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Scope and Mechanistic Insights into the Use of Tetradecyl(trihexyl)phosphonium Bistriflimide: A Remarkably Selective Ionic Liquid Solvent for Substitution Reactions

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Abstract: A survey of substitution reactions conducted in a phosphonium bistriflimide ionic liquid is presented. The results demonstrate high selectivity favoring substitution over typically competitive elimination and solvolytic processes even when challenging secondary and tertiary electrophiles are employed. The first reports of Kornblum substitution reactions in an ionic liquid are described that proceed with very high chemoselectivity in favor of nitro over nitroso products and elimination side products. The structure–reactivity study indicates that these reactions proceed through a narrow spectrum of pathways ranging from straight S_N2 to a preassociation pathway along a saddle point that approaches the S_N1 limit. The barrier to the formation of dissociated carbocations is attributed to the structural features of this ionic liquid that favor intervention of the associated nucleophile over dissociation, also preventing cross over to E1 processes. The lack of any basic entity in the phosphonium bistriflimide ionic liquid appears to prevent any potential base-mediated elimination reactions, which makes this a highly selective medium for use in general substitution reactions.

Keywords: chemoselectivity · green chemistry · ionic liquids · phosphonium salts · substitution reactions

Introduction

Room-temperature ionic liquids (ILs) have attracted considerable attention as novel reaction media over the last decade or so.[1,2] Ionic liquids may offer significant advantages in the development of environmentally benign chemical reactions by virtue of their nonflammability, thermal stability, and nonvolatility. However, these properties are also highly dependent upon the precise nature (structure and thermal/chemical stability) of the cationic–anionic pairing involved. In our view, this "designer" nature, or what may be called "task-specific" ILs, is one of the most attractive features and allows the particular IL to be tailored to a given reaction under investigation. The ability of ILs to form three liquid phases through the addition of water or methanol/water mixtures and a nonpolar solvent such as hexane or ether provides further advantages in chemical processing that are not possible with standard solvents. This, and the potential for reuse, including the recycling of toxic and/or expensive transition-metal catalysts, is a strong impetus in the development of "green" chemical processes. In addition, intrinsically novel chemical reactivities are being discovered in ILs at an increasing rate.[3] Not surprisingly, these materials have moved from being mere curiosities a decade or so ago to being commodity materials readily available on a large scale.[4,5] At least three large-scale industrial applications of ILs have been implemented and several others are reported to be in the developmental pipeline.[4]

Structurally, most of the ILs that have been investigated to date contain quaternary nitrogen cores involving imidazolium, ammonium, or pyridinium ions. In addition to the cationic core itself, further room exists for the engineering of these species through anionic exchange reactions, which allows the manipulation of properties such as density, viscosity, Lewis acidity, and hydrophobicity, thus tailoring the IL to the precise reaction or process of interest.[6] A striking example demonstrating the significant role of the anion on the

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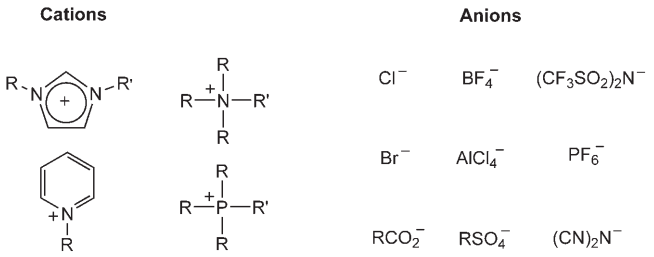
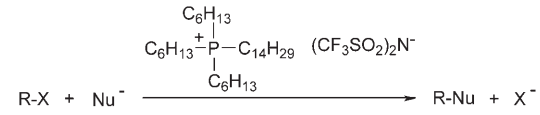
solubility of carbohydrates in imidazolium ILs was recently described by Sheldon and co-workers.[7] Scheme 1 summarizes some of the most commonly employed cationic and anionic partners that have been combined to prepare ionic liquids, thus highlighting the number of combinations that are possible.



Scheme 1. Commonly employed IL structural units.

By far, most ILs that have been investigated are based on imidazolium cations. Although beneficial in many cases, these cations have been shown to degrade under a variety of situations[8] including exposure to base and sonication. In addition, these aromatic rings have been shown to be susceptible to aromatic substitution reactions, which limits their scope in electrophilic processes.[9] For these reasons, over the last few years we have been focused on developing processes in phosphonium-salt-based ILs with the view of exploring their general scope and exploiting their unique capabilities. Phosphonium-based ILs are less expensive to manufacture than imidazolium-based ILs and are available on an industrial scale.[5] We have previously demonstrated phosphonium-based ILs to be efficient and recyclable media for Pd-mediated cross-coupling reactions.[10,11] We also demonstrated the ability of the quaternary phosphonium ion to expand its valency and function as a mild Lewis acid,[12] thus promoting carbonyl-addition reactions. Phosphonium-based ILs are very stable thermally,[13] are stable towards strongly basic reagents including Grignard reagents (it has been shown that ylide formation does not occur readily in the pure IL, even in the presence of strongly basic Grignard reagents),[14] and are not susceptible to aromatic substitution chemistry.[15] For these reasons they offer greater practicality and scope than imidazolium ILs and deserve far more consideration as unique reaction media than has been afforded them in the ILs field thus far.

One particular ion pairing we considered to be of interest was the case of a standard tetradecyl(trihexyl)phosphonium cation paired with a nonbasic and non-nucleophilic anion, such as bistriflimide (Scheme 2). The low nucleophilicity of the bistriflimide anion should prevent any nucleophilic interference from this species in substitution reactions. The absence of a basic lone pair of electrons, or of ease of formation[14] of the same in such a pairing was expected to endow these ionic solvents with potentially novel reactivity and selectivity in substitution reactions. For example, it is difficult to see how such species could be expected to participate significantly in the stabilization of dissociated carbocations. It is well known that dipolar solvents such as DMF are valuable media for alkylation reactions. Because ionization to form carbocationic intermediates is possible in most dipolar solvents, elimination processes can become competitive. In addition, many dipolar solvents are capable of shuttling protons, which further affects elimination reactions. Based on this consideration, a working hypothesis in terms of simple substitution reactions involving primary, and more importantly, secondary or tertiary electrophiles capable of ionizing (halides, tosylates, mesylates, etc.), is that higher selectivity in favor of substitution over elimination might be expected in such phosphonium salt ILs. We recently[16] reported that the phosphonium bistriflimide IL is superior as a reaction medium for substitution reactions with weakly nucleophilic carboxylate anions, including selective substitution reactions with electrophiles prone to elimination. In this paper, we report on a more extensive structure–reactivity study on this particular IL pairing, challenging the media to a range of substrates to reveal the scope of and gain some mechanistic insights into this selective substitution process.



Scheme 2. General substitution in phosphonium bistriflimide ionic liquid.

Results and Discussion

To begin, we investigated the substitution reactions of the challenging 2-phenylethyl electrophiles, including the bromide, mesylate, and tosylate derivatives, with a range of nucleophiles in the tetradecyl(trihexyl)phosphonium bistriflimide ionic liquid.[17] The chosen nucleophiles ranged from the strongly nucleophilic azido and cyanide anions, a basic and nucleophilic primary amine, to weakly nucleophilic phenolate, nitrite, and carboxylate anions. The phenylethyl substrate was chosen because styrene formation is expected to occur in the event of any of the possible elimination pathways being operative and this would be readily detected. We also noted significant amounts of solvolysis in the attempted substitution reactions of β-aryl halides when they were conducted in the dipolar solvent DMF. The results of the present investigation are summarized in Table 1. The reactions involving the strongly nucleophilic azido and cyanide anions with either the bromide, mesylate, or tosylate derivatives proved to be straightforward, and all reactions were complete at 80 °C in under 6 h. The substitution product was obtained in about 90 % isolated yield. These conversions are somewhat higher on average than similar nucleophilic displacements conducted in nitrogen-based ILs.[18]

N-Benzyl (Bn) groups are very useful protecting and modulating groups for amines, and are removable through hydrogenolysis.[19] It was thus desirable to investigate the double alkylation of benzylamine in the IL. The reaction of

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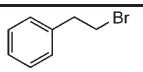
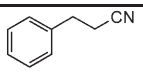
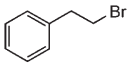
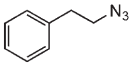
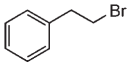
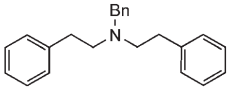
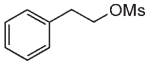
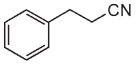
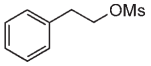
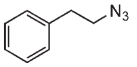
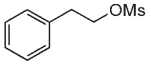
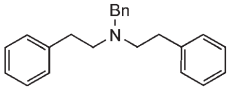
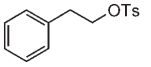
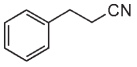
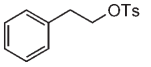
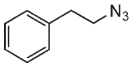
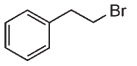
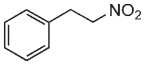
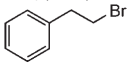
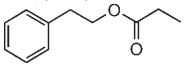
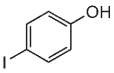
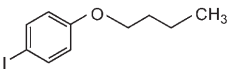
Table 1. Alkylation reactions in tetradecyl(trihexyl)phosphonium bistriflimide.

Entry	Electrophile	Nucleophile	T [°C]	Product	Yield [%]
1		KCN	80		92
2		NaN_3	80		95
3		Bn-NH_2	80		96
4		KCN	80		85
5		NaN_3	80		87
6		Bn-NH_2	80		90
7		KCN	80		84
8		NaN_3	80		86
9		$NaNO_2$	80		80
10	$CH_3(CH_2)_6$-Br	$NaNO_2$	90	$CH_3(CH_2)_6$-NO_2	90
11	$CH_3(CH_2)_7$-Br	$NaNO_2$	90	$CH_3(CH_2)_7$-NO_2	90
12	$CH_3(CH_2)_{11}$-Br	$NaNO_2$	90	$CH_3(CH_2)_{11}$-NO_2	90
13		$CH_3CH_2CO_2H$	75		98
14	$CH_3(CH_2)_3$-Br		70		87

either the 2-phenylethyl bromide or mesylate substrate with one half equivalent of benzylamine provided the double-alkylated amine in high yields (Table 1, entries 3 and 6). These results demonstrate high selectivity of the substitution reaction, and no styrene formation was detected under these conditions in the presence of basic amines, which confirms the noninvolvement of E2 or E1cB pathways. Recently, benzylation of primary amines with dibenzyl carbonate has been shown to be catalyzed by using phosphonium salt catalysts.[20] In our case it is clear that the rate of substitution is much faster than any of the possibly elimination pathways.

We next extended the substitution reaction to weaker nucleophiles including nitrite, carboxylate, and phenolate anions as indicated in Table 1 (entries 9–14). Nitroalkanes are amongst the most versatile of intermediates in organic synthesis in view of their high reactivity and versatility in terms of the subsequent conversions that are possible.[21] The Kornblum reaction involving the substitution reaction of an alkyl electrophile with potassium or sodium nitrite in a dipolar solvent such as DMF or DMSO is perhaps the most direct route to nitroalkanes.[22] Unfortunately, this route usually gives mixtures of nitro and nitroso substitution products through N-alkylation and O-alkylation of nitrite, respectively.[23] We were thus delighted to find (Table 1, entries 9–12) that the weakly nucleophilic nitrite anion participated in the reaction in the phosphonium salt IL without formation of any nitroso side product. We speculate that the high chemoselectivity in favor of nitro substitution is due to the oxyphilic nature of the phosphonium ion, which solvates the nitrite anion and allows the free nitrogen lone pair to function as the active nucleophile. The substitution reaction proceeded with aliphatic primary bromides at 80 to 90 °C to give aliphatic nitro compounds in about 90 % isolated yield (Table 1, entries 10–12). However, for the first time we noted some styrene formation in the case of the mechanistically challenging 2-phenyl bromoethane, but only if the reaction was performed at temperatures exceeding 85 °C. An 80 % yield of the nitro substitution product (entry 9) was obtained when the temperature was controlled at 80 °C. The weakly basic nature of the nitrite anion and the absence of any other appreciably basic species appears to preclude E2 and E1cB pathways for this elimination. Non-β-aryl halides do not undergo elimination under these conditions at temperatures above 85 °C (see Table 1, entries 10–12). The elimination result is consistent with a thermal aryl-assisted ionization pathway involving a phenonium ion, with direct nucleophilic substitution being kinetically favored. Although Kornblum substitution reactions have recently been described in aqueous media,[24] to the best of our knowledge, this is the first report of this type of substitution process in an ionic liquid. In general, the yields obtained in the IL are 10 to 25 % higher than those reported in aqueous media with identical or similar substrates. Finally, the reaction of a carboxylic acid and functionalized phenol with primary bromides proceeded without incident to give the ester and ether alkylation products in good isolated yields (Table 1, entries 13 and 14).

The high isolated yield obtained in the alkylative esterification example (Table 1, entry 13) and our interest in chemo- and stereocontrolled ester bond-formation processes[25–27] motivated us to investigate this process in greater detail. Esterification processes are of considerable commercial significance in the synthesis of high production volume

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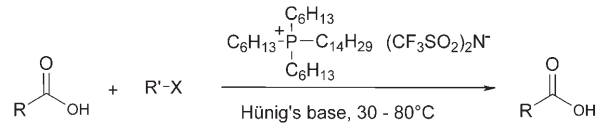
(HPV) esters including fragrances, monomers, plasticizers, as well as lower-volume high-value intermediates and end products. It appeared to be of great interest to explore this process in detail given the potential advantages of using a recyclable IL. Savelli and co-workers have recently reported on the use of imidazolium ILs in the coupling of active alkylating agents with carboxylates,[28a,b] and a preliminary communication of the present esterification work recently appeared.[16] The carboxylate alkylation reaction performed in conventional solvents, outlined in Scheme 1, was first generalized by Mehta[29,30] based on the previous findings of the groups of Alvarez[31] and Raphael.[32] In general, this reaction takes place through the addition of an alkylating agent to the carboxylic acid in a dipolar aprotic solvent in the presence of a base (Scheme 3).



Scheme 3. Esterification in ionic liquids.

The reaction is most general for the preparation of methyl esters for which iodomethane or dimethyl sulfate is employed as the alkylating agent.[30b] Several variants of the process have been shown to proceed with inversion of configuration when chiral secondary electrophiles are employed, thus indicating the involvement of a general S_N2 process.[33] As such, the reaction is sensitive to steric effects although cases involving, separately, hindered acids[30b] and tertiary alkyl halides[34] have been reported.

In the present work, we began with an investigation of the reaction of propanoic acid with 1-bromooctane in the tetradecyl(trihexyl)phosphonium bistriflimide ionic liquid[35] with diisopropylethyl amine (Hünig's base). A highly general process was developed that allows alkylative esterification of carboxylates under mild conditions. The overall results from our study are reported in Table 2.

Simple aliphatic and aromatic acids react with primary bromides to give the corresponding

Table 2. Esterification reactions in phosphonium bistriflimide ionic liquid.

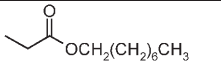
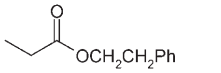
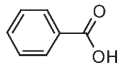
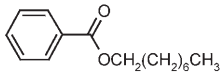
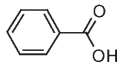
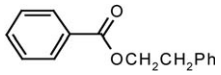
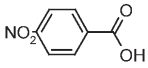
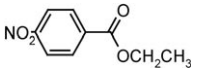
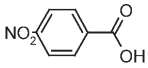
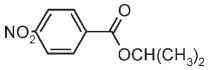
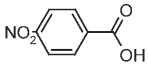
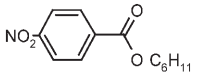
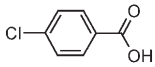
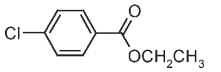
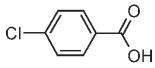
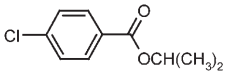
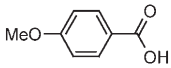
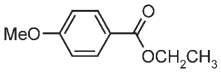
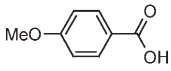
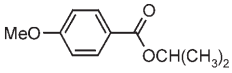
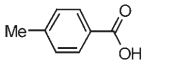
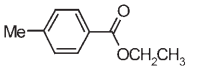
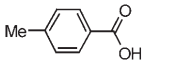
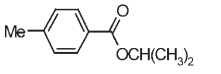
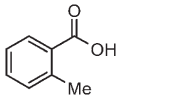
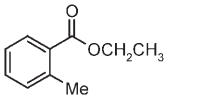
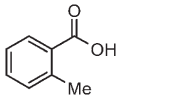
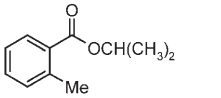
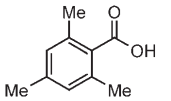
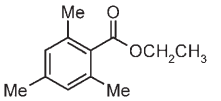
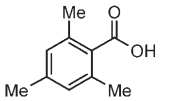
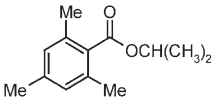
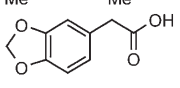
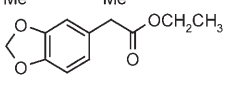
Entry	R–CO_2H	Alkylating agent	T [°C]	Product	Yield [%]
1		1-bromooctane	75		98
2		2-phenyl-1-bromoethane	75		98
3		1-bromooctane	75		98
4		2-phenyl-1-bromoethane	75		98
5		bromoethane	30		95
6		2-bromopropane	40		94
7		bromocyclohexane	70		80
8		bromoethane	30		94
9		2-bromopropane	40		93
10		bromoethane	30		94
11		2-bromopropane	40		92
12		bromoethane	30		91
13		2-bromopropane	40		92
14		bromoethane	30		89
15		2-bromopropane	40		88
16		bromoethane	30		86
17		2-bromopropane	40		85
18		bromoethane	30		95

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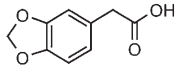
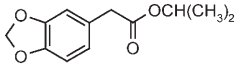
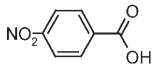
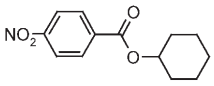
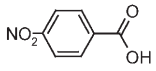
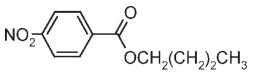
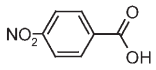
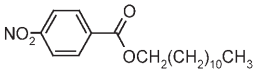
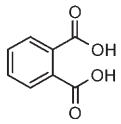
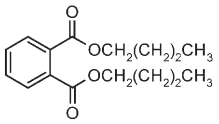
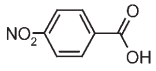
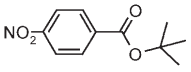
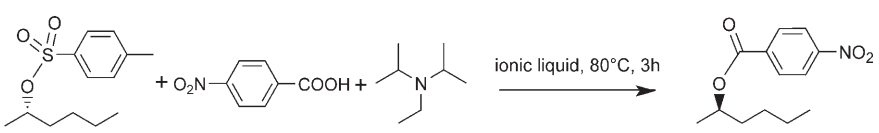
Table 2. (Continued)

Entry	R–CO_2H	Alkylating agent	T [°C]	Product	Yield [%]
19		2-bromopropane	40		93
20		cyclohexyl-*p*-tosylate	80		77
21		1-butyl-*p*-tosylate	80		95
22		bromododecane	80		98
23		1-bromobutane	80		86
24		*tert*-butyl bromide	50		70

esters in high isolated yield. Entries 2 and 4 indicate that no competitive E2-type elimination occurs with the alkyl halide under these conditions. Electronic effects were investigated for a series of 4-substituted benzoic acids reacting with alkyl bromides (entries 5–13) and determined to be minor. Both primary and secondary bromides react without difficulty and even problematic[36] cyclohexyl halides such as bromocyclohexane provided a respectable yield of the cyclohexyl ester (entry 7). Steric effects were shown to be only slightly detrimental to the efficiency of the process (entries 14–17). Even the hindered 2,4,6-trimethylbenzoic acid reacted with the secondary halide 2-bromopropane to provide the ester in 85% isolated yield.[37] β-Aryl acids, for which we have observed decarboxylation under Fischer esterification conditions, also reacted readily with primary and secondary bromides to give high yields of the ester (entries 18 and 19). In addition to bromides, we were delighted to find that tosylates, including the cyclic, secondary cyclohexyl-*p*-toluenesulfonate, readily entered into the reaction under similar conditions (entries 20 and 21). The use of potassium carbonate as base was shown to be an effective substitute for Hünig's base (entry 22). The dicarboxylic acid phthalic acid also reacted with four equivalents of bromobutane to give the dibutyl ester in 86% isolated yield (entry 23). Dialkyl phthalates are HPV chemicals utilized both as insect repellents and plasticizers. Most interestingly, the reaction was also successful and very efficient using *tert*-butyl bromide as the electrophile (entry 24). The conventional esterification reaction generally fails[35,37] with tertiary halides when conducted in standard solvents. In one report, it was successful when using a large excess (48 equiv) of *tert*-butyl bromide.[34] Using the standard IL protocol outlined here and employing only two equivalents of *tert*-butyl bromide, an unoptimized 70% yield of the *tert*-butyl-4-nitrobenzoate ester was realized. The success of this result with only two equivalents of *tert*-butyl bromide indicates that surprisingly little E1-type elimination takes place in the IL under these conditions. This IL result does not agree well with the involvement of a solvent-separated carbocation but is consistent with the related results of Chiappe and co-workers[18] involving a preassociation mechanism. As expected, the reaction is slower when chloroalkanes are employed and particularly sluggish with secondary chloroalkanes. For example, 2-bromohexane reacted with 4-nitrobenzoic acid (50 °C, 3 h) in the presence of Hünig's base to give the ester (81% yield), whereas under the same conditions 2-chlorohexane gave a 12% conversion.

One criticism that has been applied to the use of ILs is that often a volatile organic solvent is employed in the workup or product isolation,[38] partially defeating the original purpose and "green" credentials of the process.[39] This is essentially a process chemistry issue that on an industrial scale would require establishing a suitable protocol for isolation of the specific product under solvent-free conditions and allow reuse of the IL. To demonstrate process chemistry that would effect such solvent-free product isolation and IL recycling, the synthesis of the commodity ester butyl acetate was investigated. The reaction of acetic acid (1.10 equiv) and potassium carbonate (1.10 equiv) with bromobutane (1.0 equiv) was conducted in the phosphonium salt IL under slightly modified conditions. Thin-layer chromatography indicated clean conversion to the ester, which was isolated in 74% yield by direct distillation from the reaction mixture. Residual ester remains in the IL phase and no attempt at exhaustive distillation was made. The ionic-liquid phase was washed with water, dried, and a second esterification cycle was conducted. Butyl acetate was isolated in 85% yield after the second cycle. The low volatility and thermal stability of phosphonium salt ILs should allow direct solvent-free isolation of many desirable products in this manner.

Lastly, we investigated the stereochemical outcome of the alkylative esterification using the tosylate compound derived from (2*S*)-hexanol in reaction with 4-nitrobenzoic acid (Scheme 4). The reaction proceeded in the bistriflimide IL



Scheme 4. Alkylative esterification with (2*S*)-2-hexyl tosylate.

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in the presence of Hünig's base (80 °C, 3 h) to give the ester in 82 % isolated yield with a high degree of inversion of stereochemistry (er 4:96, retention/inversion). The reaction was slower at 50 °C but gave complete (>99 %) inversion of configuration. These results are consistent with the involvement of essentially an S_N2-type process with some ionization (and racemization) occurring at higher temperatures. This result is in agreement with earlier work carried out in conventional solvents.[33]

The standard phosphonium salt tetradecyl(trihexyl)phosphonium bistriflimide has been shown to be a highly effective medium for promoting various substitution reactions in an atom-economical, chemo- and stereoselective fashion. The reaction of primary electrophiles with a variety of nucleophiles proceeds without incident to give the expected S_N2 substitution product in high yields. This is not surprising when good nucleophiles (cyanide or azido) are employed, however, substitution is still the preferred pathway when both basic and weak nucleophiles (primary amines, carboxylate and phenoxide nucleophiles) are employed on a β-phenylethyl substrate prone to elimination. We have observed both elimination and solvolysis products by using β-aryl primary halides in conventional media such as DMF, most likely through involvement of a phenonium ion. It appears that ionization of such primary electrophiles is impeded in the IL at temperatures below 80 °C. The efficient substitution reactions with secondary bromides (see Table 2) and the reaction of the chiral secondary tosylate investigated are also consistent with a general S_N2 process with partial racemization being observed only at higher temperatures. Although the latter reaction is slow at 50 °C, clean inversion and no elimination byproducts were observed at this temperature. As substitution reactions in solvents of high polarity typically proceed through the borderline S_N1/S_N2 region,[18] this result is consistent with recent polarity measurements that indicate imidazolium bistriflimide IL solvent polarity to be similar to that of acetonitrile[17a] and highlights the fact that ILs are not as polar as is often assumed.[4,17b] We believe that the lack of elimination and racemization seen in this case are key observations that free, dissociated or solvent-separated carbocations are not readily formed in the phosphonium bistriflimide. We attribute this to the lack of basic lone pairs in this moderately polar solvent, in contrast to typical dipolar media (DMF, DMSO) that would hinder complete ionization.

Conclusion

In conclusion, general substitution reactions conducted in tetradecyl(trihexyl)phosphonium bistriflimide IL proceed through a narrow spectrum[40] of pathways that, depending upon the structure of the electrophile, range from straightforward S_N2 to those that proceed through preassociation[18] involving a nucleophilically assisted saddle point approaching the S_N1 limit.[41] The results indicate that free, dissociated carbocations are only formed under forcing conditions, thus allowing for high chemoselectivity favoring substitution over elimination, and stereoselectivity in favor of inversion. These results are consistent with our hypothesis that the phosphonium bistriflimide IL would offer little in terms of carbocation stabilization in contrast to standard dipolar solvents. In those cases in which the reaction proceeds through a preassociation pathway, cross over to competitive E1 pathways are hindered due to the nonbasic nature of the media and the lack of a donor that might affect proton shuttling as this limit is approached. We report the first examples of highly chemoselective Kornblum-type substitution reactions in an IL that provide nitro-substitution products exclusively with simple aliphatic primary halides and problematic β-aryl halides. Lastly, imidazolium salts have been shown to exist as supramolecular aggregates in crystalline form and to retain these structures to some extent in solution. Such nanostructured materials may possess catalytically active sites that act in synergy for example by polarizing a carbon–halogen bond through electrophilic activation, thus lowering the barrier for incoming nucleophilic attack without compromising elimination or other side reactions. The precise nature of the present phosphonium bistriflimide IL is currently being investigated and further applications of the selective methodology described towards the synthesis of biologically important targets is under active investigation in our laboratories.

Experimental Section

Tetradecyl(trihexyl)phosphonium bis(trifluoromethylsulfonyl)imide[35] (note: the anion is commonly referred to as "bistriflimide") was prepared according to the literature method.[43] This material was washed until no halide could be detected (using $AgNO_3$) and was dried under high vacuum for several hours before each use. IR spectra were measured on a Bio-Rad FTS-40 series spectrometer in dry film (NaCl). CIMS were run on a Micromass Quattro Ultima spectrometer fitted with a direct injection probe (DIP) with ionization energy set at 70 eV and HRMS (CI) were performed with a Micromass Q-Tof Ultima spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker 500 or AV 700 spectrometer in $CDCl_3$ with TMS as internal standard, chemical shifts are reported in units of δ (ppm) and coupling constants (J) are expressed in Hz.

General procedure for alkylation (i.e., Table 1): The electrophile (1 mmol) and nucleophile (2 mmol) were added to the ionic liquid (0.5 g) followed by the addition of 0.3 mL water (for nitration, cyanylation, and azidonation reactions only), and the reaction mixture was stirred at 80 or 90 °C. After analysis by TLC indicated that the reaction was complete (in all cases within 6 h), the mixture was poured into a methanol/water (3:2) solution (5 mL) and extracted with *n*-hexane (3×5 mL), which partitioned the ionic-liquid layer between the upper organic and lower aqueous phases. The combined hexane fractions were dried over anhydrous Na_2SO_4, diluted with 5 % ethyl acetate, filtered through a plug of silica gel, and the solution was concentrated under reduced pressure to give the alkylated product in 80–90 % yield.

3-Phenylpropionitrile (Table 1, entries 1, 4, and 7): ^1H NMR ($CDCl_3$, 200 MHz): $\delta = 7.31$ (m, 5H), 2.96 (t, $J = 7.4$, 7.3 Hz, 2H), 2.62 ppm (t, $J = 7.4$, 7.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 145.0$, 135.7, 135.6, 135.1, 135.0, 134.1, 126.5, 38.4, 26.2 ppm; IR (NaCl): $\tilde{\nu} = 2927$, 2248, 1604, 1559, 1456 cm^{-1}; EIMS (70 eV): m/z (%): 131 (20) [M^+], 120 (100), 91 (50); HRMS (EI): m/z calcd for C_9H_9N: 131.0735; found: 131.0713.

2-Phenyl azidoethane (Table 1, entries 2, 5, and 8): ^1H NMR ($CDCl_3$, 200 MHz): $\delta = 7.29$ (m, 5H), 3.52 (t, $J = 7.4$, 7.3 Hz, 2H), 2.91 ppm (t, $J =$

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7.4, 7.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ=145.0, 135.6, 135.5, 135.4, 135.3, 133.6, 59.3, 42.2 ppm; IR (NaCl): $\tilde{\nu}$=2927, 2098, 1604, 1559, 1460 cm^{-1}; EIMS (70 eV): *m*/*z* (%): 147 (5) [M^+], 119 (42), 105 (32), 91 (100); HRMS (EI): *m*/*z* calcd for $C_8H_9N_3$: 147.0875; found: 147.0865.

Bis(2-phenylethyl) benzylamine (Table 1, entries 3 and 6): ^{1}H NMR ($CDCl_3$, 200 MHz): δ=7.21 (m, 15H), 3.76 (s, 2H), 2.81 ppm (s, 8H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ=147.5, 147.4, 146.5, 135.7, 135.6, 135.5, 135.4, 135.3 (2C), 135.2 (2C), 135.1 (2C), 135.0 (2C), 133.7, 132.8, 132.7, 65.3, 62.5, 62.4, 40.4, 40.3 ppm; IR (NaCl): $\tilde{\nu}$=2929, 1603, 1544, 1454, 503 cm^{-1}; EIMS (70 eV): *m*/*z* (%): 315 (5) [M^+], 224 (10), 206 (10), 191 (40), 149 (5), 120 (8), 105 (100); HRMS (EI): *m*/*z* calcd for $C_{23}H_{25}N$: 315.4581; found: 315.4568.

2-Nitroethylbenzene (Table 1, entry 9): ^{1}H NMR ($CDCl_3$, 200 MHz): δ= 7.26 (m, 5H), 4.61 (t, *J*=7.3, 7.4 Hz, 2H), 3.32 ppm (t, *J*=7.4, 7.4 Hz, 2H); ^{13}C NMR (CD_3OD, 50 MHz): δ=139.5, 128.5 (2C), 127.4 (2C), 126.0, 76.3, 33.4 ppm; IR (NaCl): $\tilde{\nu}$=2997, 2881, 1553, 1480, 1443, 1403, 1357 cm^{-1}; CIMS (70 eV): *m*/*z* (%): 151 (10) [M^+], 135 (10), 104 (100), 77.0 (20); HRMS (CI): *m*/*z* calcd for $C_8H_9NO_2$: 151.0633; found: 151.0635 [M^+−H].

1-Nitroheptane (Table 1, entry 10): ^{1}H NMR ($CDCl_3$, 200 MHz): δ=4.37 (t, *J*=7.0 Hz, 2H), 2.00 (m, 2H), 1.27 (m, 8H), 0.88 ppm (t, *J*=6.1, 6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ=75.6, 32.0, 31.5, 29.6, 28.1, 22.6, 14.1 ppm; IR (NaCl): $\tilde{\nu}$=2970, 2876, 2829, 1577, 1457, 1350 cm^{-1}; CIMS (70 eV): *m*/*z* (%): 144 (100) [M^+], 128 (10), 45 (20), 31 (10); HRMS (CI): *m*/*z* calcd for $C_7H_{14}NO_2$: 144.1025; found: 144.1002 [M^+−H].

1-Nitrooctane (Table 1, entry 11): ^{1}H NMR ($CDCl_3$, 200 MHz): δ=4.37 (t, *J*=7.0 Hz, 2H), 1.96 (m, 2H), 1.26 (m, 10H), 0.87 ppm (t, *J*=6.1, 6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ=75.7, 31.9, 29.6, 28.9, 27.4, 26.2, 22.5, 14.0 ppm; IR (NaCl): $\tilde{\nu}$=2925, 2855, 1526, 1465, 1378 cm^{-1}; CIMS (70 eV): *m*/*z* (%): 158 (50) [M^+], 124 (10), 74 (70), 45 (100); HRMS (CI): calcd for $C_8H_{16}NO_2$: 158.1181; found: 158.1184 [M^+−H].

1-Nitrododecane (Table 1, entry 12): ^{1}H NMR ($CDCl_3$, 200 MHz): δ= 4.36 (t, *J*=7.0, 7.0 Hz, 2H), 1.99 (m, 2H), 1.25 (m, 18H), 0.87 ppm (t, *J*= 6.0, 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ=75.7, 31.9, 29.7 (3C), 29.5, 29.4, 28.8, 27.4, 26.2, 22.7, 14.1 ppm; IR (NaCl): $\tilde{\nu}$=2928, 2855, 1550, 1468, 1380 cm^{-1}; CIMS (70 eV): *m*/*z* (%): 214 (100) [M^+], 198 (15), 177 (5), 45 (10); HRMS (CI): *m*/*z* calcd for $C_{12}H_{24}NO_2$: 214.1807; found: 214.1846 [M^+−H].

1-Butoxy-4-iodobenzene (Table 1, entry 14): ^{1}H NMR ($CDCl_3$, 200 MHz): δ=7.52 (d, *J*=6.9 Hz, 2H), 6.65 (d, *J*=6.9 Hz, 2H), 3.90 (t, *J*=6.3, 6.4 Hz, 2H), 1.75 (m, 2H), 1.45 (m, 2H), 0.87 ppm (t, *J*=7.2, 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ=159.0, 138.1 (2C), 116.9 (2C), 82.4, 67.8, 31.2, 19.2, 13.8 ppm; IR (NaCl): $\tilde{\nu}$=2960, 2873, 1587, 1572, 1486, 1474, 1283, 1245, 1174, 1000, 819 cm^{-1}; CIMS (70 eV): *m*/*z* (%): 276 (70) [M^+], 219 (100), 150 (10), 83 (10); HRMS (CI): *m*/*z* calcd for $C_{10}H_{13}OI$: 276.0011; found: 276.0016.

General procedure for esterification (i.e., Table 2)

Ethyl 4-bromobenzoate (Table 2, entry 5): 4-Nitrobenzoic acid (40 mg, 0.24 mmol), Hünig's base (0.48 mmol), and tetradecyl-(trihexyl)phosphonium bistriflimide IL (0.50 g) were stirred at 30°C under Ar for 10 min whereupon bromoethane (0.48 mmol) was added. After analysis by TLC indicated that the reaction was complete (in all cases within 12 h), the reaction mixture was poured into a methanol/water (3:2) solution (5 mL) and extracted with *n*-hexane (3×5 mL). The hexane fractions were dried over anhydrous sodium sulfate, diluted with 5% v/v ethyl acetate, and the solution was filtered through a plug of silica gel. Concentration of the filtrate gave the ester product in 95% yield. All compounds reported were characterized by using ^{1}H and ^{13}C NMR spectroscopy as well as MS and high-resolution (HR) MS data.

Octyl propionate (Table 2, entry 1): ^{1}H NMR ($CDCl_3$, 200 MHz): δ=4.03 (t, *J*=6.6, 6.7 Hz, 2H), 3.37 (t, *J*=6.8, 6.8 Hz, 2H), 2.27 (m, 2H), 1.82 (m, 2H), 1.59 (m, 2H), 1.13 (t, *J*=6.6, 6.7 Hz, 3H), 1.24 ppm (m, 12H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ=174.3, 64.3, 33.7, 32.8, 31.7, 29.1, 28.6, 27.5, 25.8, 22.5, 13.9 ppm; IR (NaCl): $\tilde{\nu}$=2958, 2929, 1741, 1465, 1185, 1084 cm^{-1}; EIMS (70 eV): *m*/*z* (%): 187 (5) [M^+], 112 (50), 205 (20), 83 (70), 57 (100); HRMS (EI) calcd for $C_{11}H_{23}O_2$: 187.1698; found: 187.1682.

Phenylethyl propionate (Table 2, entry 2): ^{1}H NMR ($CDCl_3$, 200 MHz): δ=7.28 (m, 5H), 4.29 (t, *J*=7.0, 7.0 Hz, 2H), 2.94 (t, *J*=7.0, 7.0 Hz, 2H), 2.33 (q, *J*=7.5, 7.5, 7.5 Hz, 2H), 1.12 ppm (t, *J*=7.5, 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ=174.3, 137.9, 128.9 (2C), 128.4 (2C), 126.5, 64.7, 35.1, 27.5, 9.1 ppm; IR (NaCl): $\tilde{\nu}$=3030, 2349, 1738, 1498, 1384, 1349 cm^{-1}; EIMS (70 eV): *m*/*z* (%): 178 (10) [M^+], 104 (100), 91 (15), 57 (80), 51 (10); HRMS (EI): *m*/*z* calcd for $C_{11}H_{14}O_2$: 178.0994; found: 178.0988.

Octyl benzoate (Table 2, entry 3): ^{1}H NMR ($CDCl_3$, 200 MHz): δ=8.06 (d, *J*=7.4 Hz, 2H), 7.51 (m, 3H), 4.34 (t, *J*=6.6, 6.6 Hz, 2H), 1.76 (m, 2H), 1.29 (m, 10H), 0.96 ppm (m, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ= 164.9, 133.1 (2C), 128.9, 128.7, 127.9, 127.8, 63.4, 31.9, 30.1, 27.6, 27.1, 24.4, 21.0, 12.4 ppm; IR (NaCl): $\tilde{\nu}$=2929, 2858, 1719, 1603, 1274, 1113 cm^{-1}; EIMS (70 eV): *m*/*z* (%): 234 (5) [M^+], 123 (100), 105 (90), 77 (75), 70 (20); HRMS (EI): *m*/*z* calcd for $C_{15}H_{22}O_2$: 234.1620; found: 234.1609.

2-Phenylethyl benzoate (Table 2, entry 4): ^{1}H NMR ($CDCl_3$, 200 MHz): δ=8.05 (d, *J*=7.3 Hz, 2H), 7.43 (m, 8H), 4.55 (t, *J*=7.0, 6.9 Hz, 2H), 3.09 ppm (t, *J*=6.9, 6.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ=166.4, 137.9, 132.9, 130.3, 129.5 (2C), 128.9 (2C), 128.5 (2C), 128.3 (2C), 127.8, 65.4, 35.2 ppm; IR (NaCl): $\tilde{\nu}$=3030, 2966, 2925, 1719, 1603, 1274 cm^{-1}; EIMS (70 eV): *m*/*z* (%): 234 (100) [M^+], 211 (10), 183 (15), 178 (15), 176 (10); HRMS (EI): *m*/*z* calcd for $C_{15}H_{14}O_2$: 226.0994; found: 226.0988.

Ethyl 4-nitrobenzoate (Table 2, entry 5): ^{1}H NMR ($CDCl_3$, 200 MHz): δ=8.29 (d, *J*=9.0 Hz, 2H), 8.21 (d, *J*=9.0 Hz, 2H), 4.43 (q, *J*=7.0, 14.1 Hz, 2H), 1.43 ppm (t, *J*=7.0, 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ=172.2, 157.4, 142.7, 137.5, 137.4, 130.3, 130.2, 68.8, 21.1 ppm; IR (NaCl): $\tilde{\nu}$=2993, 1717, 1605, 1526, 1474, 1457, 1368 cm^{-1}; EIMS (70 eV): *m*/*z* (%): 195 (31) [M^+], 166 (42), 150 (100); HRMS (EI): *m*/*z* calcd for $C_9H_9NO_4$: 195.0532; found: 195.0512.

Isopropyl 4-nitrobenzoate (Table 2, entry 6): ^{1}H NMR ($CDCl_3$, 200 MHz): δ=8.28 (d, *J*=9.1 Hz, 2H), 8.19 (d, *J*=9.1 Hz, 2H), 5.29 (m, 1H), 1.39 ppm (d, *J*=6.6 Hz, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ=171.0, 157.8, 142.7, 137.5, 137.4, 130.3, 130.2, 76.5, 28.7, 28.6 ppm; IR (NaCl): $\tilde{\nu}$=2988, 1718, 1608, 1529, 1469, 1350 cm^{-1}; EIMS (70 eV): *m*/*z* (%): 209 (10) [M^+], 173 (3), 150 (100); HRMS (EI): *m*/*z* calcd for $C_{10}H_{11}NO_4$: 209.2020; found: 209.2010.

Cyclohexyl 4-nitrobenzoate (Table 2, entry 7): ^{1}H NMR ($CDCl_3$, 200 MHz): δ=8.28 (d, *J*=9.2 Hz, 2H), 8.20 (d, *J*=9.2 Hz, 2H), 5.06 (m, 1H), 1.96 (m, 2H), 1.78 (m, 2H), 1.57 (m, 2H), 1.41 ppm (m, 4H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ=170.9, 157.3, 143.2, 137.5, 137.4, 130.3, 130.2, 81.2, 38.4, 38.3, 32.2, 30.5, 30.4 ppm; IR (NaCl): $\tilde{\nu}$=2939, 1722, 1608, 1530, 1452, 1349 cm^{-1}; EIMS (70 eV): *m*/*z* (%): 249 (1) [M^+], 233 (1), 194 (1), 168 (8), 150 (50), 120 (30), 104 (86), 82 (100); HRMS (EI): *m*/*z* calcd for $C_{13}H_{15}NO_4$: 249.1001; found: 249.1008.

Ethyl 4-chlorobenzoate (Table 2, entry 8): ^{1}H NMR ($CDCl_3$, 200 MHz): δ=7.99 (d, *J*=8.4 Hz, 2H), 7.40 (d, *J*=8.2 Hz, 2H), 4.37 (q, *J*=7.1, 14.0 Hz, 2H), 1.38 ppm (t, *J*=7.0, 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ=166.0, 138.1, 131.1, 131.0, 129.0, 128.8, 128.7, 61.3, 14.4 ppm; IR (NaCl): $\tilde{\nu}$=2927, 1724, 1596, 1461, 1368, 761 cm^{-1}; EIMS (70 eV): *m*/*z* (%): 184 (5) [M^+], 164 (15), 135 (40), 119 (100); HRMS (EI): *m*/*z* calcd for $C_9H_9ClO_2$: 184.0291; found: 184.0302.

Isopropyl 4-chlorobenzoate (Table 2, entry 9): ^{1}H NMR ($CDCl_3$, 200 MHz): δ=7.97 (d, *J*=8.7 Hz, 2H), 7.40 (d, *J*=8.7 Hz, 2H), 5.24 (m, 1H), 1.36 ppm (d, *J*=6.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ=172.0, 146.0, 137.7, 137.6, 136.2, 135.4, 135.3, 75.5, 28.7, 28.6 ppm; IR (NaCl): $\tilde{\nu}$=2983, 1720, 1595, 1469, 1375, 762 cm^{-1}; EIMS (70 eV): *m*/*z* (%): 198 (5) [M^+], 155 (19), 138 (48), 135 (100); HRMS (EI): calcd for $C_{10}H_{11}ClO_2$: 198.0448; found: 198.0446.

Ethyl 4-methoxybenzoate (Table 2, entry 10): ^{1}H NMR ($CDCl_3$, 200 MHz): δ=7.99 (d, *J*=8.1 Hz, 2H), 6.91 (d, *J*=8.0 Hz, 2H), 4.33 (q, *J*=7.0, 14.1 Hz, 2H), 3.86 (s, 3H), 1.38 ppm (t, *J*=7.0, 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ=173.0, 170.0, 138.4, 138.3, 130.0, 120.3, 120.2, 67.5, 62.2, 21.2 ppm; IR (NaCl): $\tilde{\nu}$=2982, 1713, 1608, 1512, 1464,

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1368 cm^{-1}; EIMS (70 eV): m/z (%): 180 (5) [M^+], 164 (50), 136 (10), 118 (100); HRMS (EI): m/z calcd for $C_{10}H_{12}O_3$: 180.0786; found: 180.0757.

Isopropyl 4-methoxybenzoate (Table 2, entry 11): ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.99 (d, J = 9.0 Hz, 2H), 6.90 (d, J = 9.0 Hz, 2H), 5.22 (m, 1H), 3.85 (s, 3H), 1.34 ppm (d, J = 6.7 Hz, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 172.5, 170.0, 138.3, 138.2, 130.2, 120.3, 120.2, 74.8, 62.2, 28.8, 28.7 ppm; IR (NaCl): $\tilde{\nu}$ = 2981, 1711, 1608, 1512, 1465, 1374 cm^{-1}; EIMS (70 eV): m/z (%): 194 (15) [M^+], 179 (5), 152 (37), 135 (100); HRMS (EI): m/z calcd for $C_{11}H_{14}O_3$: 194.0943; found: 194.0949.

Ethyl 4-methylbenzoate (Table 2, entry 12): ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.94 (d, J = 8.1 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 4.35 (q, J = 7.0, 14.0 Hz, 2H), 2.40 (s, 3H), 1.37 ppm (t, J = 7.0, 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 167.5, 144.7, 130.3, 130.2, 129.8, 129.7, 128.0, 61.5, 22.4, 15.1 ppm; IR (NaCl): $\tilde{\nu}$ = 2958, 1735, 1618, 1522, 1459, 1385 cm^{-1}; EIMS (70 eV): m/z (%): 164 (5) [M^+], 136 (47), 118 (100); HRMS (EI): calcd for $C_{10}H_{12}O_2$: 164.2040; found: 164.2044.

Isopropyl 4-methylbenzoate (Table 2, entry 13): ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.92 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 8.2 Hz, 2H), 5.23 (m, 1H), 2.40 (s, 3H), 1.35 ppm (d, J = 6.7 Hz, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 166.5, 143.4, 129.6, 129.5, 129.1, 129.0, 128.0, 68.2, 22.1, 22.0, 21.7 ppm; IR (NaCl): $\tilde{\nu}$ = 2927, 1718, 1653, 1559, 1459, 1376 cm^{-1}; EIMS (70 eV): m/z (%): 178 (16) [M^+], 136 (37), 119 (100); HRMS (EI): m/z calcd for $C_{11}H_{14}O_2$: 178.0994; found: 178.0986.

Ethyl 2-methylbenzoate (Table 2, entry 14): ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.90 (d, J = 7.5 Hz, 1H), 7.37 (d, J = 7.6 Hz, 1H), 7.25 (m, 2H), 4.33 (q, J = 7.1, 14.0 Hz, 2H), 2.60 (s, 3H), 1.39 ppm (t, J = 7.0, 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 174.8, 147.0, 138.6, 138.5, 137.3, 137.1, 132.5, 67.5, 28.5, 21.2 ppm; IR (NaCl): $\tilde{\nu}$ = 2925, 1738, 1653, 1560, 1460, 1380 cm^{-1}; EIMS (70 eV): m/z (%): 164 (15) [M^+], 135 (100), 119 (44); HRMS (EI): m/z calcd for $C_{10}H_{12}O_2$: 164.0837; found: 164.0836.

Isopropyl 2-methylbenzoate (Table 2, entry 15): ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.87 (d, J = 7.4 Hz, 1H), 7.36 (d, J = 7.4 Hz, 1H), 7.24 (m, 2H), 5.24 (m, 1H), 2.59 (s, 3H), 1.32 ppm (d, J = 6.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 167.7, 140.5, 131.9, 131.8 (2C), 130.7, 125.9, 68.4, 22.2, 22.1, 22.0 ppm; IR (NaCl): $\tilde{\nu}$ = 2926 (CH), 1735, 1653, 1559, 1461, 1379 cm^{-1}; EIMS (70 eV): m/z (%): 178 (5) [M^+], 155 (86), 138 (100); HRMS (EI): m/z calcd for $C_{11}H_{14}O_2$: 178.0994; found: 178.0993.

Ethyl 2,4,6-trimethylbenzoate (Table 2, entry 16): ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 6.85 (s, 2H), 4.36 (q, J = 7.0, 14.0 Hz, 2H), 2.28 (s, 9H), 1.38 ppm (t, J = 7.0, 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 177.4, 146.5, 141.2, 141.1, 137.7, 135.2, 135.1, 67.6, 27.9, 26.5, 26.4, 21.1 ppm; IR (NaCl): $\tilde{\nu}$ = 2981, 1727, 1613, 1449, 1366 cm^{-1}; EIMS (70 eV): m/z (%): 192 (38) [M^+], 163 (20), 147 (100), 119 (26); HRMS (EI): m/z calcd for $C_{12}H_{16}O_2$: 192.1150; found: 192.1150.

Isopropyl 2,4,6-trimethylbenzoate (Table 2, entry 17): ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 6.84 (s, 2H), 5.28 (m, 1H), 2.29 (s, 6H), 2.27 (s, 3H), 1.35 ppm (d, J = 6.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 146.2, 141.5, 141.4, 141.3, 138.2, 135.2, 135.1, 75.1, 28.7, 28.6, 27.9, 26.4, 26.3 ppm; IR (NaCl): $\tilde{\nu}$ = 2980, 1723, 1613, 1559, 1457, 1376 cm^{-1}; EIMS (70 eV): m/z (%): 206 (22) [M^+], 164 (25), 147 (100), 119 (23); HRMS (EI): m/z calcd for $C_{13}H_{18}O_2$: 206.1307; found: 206.1301.

Ethyl 2-(3,4-methylenedioxyphenyl) acetate (Table 2, entry 18): ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 6.76 (d, J = 9.0 Hz, 2H), 6.68 (s, 1H), 5.93 (s, 2H), 4.14 (q, J = 7.0, 14.1 Hz, 2H), 3.51 (s, 2H), 1.25 ppm (t, J = 7.1, 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 178.0, 155.0, 153.0, 134.7, 129.2, 116.3, 115.1, 107.8, 67.7, 47.8, 21.0 ppm; IR (NaCl): $\tilde{\nu}$ = 2984, 1735, 1610, 1504, 1446, 1368, 932 cm^{-1}; EIMS (70 eV): m/z (%): 208 (30) [M^+], 180 (1), 159 (1), 135 (100); HRMS (EI): m/z calcd for $C_{11}H_{12}O_4$: 208.0736; found: 208.0738.

Isopropyl 2-(3,4-methylenedioxyphenyl) acetate (Table 2, entry 19): ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 6.75 (d, J = 9.1 Hz, 2H), 6.72 (s, 1H), 5.93 (s, 2H), 5.00 (m, 1H), 3.48 (s, 2H), 1.22 ppm (d, J = 6.3 Hz, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 177.8, 154.8, 153.0, 134.8, 129.2, 116.5, 115.1, 107.8, 75.0, 48.1, 28.6, 28.5 ppm; IR (NaCl): $\tilde{\nu}$ = 2984, 1735, 1653, 1506, 1446, 1370, 932 cm^{-1}; EIMS (70 eV): m/z (%): 222 (15) [M^+], 208 (12), 180 (1), 135 (100); HRMS (EI): m/z calcd for $C_{12}H_{14}O_4$: 222.0892; found: 208.0896.

Butyl 4-nitrobenzoate (Table 2, entry 21): ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 8.29 (d, J = 8.0 Hz, 2H), 8.20 (d, J = 8.0 Hz, 2H), 4.38 (t, J = 6.1, 6.2 Hz, 2H), 1.78 (m, 2H), 1.50 (m, 2H), 0.99 ppm (t, J = 6.2, 6.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 172.0, 157.2, 142.6, 137.5, 137.4, 130.3, 130.2, 72.6, 37.4, 26.0, 20.5 ppm; IR (NaCl): $\tilde{\nu}$ = 2963, 1727, 1608, 1530, 1466, 1351 cm^{-1}; EIMS (70 eV): m/z (%): 223 (1) [M^+], 207 (1), 168 (5), 150 (15), 119 (5), 83 (100); HRMS (EI): m/z calcd for $C_{11}H_{13}NO_4$: 223.0845; found: 223.0839.

Dodecyl 4-nitrobenzoate (Table 2, entry 22): ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 8.29 (d, J = 9.0 Hz, 2H), 8.20 (d, J = 9.0 Hz, 2H), 4.36 (t, J = 6.1, 6.2 Hz, 2H), 1.80 (m, 2H), 1.26 (m, 20H), 0.87 ppm (t, J = 6.2, 6.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 172.0, 157.0, 142.5, 137.5, 137.4, 130.3, 130.2, 72.9, 38.7, 36.4, 36.3, 36.2 (2C), 36.1 (2C), 35.4, 32.8, 29.5, 20.9 ppm; IR (NaCl): $\tilde{\nu}$ = 2960, 1717, 1606, 1527, 1470, 1351 cm^{-1}; EIMS (70 eV): m/z (%): 335 (2) [M^+], 305 (33), 289 (1), 278 (1), 169 (50), 137 (100), 119 (21); HRMS (EI): m/z calcd for $C_{19}H_{29}NO_4$: 335.2097; found: 335.2101.

Dibutyl phthalate (Table 2, entry 23): ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.70 (d, J = 3.2 Hz, 1H), 7.53 (d, J = 3.3 Hz, 1H), 4.29 (t, J = 6.5, 6.0 Hz, 2H), 1.71 (m, 2H), 1.48 (m, 2H), 1.13 ppm (m, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 167.6 (2C), 132.2 (2C), 130.8 (2C), 128.8 (2C), 65.5 (2C), 30.5 (2C), 19.1 (2C), 13.7 ppm (2C); IR (NaCl): $\tilde{\nu}$ = 1750, 1600, 1290, 1122, 1075, 745 cm^{-1}; EIMS (70 eV): m/z (%): 278 (10) [M^+], 223 (20), 205 (20), 150 (10), 149 (100), 31 (50); HRMS (EI): m/z calcd for $C_{16}H_{22}O_4$: 278.1518; found: 278.1523.

***tert*-Butyl 4-nitrobenzoate (Table 2, entry 24)**: ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 8.26 (d, J = 9.0 Hz, 2H), 8.14 (d, J = 9.0 Hz, 2H), 1.61 ppm (s, 9H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 171.0, 157.5, 144.8, 137.3, 137.2, 130.2, 130.1, 89.8, 34.9, 34.8, 34.7 ppm; IR (NaCl): $\tilde{\nu}$ = 2982, 1717, 1607, 1527, 1460, 1350 cm^{-1}; EIMS (70 eV): m/z (%): 223 (5) [M^+], 185 (1), 150 (100), 135 (5), 120 (10), 104 (40); HRMS (EI): m/z calcd for $C_{11}H_{13}NO_4$: 223.0845; found: 223.0838.

(2*R*)-2-Hexyl-4′-nitrobenzoate (Scheme 4): Hünig's base (0.015 mL, 0.089 mmol) was added to a solution of 4-nitrobenzoic acid (14.7 mg, 0.089 mmol) in tetradecyl(trihexyl)phosphonium bistriflimide ionic liquid (100 mg) at room temperature under Ar. The reaction mixture was stirred for 10 min followed by addition of (2*S*)-2-hexyl-4′-methylbenzenesulfonate (15 mg, 0.059 mmol). The reaction mixture was then stirred at 80 °C for 3 h or at 50 °C for 10 h. The product was extracted from the ionic liquid with hexane (5.0 mL) and saturated aqueous Na_2CO_3 (1.0 mL) five times. The combined hexane layers were concentrated and purified on a short silica gel column (10 × 1 cm; eluant: hexane/EtOAc 9:1) to give 2-hexyl-4′-nitro benzoate in 82% and 33% isolated yield, respectively. ^{1}H NMR ($CDCl_3$): δ = 8.17 (AB, J = 8.7 Hz, 4H), 5.11 (m, 1H), 1.80–1.33 (m, 2H), 1.29 (d, J = 6.2 Hz, 3H), 1.32–1.25 (m, 4H), 0.83 ppm (t, J = 6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 164.7, 150.8, 136.7, 131.0, 123.9, 73.5, 36.0, 27.9, 22.9, 20.4, 14.4 ppm. Enantiomeric purity of the esters (retention/inversion 4:96 for the reaction at 80 °C and >99% inversion at 50 °C) was determined by means of direct chiral GC on an Astec β-PM capillary column (30 m × 0.25 mm; flow rate = 0.5 mL min^{-1}; T = 135 °C). Standard retention times were 143.0 min for (2*S*)-2-hexyl-4′-nitrobenzoate, and 144.5 min for (2*R*)-2-hexyl-4′-nitrobenzoate.

Ionic-liquid recycling protocol

Synthesis of n-butyl acetate: Glacial acetic acid (1.10 g, 18.3 mmol) and K_2CO_3 (2.53 g, 18.3 mmol) were dissolved in an ionic liquid (10.0 mL) and the solution was stirred at 70 °C for 30 min under Ar and then bromobutane (1.79 mL, 16.6 mmol) was added. After 6 h the reaction was complete. The temperature was then raised to 130 °C and the *n*-butyl acetate was distilled (127–128 °C) directly from the reaction mixture yielding 1.42 g (74%). The IL was subsequently cooled to RT, partitioned with water (3 × 20 mL), and dried under vacuum. A second identical reaction was then carried out in the recycled IL to yield butyl acetate in an overall 85% yield after distillation.

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