28] However, some of these methods require an absolutely anhydrous system under an inert atmosphere, and some reagents and solvents are costly, moisture sensitive, and toxic. During the past few decades, great efforts have been made to explore environmentally benign systems for the pinacol reaction. Different catalysts/co-catalysts in aqueous media including $InCl_3$/Al, $TiCl_3$, VCl_3/Al, Mn/AcOH, *etc.* have been reported with promising results.[29–31] Electrochemical pinacol coupling in RTILs can provide convenient and environmentally friendly conditions for this reaction.

Table 1 Comparison of solvents for electrochemical pinacol coupling reaction[a]



Entry	Solvent system	Percent yield of **1**[b] (%)	Percent yield of **2**[b] (%)
1	[BMIM][BF_4]	28	20
2	[BMIM][PF_6]	12	5
3	80% [BMIM][BF_4]–H_2O	95	91
4	70% [BMIM][BF_4]–H_2O	89	80
5	50% [BMIM][BF_4]–H_2O	65	61
6	80% [BMIM][PF_6]–H_2O	62	54
7	70% [BMIM][PF_6]–H_2O	60	48
8	50% [BMIM][PF_6]–H_2O	32	24
9	80% [BMIM][BF_4]–CH_3CN	46	33
10	80% [BMIM][PF_6]–CH_3CN	26	18

[a] Electrolysis was performed using the carbonyl compound (0.035 mmol) in 5.0 mL of the solvent, and applying a constant voltage of −2.0 V *vs.* Ag/AgCl for 5 h. [b] Isolated yields.

Table 2 Physical property comparison for RTILs

Ionic liquid	Viscosity (mPa s)	Conductivity (S m^{-1})	Molecular weight (g mol^{-1})	Density (g cm^{-3})
[BMIM][BF_4][32]	154	0.35	226.01	1.26
[BMIM][PF_6][32]	308	0.146	284.18	1.35
80% [BMIM][BF_4]–H_2O[33]	7.5	3.35	—	—

Results and discussion

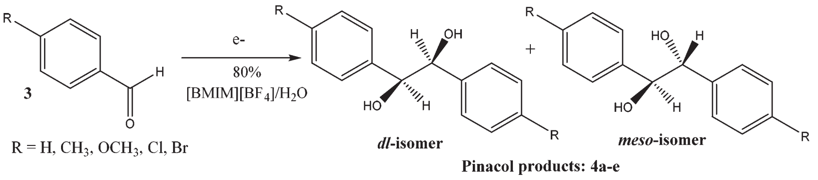
Initially, two of the most commonly used RTILs, 1-butyl-3-methylimidazolium tetrafluoroborate, [BMIM][BF_4], and 1-butyl-3-methylimidazolium hexafluorophosphate, [BMIM][PF_6], were chosen as the solvents for electrochemical pinacol coupling reactions. Carbonyl compounds, benzaldehyde and acetophenone were used to develop the electrolysis conditions. However, after five hours of electrolysis in these RTILs, the reactions did not proceed to completion, thus providing lower yields (Table 1, entries 1–2).

Even though ionic liquids are comprised entirely of ions, RTIL itself was not efficient enough as an electric conductor. The high viscosity of RTILs would limit the ion mobility, resulting in an important ohmic drop, and therefore a high cell voltage when the current intensity is increased.[14] The mass transfer of the substrate in the solution to the electrode surface is also slower in high viscous ionic liquids. The viscosities for [BMIM][BF_4] and [BMIM][PF_6] are given in Table 2. The ionic liquid, [BMIM][PF_6], displays higher viscosity and lower conductivity than [BMIM][BF_4] and the pinacol coupling conducted in [BMIM][PF_6] resulted in a lower yield than the reaction conducted in [BMIM][BF_4] (Table 1, entries 1–2). Therefore, both water and acetonitrile were tested as co-solvents for this electrosynthesis. The addition of a co-solvent substantially increased the yields of pinacol coupling in both RTILs (Table 1, entries 3–10). However, the combination of the ionic liquid, [BMIM][BF_4], with the co-solvent, H_2O, resulted in the best yields (Table 1, entries 3–5).

The conductivity and viscosity of RTILs can be changed by adding a co-solvent. The viscosity for the 80% [BMIM][BF_4]–H_2O mixture which gave the best yields was determined to be substantially lower than that of the pure ionic liquid (Table 2). Seddon *et al.* reported an equation that can be used to predict the viscosity for ionic liquid–cosolvent mixtures.[34] The experimentally determined viscosity for the 80% [BMIM][BF_4]–H_2O mixture is closely similar to that of the calculated value. The decrease in the viscosity of ionic liquids by the addition of co-solvents varies due to the differences in polarities which lead to different interactions with the ions in the ionic liquids.[35] The conductivity for the 80% [BMIM][BF_4]–H_2O mixture was measured to be about ten times higher than the conductivity of pure ionic liquid (Table 2). The co-solvent can increase the conductivity by solvating the constituent ions of the ionic liquid. This solvation reduces the ion pairing or ion aggregation in the ionic liquid, resulting in an increase in the number of available charge carriers and an increase in the mobility of these charge carriers. However, it is worth noting that the electrochemical potential window was decreased with the addition of water as the co-solvent.[36]

After the initial studies, the 80% [BMIM][BF_4]–H_2O mixture was used as the electrolyte for subsequent pinacol coupling reactions. The reduction potentials for aromatic aldehydes and ketones ranged between −1.8 V and −1.2 V *vs.* the Ag/AgCl reference in 80% [BMIM][BF_4]–H_2O. A controlled potential of −2 V was applied against Ag/AgCl at a platinum cathode for 5 hours. The resulting pinacol products were separated and characterized using spectroscopic techniques. The results of the electrochemical pinacol coupling of aromatic aldehydes are shown in Table 3.

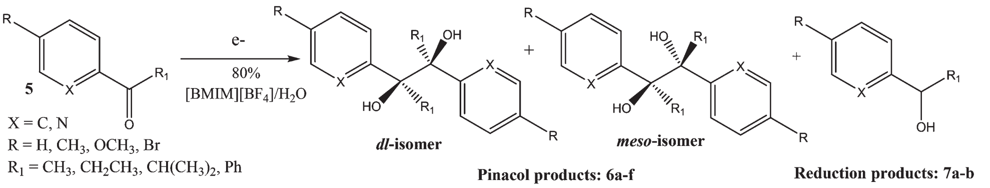
Table 3 Results of the pinacol coupling reactions of aldehydes[a]



Entry	Aldehyde	Product R-group	Yield[b] (%)	*meso*/*dl*[c]
1	Benzaldehyde	(**4a**) H	95	31/69
2	4-Tolualdehyde	(**4b**) CH_3	97	56/44
3	4-Anisaldehyde	(**4c**) OCH_3	93	18/82
4	4-Chlorobenzaldehyde	(**4d**) Cl	56	40/60
5	4-Bromobenzaldehyde	(**4e**) Br	62	45/55

[a] Electrolysis was performed using the aldehyde (0.35 mmol) in 5.0 mL of the 80% $[BMIM][BF_4]$–H_2O mixture and applying a constant voltage of −2.0 V *vs.* Ag/AgCl for 5 h. [b] Isolated yields. [c] Determined by NMR spectroscopy.

Table 4 Results of the pinacol coupling reactions of ketones[a]



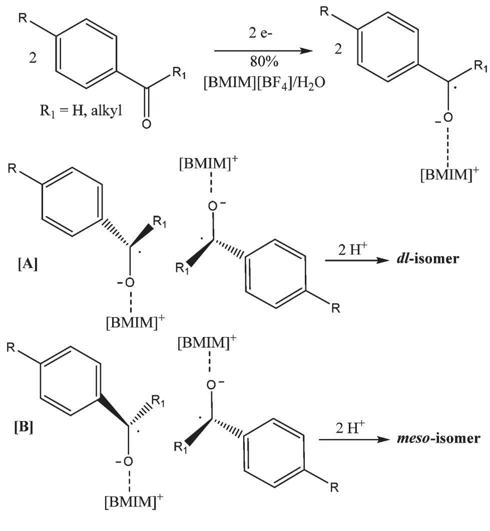
Entry	Ketone	Product structure R, R_1, X	Yield of the pinacol product[b] (%)	*meso*/*dl* ratio for the pinacol product[c]	Yield of the reduction product[b] (%)
1	Acetophenone	(**6a**) H, CH_3, C	91	21/79	—
2	4-Methylacetophenone	(**6b**) CH_3, CH_3, C	86	11/89	—
3	4-Methoxyacetophenone	(**6c**) OCH_3, CH_3, C	50	14/86	—
4	4-Bromoacetophenone	(**6d**) Br, CH_3, C	48	17/83	—
5	2-Acetylpyridine	(**6e**) H, CH_3, N	88	42/58	—
6	Propiophenone	(**6f**) H, CH_2CH_3, C	83	50/50	—
7	Isobutyrophenone	(**7a**) H, $CH(CH_3)_2$, C	—	NA	85
8	Benzophenone	(**7b**) H, Ph, C	—	NA	96

[a] Electrolysis was performed using the ketone (0.35 mmol) in 5.0 mL of the 80% $[BMIM][BF_4]$–H_2O mixture and applying a constant voltage of −2.0 V *vs.* Ag/AgCl for 5 h. [b] Isolated yields. [c] Determined by NMR spectroscopy.

The pinacol coupling of substituted benzaldehydes under developed conditions afforded excellent to good yields. For the electroreductive coupling of 4-chloro- and 4-bromobenzaldehydes, the starting materials were remaining after five hours of electrolysis and the pinacol products were separated by flash column chromatography (Table 3, entries 4–5). The Faradic efficiency for these reactions varied in the range of 72–87%. In the presence of water, it is a probability that some side reactions such as hydrogen generation can take place at the Pt cathode. This may have contributed to a somewhat low faradic efficiency of these reactions. However, a Pt cathode–Sn anode combination has been successfully used previously in the presence of water (acetonitrile–H_2O) for reductive coupling reactions.[5,37] As a comparison, a pinacol coupling of benzaldehyde in 80% $[BMIM][BF_4]$–H_2O was conducted using the RVC cathode.[38] The Faradic efficiency and the percent yield were found to be equal to those from the experiment that used a Pt cathode. The resulting 1,2-diols were characterized by spectroscopic methods. According to NMR spectroscopy, a mixture of *dl* and *meso* isomers was formed for each synthesis with very low diastereoselectivity.

The electrochemical pinacol coupling of aromatic ketones was also carried out using 80% $[BMIM][BF_4]$–H_2O as the electrolytic medium. The coupling products were obtained in high yields with low to moderate diastereoselectivity, confirmed by NMR spectroscopy (Table 4). After five hours of electrolysis, unreacted starting ketone was still remaining for 4-methoxyacetophenone and 4-bromoacetophenone, and the pinacol product was separated by flash column chromatography (Table 4, entries 3–4). Interesting results were obtained when the methyl group (R_1) of acetophenone was changed with different alkyl and aryl groups. Both acetophenone and propiophenone resulted in the corresponding pinacol product as expected in 91% and 83% yields respectively (Table 4, entries 1, 6). However, when isobutyrophenone and benzophenone were subjected to electrolysis under these conditions, the pinacol coupling products were not formed, but the corresponding alcohols, 2-methyl-1-phenylpropanol (**7a**) and diphenylmethanol (**7b**), were produced in good yields (Table 4, entries 7–8). The steric hindrance from large substituents (isobutyl and phenyl) prevents the pinacol coupling and promotes the reduction at the carbonyl group under these conditions.

The developed method uses a Sn sacrificial anode in the electrochemical cell. It has been previously reported that the cations formed by sacrificial anodes can stabilize the anionic intermediates by ion-bridge formation.[37,39] Such ion-bridge formation between Sn cations and two radical anions should increase the diastereoselectivity of the reaction favoring the *dl* isomers. However, the pinacol coupling of both aldehydes and ketones underwent very low diastereoselectivity. In this situation, it is possible that ion-bridging with Sn cations is not favored and an ion-pair is more efficiently formed between one radical anion and the imidazolium cation. It has been reported that the 1-butyl-3-methylimidazolium cation demonstrates an unusual ion pairing tendency when compared to tetraalkylammonium ions.[40] The moderate diastereoselectivity for the pinacol product of acetophenone in [BMIM][NTf$_2$] was also reported by Lagrost *et al.*[41] The observed moderate diastereoselectivity is a result of the strongly-bound ion-pairs formed between the imidazolium cation and the radical anions of the carbonyl compounds formed after the first electron transfer (Scheme 1). The negatively charged carbonyl oxygen can closely face the imidazolium cation due to the planar geometry of a cationic ring. This minimizes the cation–anion distance in the ion pair leading to strong interactions. Another reason for the strong interactions between the imidazolium cation and the radical anion is the hydrogen bond formation between the hydrogen at the C-2 position of the imidazolium cation and the carbonyl oxygen in the radical anion.[42] These tightly-bound complexes promote coupling with a head-to-tail orientation of the radical anion, in order to avoid strong interactions from large imidazolium cations. The charge stabilization by ion pairing also allows a fast dimerization step between two radical anions. The coupling arrangement [A] leads to the *dl* isomer while the arrangement [B] leads to the *meso* isomer (Scheme 1). Both approaches of the radical anions could be identically involved thereby decreasing the stereoselectivity.



Scheme 1 Mechanism for the electrochemical pinacol coupling of carbonyl compounds in [BMIM][BF$_4$].

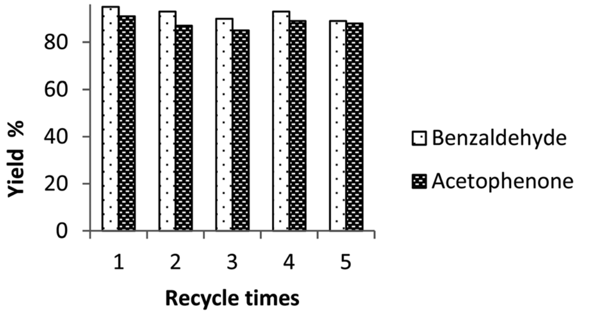


Fig. 1 Reuse of [BMIM][BF$_4$] in electrochemical pinacol coupling reactions. Reaction conditions as Table 1, entry 3.

Room temperature ionic liquids are known for their recyclability.[43,44] In this study, the possibility of recycling the ionic liquid electrolytic medium was also investigated. The RTIL was recycled using the method reported in the Experimental section. The NMR spectroscopy of the recovered ionic liquid indicated no change in the structure. The electrochemical pinacol coupling reactions of benzaldehyde and acetophenone conducted in the recovered ionic liquids showed no significant decrease in yields or selectivity for up to five cycles (Fig. 1). This indicates that the ionic liquid as an electrolyte for pinacol coupling of aromatic aldehydes and ketones is recyclable.[45]

Conclusion

We have demonstrated that the electrochemical pinacol coupling of aromatic aldehydes and ketones can effectively be performed using 80% [BMIM][BF$_4$]–H$_2$O as the electrolytic medium. The resulting products were obtained in high yields with moderate diastereoselectivity. The developed electrochemical method avoids the use of a catalyst–co-catalyst systems for reductive coupling, thereby preventing the formation of any metallic byproducts. Owing to the inherent ionic nature of the RTILs, the use of a supporting electrolyte for the electrolysis was also not needed which avoided the salt byproducts and simplified the separation and purification steps. With the ease of product recovery, this method provides a simple synthetic route to 1,2-diols. The electrolyte can be recycled and reused at least up to five cycles. Efforts are currently underway to utilize chiral RTILs in stereoselective electrosynthesis.

Experimental

The RTILs [BMIM][BF$_4$] and [BMIM][PF$_6$] were synthesized using a previously reported method.[46]

The final ionic liquids were dried in a vacuum line (~0.1 Torr) for 48 h and kept under a nitrogen atmosphere. The amount of residual water was determined to be 500–700 ppm using Karl-Fisher coulometric titration (Karl Fisher 652 Metrohm).

General procedure for the electrochemical pinacol coupling reaction

The carbonyl compound (0.35 mmol) and a mixture of 80% [BMIM][BF_4]–H_2O (4.0 mL of [BMIM][BF_4] and 1.0 mL of H_2O) were placed in an electrochemical cell fitted with a sacrificial tin foil anode (1.0 cm^2) and a platinum plate cathode (1.0 cm^2). The mixture was stirred and degassed by bubbling nitrogen for 30 minutes. A controlled potential of −2.0 V *vs.* the Ag/AgCl reference electrode was applied under a nitrogen atmosphere for 5 hours using a BASi PWR-3 potentiostat. The resulting solution was filtered to remove any insoluble tin salts and extracted with diethyl ether (2 × 5 mL). The ether extract was dried with anhydrous sodium sulfate, filtered and concentrated *in vacuo*. When necessary, the residue was purified *via* silica gel flash column chromatography (10% ethyl acetate in a hexane eluent) to afford the final product. The product structures and diastereomeric ratios were confirmed by NMR spectroscopy. The NMR spectra were recorded on a JOEL eclipse 400 MHz spectrometer in chloroform-*d*.

Recycling of RTIL

After extraction of the pinacol product, 5.0 mL of methylene chloride was added to the separatory funnel containing a [BMIM][BF_4]–aqueous layer. The organic layer was separated and the aqueous layer was extracted with another portion of methylene chloride (5.0 mL). The combined organic layers were dried with anhydrous sodium sulfate, filtered and concentrated using a rotary evaporator. The RTIL was then dried in a vacuum line for 24 h prior to use in the next experiment.

Product characterization

1,2-Diphenylethane-1,2-diol [4a] (*meso*/*dl* mixture). White solid (0.035 g, 95%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.75 (br s, 2H, OH), 4.63 (s, 2H, *dl*), 4.77 (s, 2H, *meso*), 7.05–7.26 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 78.1, 79.2, 127.1, 127.2, 127.9, 128.1, 128.2, 128.3, 139.9, 139.9; IR (ν/cm^{-1}) 3368, 3040, 2920, 1648, 1510, 764.

1,2-Di(4-methylphenyl)ethane-1,2-diol [4b] (*meso*/*dl* mixture). White solid (0.041 g, 97%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.30 (s, 6H, *dl*), 2.92 (s, 6H, *meso*), 2.41 (s, 2H, OH), 4.57 (s, 2H, *dl*), 4.68 (s, 2H, *meso*), 6.98–7.08 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.3, 78.1, 79.1, 127.0, 127.2, 128.9, 128.2, 129.0, 130.0, 130.1, 137.1, 137.8; IR (ν/cm^{-1}) 3360, 3028, 2923, 1650, 1606, 1450, 909.

1,2-Di(4-methoxylphenyl)ethane-1,2-diol [4c] (*meso*/*dl* mixture). White solid (0.045 g, 93%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.01 (br s, 2H, OH), 3.77 (s, 6H, *dl*), 3.82 (s, 6H, *meso*), 4.58 (s, 2H, *dl*), 4.71 (s, 2H, *meso*), 6.73 (d, *J* = 8 Hz, 4H), 7.01 (d, *J* = 8 Hz, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.3, 79.0, 113.6, 128.3, 132.2, 159.2; IR (ν/cm^{-1}) 3320, 3012, 2959, 1681, 1601, 1513, 1463, 1249, 1035.

1,2-Di(4-chlorophenyl)ethane-1,2-diol [4d] (*meso*/*dl* mixture). White solid (0.028 g, 56%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.64 (s, 2H, *dl*), 4.86 (s, 2H, *meso*), 7.03–7.28 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 76.8, 78.6, 128.4, 128.5, 128.8, 133.9, 138.1; IR (ν/cm^{-1}) 3390, 3034, 2895, 1697, 1604, 1495, 1213.

1,2-Di(4-bromophenyl)ethane-1,2-diol [4e] (*meso*/*dl* mixture). White solid (0.040 g, 62%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.59 (s, 2H, *dl*), 4.82 (s, 2H, *meso*), 6.98–7.24 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 78.4, 128.4, 128.7, 129.1, 133.8, 138.2; IR (ν/cm^{-1}) 3393, 3020, 3010, 2908, 1620, 1494, 1199, 1047, 912.

2,3-Diphenylbutane-2,3-diol [6a] (*meso*/*dl* mixture). White solid (0.039 g, 91%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.50 (s, 6H, *dl*), 1.58 (s, 6H, *meso*), 2.64 (s, 2H, OH), 7.23–7.25 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.0, 78.7, 78.9, 127.1, 127.2, 127.5, 143.5; IR (ν/cm^{-1}) 3480, 3070, 2980, 1640, 1446, 1062.

2,3-Di(4-methylphenyl)butane-2,3-diol [6b] (*meso*/*dl* mixture). White solid (0.044 g, 86%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.45 (s, 6H, *dl*), 1.53 (s, 6H, *meso*), 2.34 (s, 6H), 2.64 (s, 2H, OH), 7.04–7.14 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.1, 25.1, 25.3, 78.7, 79.0, 126.9, 127.4, 127.9, 128.1, 136.2, 136.5, 136.6, 140.7, 141.0; IR (ν/cm^{-1}) 3606, 2984, 2925, 1512, 1372, 909.

2,3-Di(4-methoxylphenyl)butane-2,3-diol [6c] (*meso*/*dl* mixture). White solid (0.027 g, 50%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.45 (s, 6H, *dl*), 1.54 (s, 6H, *meso*), 3.79 (s, 6H), 6.76 (d, *J* = 8 Hz, 4H), 7.09 (d, *J* = 8 Hz, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.1, 55.3, 78.7, 78.9, 112.5, 112.6, 128.2, 128.6, 135.8, 158.6; IR (ν/cm^{-1}) 3528, 2959, 2954, 1655, 1611, 1511, 1249.

2,3-Di(4-bromophenyl)butane-2,3-diol [6d] (*meso*/*dl* mixture). White solid (0.025 g, 48%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.46 (s, 6H, *dl*), 1.57 (s, 6H, *meso*), 7.16–7.19 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.9, 79.5, 126.9, 127.0, 127.1, 127.5, 129.9, 131.9, 143.8; IR (ν/cm^{-1}) 3191, 2977, 2933, 1594, 1570, 1465, 909.

2,3-Di(2-pyridinyl)butane-2,3-diol [6e] (*meso*/*dl* mixture). White solid (0.049 g, 88%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.24 (s, 6H, *dl*), 1.65 (s, 6H, *meso*), 6.90–8.47 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.3, 25.8, 78.3, 78.3, 120.5, 121.4, 122.1, 137.0, 137.4, 146.2, 146.4, 165.1, 168.1; IR (ν/cm^{-1}) 3419, 2986, 2937, 1621, 1468, 1357, 1067.

3,4-Diphenylhexane-3,4-diol [6f] (*meso*/*dl* mixture). White solid (0.043 g, 83%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.60 (t, *J* = 6 Hz, 6H), 1.71 (q, *J* = 6 Hz, 4H, *dl*), 2.07 (q, *J* = 6 Hz, 4H, *meso*), 2.67 (s, 2H, OH), 7.24–7.26 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ7.7, 27.8, 82.0, 16.9, 127.2, 128.4, 140.4; IR (ν/cm^{-1}) 3560, 3060, 2974, 1669, 1491, 970.

2-Methyl-1-phenylpropan-1-ol [7a]. Clear liquid (0.042 g, 85%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.79 (d, *J* = 7 Hz, 3H), 0.95 (d, *J* = 7 Hz, 3H), 1.94–1.97 (m, 1H), 4.35 (d, *J* = 7 Hz, 2H), 7.43–7.53 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.4, 19.7, 35.0, 80.0, 126.7, 127.2, 127.4, 144.2; IR (ν/cm^{-1}) 3609, 2966, 2932, 1620, 1445, 1369, 1166, 1011.

Diphenylmethanol [7b]. White solid (0.047 g, 96%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.05 (br s, 1H, OH), 5.83 (s, 1H), 7.31–7.36 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 76.8, 126.6, 127.7, 128.6, 143.9; IR (ν/cm^{-1}) 3605, 1617, 1493, 1454, 1381, 1096.

Scaled-up electrolysis

3.5 mmol of the carbonyl compound (benzaldehyde, 0.37 g or acetophenone, 0.42 g) and 80% [BMIM][BF$_4$]–H$_2$O (30.0 mL) were placed in an electrochemical cell fitted with a sacrificial tin foil anode (2.0 cm^2) and a platinum plate cathode (2.0 cm^2). The mixture was stirred and degassed by bubbling nitrogen for 30 minutes. A controlled potential of −2.0 V and a Ag/AgCl reference electrode was applied under a nitrogen atmosphere for 5 hours. The resulting solution was filtered to remove any insoluble tin salts and extracted with diethyl ether (2 × 15 mL). The ether extract was dried with anhydrous sodium sulfate, filtered and concentrated *in vacuo*. The residue was purified *via* silica gel flash column chromatography (10% ethyl acetate in a hexane eluent) to afford the final product. The pinacol product of benzaldehyde was obtained in 76% yields while the pinacol product of acetophenone was obtained in 68% yields.

Acknowledgements

This work was supported by a Susquehanna University Faculty Research grant. The authors thank Dr L. Viyannalage from the University at Buffalo for some electrochemical characterizations of RTILs.

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