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Review

Ionic Liquids: Advances and Applications in Phase Transfer Catalysis

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Abstract: Ionic liquids are a family of liquids that are composed entirely of ions and usually have melting points lower than 100 °C. Extensive research, along with the ever-growing interest of the scientific community, allowed for the development of a multitude of ionic liquids with low melting points. Such compounds are considered neoteric materials as well as ideal, custom-made solvents for a variety of different chemical transformations. In this regard, the importance of phase transfer catalysis is evident in a diversity of substrates and reactions. The use of phase transfer catalysts allows the reaction to proceed, facilitating the transfer of otherwise insoluble reactants to the desired phase. Recent scientific advances led to the emergence of ionic liquids, which are excellent candidates as phase transfer catalysts. The inherent fine-tuning capability of these molecules, along with the potential of phase transfer catalytic reactions, epitomize the sustainable aspect of this field of research. Herein, a cohesive report of such applications will be presented, including the period from the last decade of the 20th century up to date.

Keywords: ionic liquids; phase transfer catalysis; catalysis; green chemistry

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1. Introduction

Since the dawn of modern chemistry, scientists have been tirelessly working toward the generation of novel molecules which can be exploited in many ways, allowing for the development of various materials with notable technological and biological functions. Thermodynamic barriers such as activation energy pose challenges in the completion of chemical transformations. In this regard, the use of catalysis was a crucial advancement since they allow for the lowering of these energy barriers, increasing the rate of a reaction using a reagent that is not consumed: the catalyst. A multitude of catalysts have been implemented that allowed for the development of numerous different reactions, methodologies, and materials. Additionally, considering the ever-increasing need for sustainable pathways toward the development of new materials, catalysis can offer an alternative to traditional methodologies with respect to the pillars of "Green Chemistry". Some of the earliest examples of catalytic sustainability are the implementation of solvent-free reactions as well as the use of "green" neoteric solvents. Elaborating on that, the use of ionic liquids (ILs) in many reactions is considered a significant alternative which overcomes many of the drawbacks of standard organic solvents, such as high vapor pressure, toxicity, low biodegradability, and limitations regarding their solvation ability [1–14]. In this direction, our research group has developed protic ILs which can be used in various applications [15–19].

An important pillar of organic chemistry that over the years has attracted significant attention by the scientific community is phase transfer catalysis (PTC) which offers a more environmentally benign alternative to classic synthetic methodologies [20–28]. The focal point of this review is to highlight the application of ILs in phase transfer catalytic protocols in an attempt to develop greener synthetic methodologies. The use of ILs for such applications is an emerging research area, and this can be concluded by the number of research publications in the catalysis areas using ILs over the past two decades (Figure 1). To the best of our knowledge, it is the first attempt to enlist all the literature data regarding the use of ILs in PTC. The following presents, in chronological order and per different reactions, the literature data regarding the implementation of ILs in PTC.

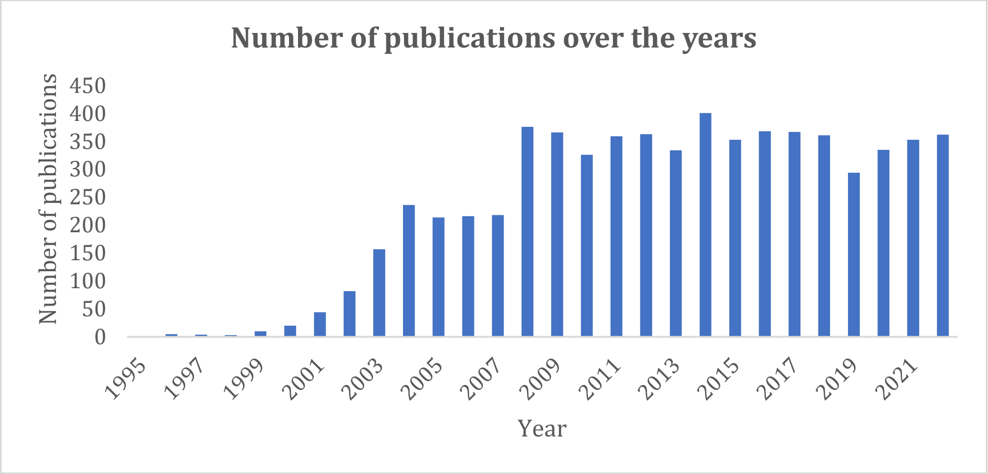


Figure 1. Graphical representation of publications per year in the domain of "*ionic liquids*" in "*catalysis*" in the period between 1995–2022. (Database: Scopus, search terms: "Ionic Liquids" AND "Catalysis", January 2023).

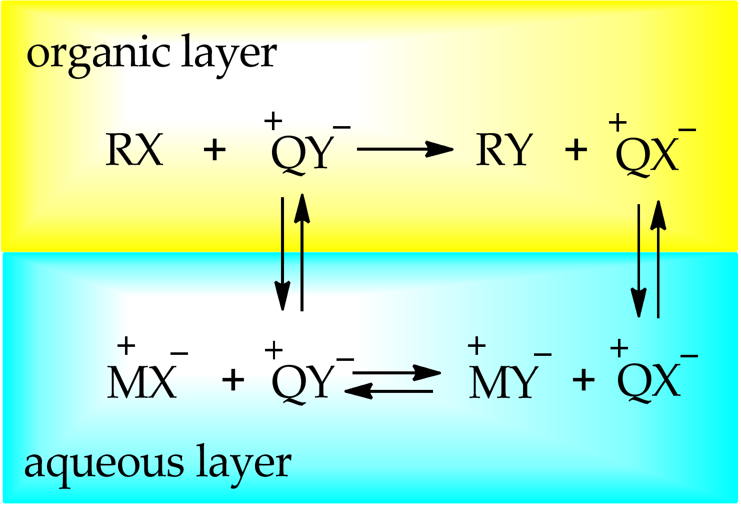
2. The Concept of Phase Transfer Catalysis

Phase transfer catalysis (PTC) is a well-known catalytic methodology in a range of chemical applications [29]. Numerous applications can be found in all fields of industrial processes, such as the production of organic dyes, fragrances, as well as the synthesis of polymers and pharmaceuticals [21,22,26,30–40]. Moreover, it is worth noting that the chemical community still emphasizes the value of PTC, especially as the demand for more sustainable and efficient catalytic protocols is growing. In that regard, PTC will probably attract the interest of the scientific community in the future.

2.1. Principles of Phase Transfer Catalysis

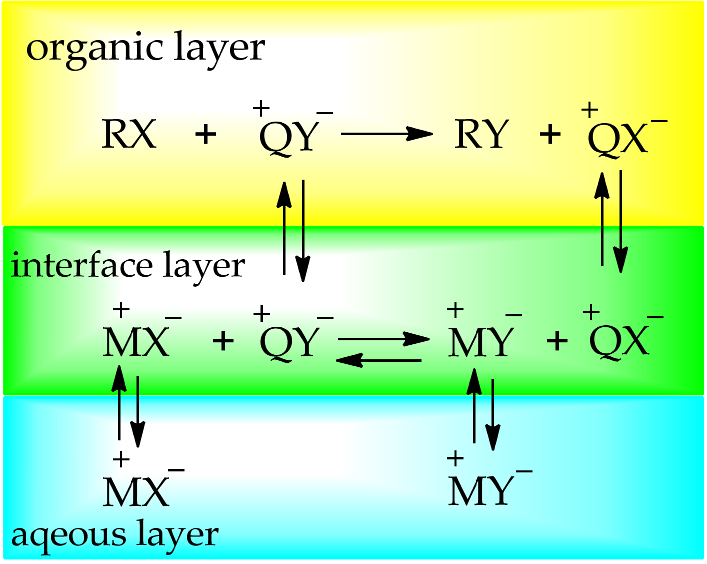
In general, PTC is capable of increasing the rate of a reaction and allows for better reaction selectivity. Additionally, it facilitates the miscibility of different reactants that would otherwise be immiscible should a PTC protocol not be followed. Organic reactions are usually performed in a homogeneous environment where all reactants are dissolved into a solvent. However, when a heterogeneous system is required, for example using an organic solvent phase and an aqueous phase, some reactions proceed slowly or no reaction is observed at all [29,41–43]. In some cases, these obstacles could be overcome if the use of polar aprotic solvents was implemented, but that would require anhydrous conditions that could be economically unfavorable in industrial production. In this context, many reactions that, under normal circumstances, require extreme conditions or have a slow rate of completion can be completed under mild conditions if a phase transfer catalyst is used. In general, two broad categories of mechanisms have been proposed for PTC which favor distinct families of reactions. It is worth noting that microemulsions are rather an antagonizing agent regarding possible applications since, macroscopically, they are homogeneous but heterogeneous microscopically. Thus, they can be regarded as an intermediate between heterogeneous PTC systems and homogeneous solutions [44].

The first mechanism is called "extractive type" and describes reactions where the transfer of nucleophiles to the organic phase occurs through a phase transfer catalyst which is miscible in both phases [38]. In this regard, it is widely applied in displacement reactions as well as alkylation, etherifications, and esterifications [29,30,45]. Elaborating on the mechanistic aspect as described by Ch. Starks [45], when all reactants are dissolved into their respective phases, PTC includes two basic steps. Firstly, the necessary species (Y^-) for the completion of the reaction are transferred from the phase in which they are dissolved to the other phase in which they would be immiscible. The interaction of the phase transfer catalyst (Q^+) and Y^- generates an ionic pair which allows for the transfer to take place. Then, the reaction between these species (Y^-) and the substrate (RX) which is present in this phase occurs, and the desired product (RY) is obtained (the mechanism is presented in Scheme 1).



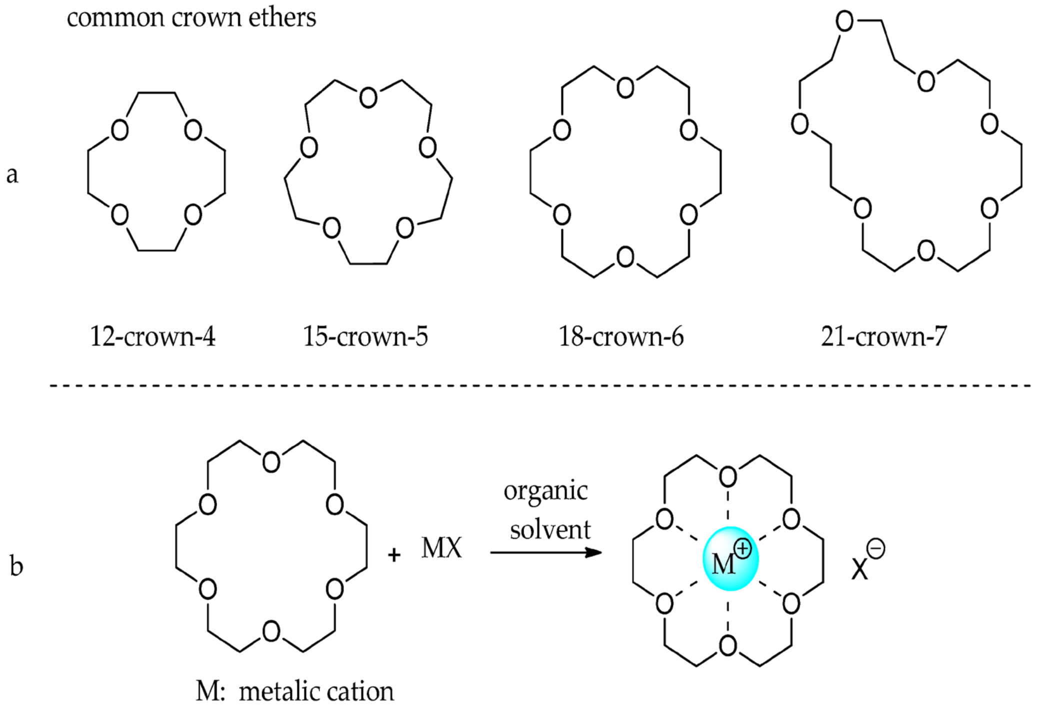
Scheme 1. General extractive mechanism for PTC reactions.

The other mechanism in which the PTC can occur is called "interface type", and it generally applies to carbene reactivity and polymerization reactions [20,30,38,41]. The key difference is the lipophilicity of the catalyst, which is not miscible in both liquid phases; thus, the catalytic species (Q^+) are dissolved only in the organic phase and the interface layer [41]. The anionic exchange between the catalyst and the water-dissolved reactant (MY) in the interface layer permits the transfer of the Y^- into the organic phase via an ionic pair with Q^+ [42]. Subsequently, the reaction between the substrate RX and Y^- species ensues the generation of the desired product (Scheme 2) [42].



Scheme 2. General interface-type mechanism for PTC reactions.

The great importance of the catalytic species is apparent when a PTC protocol is applied. Thus, different types of catalysts have been developed and utilized through the years in a multitude of applications. The earliest notable type of such catalysts is quaternary ammonium and phosphonium amphiphilic salts [46]. They are comprised from a central nitrogen or phosphorous atom connected with four alkyl chains forming the cation and an anionic counterpart. The ideal balance between hydro- and lipophilicity depends on the length of the carbon backbone of the substituents. Additionally, the catalytic activity is affected by the stereochemical factors regarding the alkyl chains. The ease of access and the great structural tunability of these catalysts have established their use in many chemical transformations both in industrial- and laboratory-scale applications. Similarly, an emerging type of phase transfer catalyst is crown ethers, which also present an interesting option taking into consideration the low price, facile synthesis, and great chemical stability of such molecules [32]. Some widely used crown ethers are depicted in Scheme 3a and present affinity with metallic salts. The greater lipophilicity of these compounds generally favors the interface-type mechanism. Regarding the mechanistic aspect, the electron-rich hole that is structurally present on these ethers stabilizes the cationic part of the ion pair thus making possible the transfer of the anionic part into nonpolar phases (Scheme 3b). Additionally, the anionic part of this system is disassociated with the cationic part; hence, it is more reactive while it remains in the organic phase. It is evident that structural differences allow for different cations to complex with the phase transfer catalyst.



Scheme 3. (**a**) Various crown ether phase transfer catalysts. (**b**) Mechanism of PTC using crown ethers.

Taking into consideration the extensive study of these catalysts, it was obvious that the heterogeneity of such catalytic systems would have been implemented in the creation of supported-type catalysts [47]. The chemical bonding of crown ethers and ammonium or phosphonium salts with inorganic materials or immobilization on organic polymers developed this new generation of catalysts. The benefits that the previously mentioned catalysts offer, along with the simplicity of recovery and reusability of a heterogeneous catalyst via filtration, provide ideal capabilities for industrial applications, which require continuous and reliable catalytic activity and stability. In the next paragraphs, the history of the development of these catalytic protocols will be explored.

2.2. The Chronicle of PTC

The first observations that suggested the great prospects of PTC took place early in the 20th century but were nonetheless underexplored [48]. The first use of the term phase transfer catalysis was by Ch. Starks in his pioneer work (Scheme 4) in which quaternary ammonium and phosphonium salts were used as catalysts for a multitude of reactions, such as displacement reactions and the oxidation of olefins by aqueous $KMnO_4$ [45]. As it is mentioned, these reactions are unfavorable due to the inability of the reagents to react since they are dissolved in different phases. With the introduction of a catalyst, the reactions proceeded to produce the desired products in high yields and with unprecedented reaction rates [43].

$$\mathrm{RX} + \mathrm{NaY} \xrightleftharpoons{\begin{array}{c}\text{PTC}\\ \text{catalyst}\\ 1\text{–}5\%\end{array}} \mathrm{RY} + \mathrm{NaX}$$

R= n-alkyl (C8–C12)

X= Cl, Br, CH_3SO_2

Y= CN, Cl, Br, I, $NO_{2,}$ NCO, OH, etc

PTC catalyst = Tricaprylylmethylammonium chloride or
Hexadecyltributylphosphonium bromide

Scheme 4. The first reported displacement reaction using quaternary ammonium/phosphonium cations.

The potential that PTC offers was explored in 1972 in the successful Hoffman carbylamine reaction for the generation of isocyanides from amines [27]. Generally, the PTC protocol that was employed offered an effective method for the synthesis of methyl and ethel isocyanides which had never been achieved in a reproducible way. In 1974, another PTC protocol for the synthesis of phenol ether was reported. The reaction produced the desired products in up to 93% isolated yields and in mild reaction conditions [49]. Additionally, in 1989, the use of anhydrous tetrabutylammonium fluoride was explored as a PTC catalyst as well as for its ability to provide fluorine anions for demanding nucleophilic displacement reactions [50].

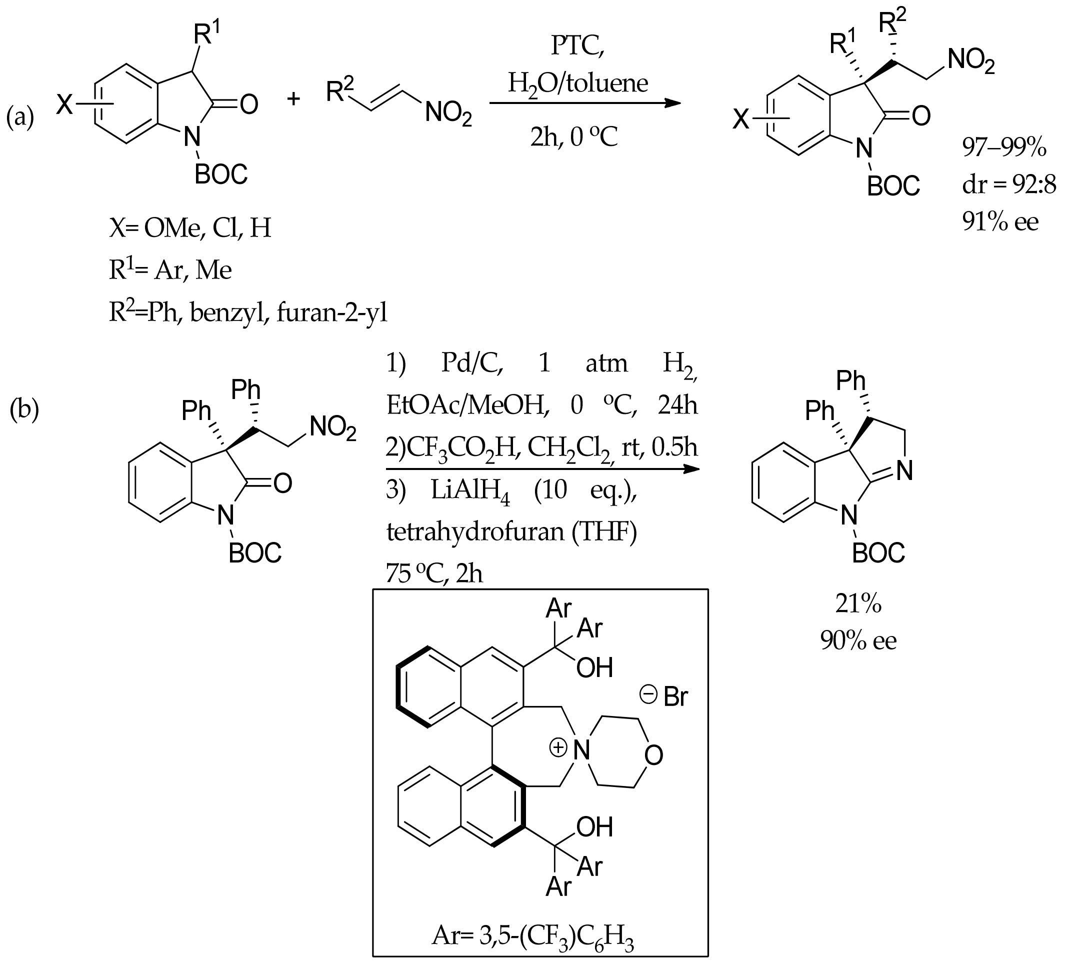
An interesting chapter in PTC was early recognized in multiphase reactions in which the interface layer is catalytically active [22,47,51]. In this regard, various polymer-supported catalysts based on quaternary ammonium–phosphonium salts and crown ethers act as solid-phase phase transfer catalysts for reactions between organic- and aqueous-layer dissolved reactants [31,47]. Additionally, ionic liquid micelles exhibit remarkable catalytic properties as phase transfer catalysts in biphasic systems with a strong dependence on temperature which can be exploited for controlled separation, drug delivery, and extraction applications [52]. In the same manner, polymer-supported ionic liquids and different metal macro-complexes offer unique synthetic strategies which are based on the thermosensitive properties of these protocols [22,36,53]. It is important to note the extensive usage of hybrid proline-based ionic liquids in a variety of different biphasic protocols [22]. More recently, the use of a triphasic PTC system for the oxidation of alcohols in aqueous H_2O_2 has been reported [51]. The application of a composite graphene oxide-immobilized polyoxometalate ionic liquid afforded the desired ketones with up to a 99.8% conversion rate. Similarly, in 2021, the utilization of Rh and Ru nanoparticles was explored in the controlled hydrogenation of ketones, alkenes, and aldehydes, which resulted in the formation of the respective products with 70–91% yield [33]. An industrially interesting concept was reported in 2015 for the hydrogenation of CO_2 to produce methanol by a Ru-[1,1,1-tris(diphenylphosphinomethyl)] catalyst [24].

In 1989, the use of a quinine-based phase transfer catalyst allowed for the fruitful production of α-aminoacids via multistep asymmetric alkylation [54]. The same methodology was also applied to the enantioselective synthesis of alkylation products [55]. Additional studies provided mechanistic insight into epoxidation reactions by a complex PTC system [56]. Epoxidation reactions were also the focal point of the Xi Zuwei et al., study [57]. In this paper, the epoxidation of propylene was achieved using a PTC protocol with up to a 91% yield. Another example of PTC was demonstrated in the oxidation of hydrocarbons, such as cyclohexene, cymene, and tetralin [39]. In the presence of multiple PTC surfactants, the autooxidation of these hydrocarbons was greatly enhanced, effectively proving the catalytic capabilities of these molecules [39]. In addition, the influence of different types of catalysts was also investigated. The oxidation of cyclic alcohols to the corresponding ketones was reported in 2014, taking advantage of the PTC properties of many ionic liquids for the generation of desired products with up to 82% yields [35].

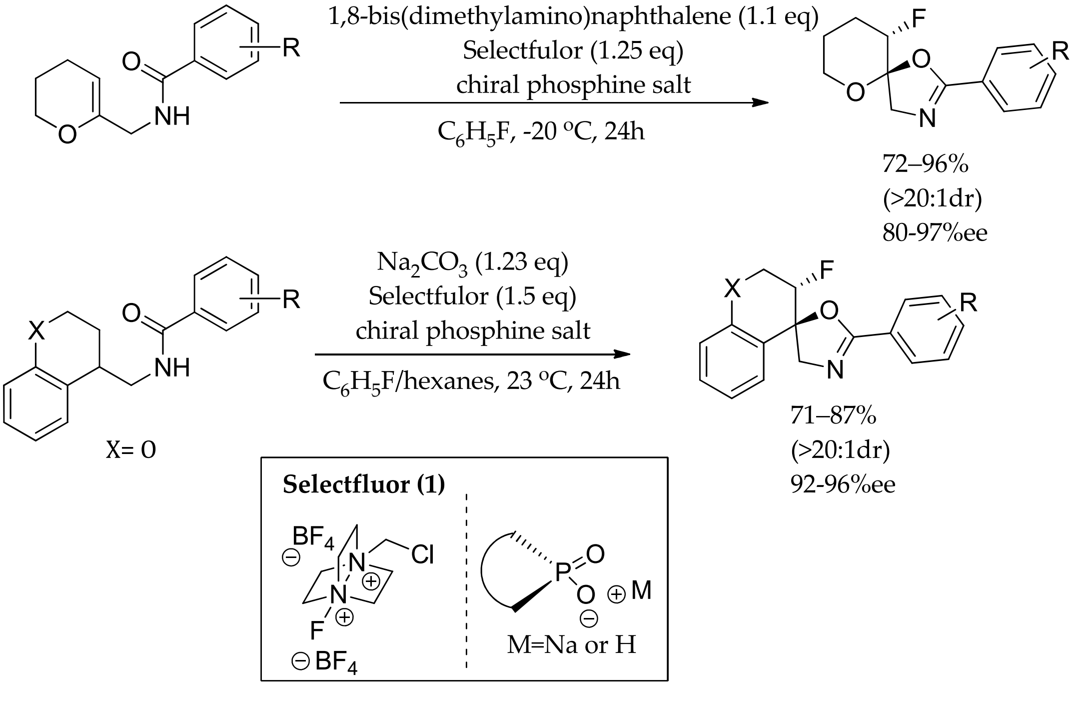
As early as 2003, the usage of phase transfer catalysis exploded, and a multitude of reactions based on PTC were reported [29,58–63]. A neoteric approach in synthesis is the implementation of microwave-assisted reactions [64]. Applications of such microwave-assisted phase transfer catalysis in the field of alkylations [65,66], nucleophilic additions [67], and various reactions were explored in an interesting review regarding these applications [64].

As has been mentioned, the usage of enantioselective PTC protocols is a well-established norm in chemical synthesis. [32,68]. PTC applications on the asymmetric Michael and Mannich reactions of 3-aryloxindole substrates are presented by He et al. The reaction resulted in the generation of the desired product with up to 99% isolated yields and up to 99% enantiomeric excess (ee) [23]. The catalyst that was developed was based on a chiral quaternary phosphonium ion scaffold. Further investigation on asymmetric PTC protocols highlighted the importance of alkaloid *cinchona*-based chiral catalysts [69]. It is worth noting that these PTCs had been developed in different generations based on the substitution of the *cinchona* base scaffold, which is meticulously described in the review of Sang-Sup Jew and Hyeung-Geun Park [69]. Additional applications of asymmetric PTC were reported in 2009 for the enantioselective conjugate addition of 3-phenyloxindole to nitrostyrene with up to a 98% isolated yield with remarkable enantioselectivity using a chiral phase transfer catalyst [70]. Surprisingly, the reaction was performed in less than 1 h at 0 °C in a simple toluene/water biphasic system without the use of any other additive (Scheme 5a). Additionally, the synthetic potential of this transformation was explored in the production of molecules that bear the alkaloid scaffold (Scheme 5b). In a spectacular PTC approach, the tandem enantioselective fluorocyclization of olefins was accomplished in remarkably low temperatures by Vivek Rauniyar et al. (Scheme 6) [71]. This transformation was achieved using a specialized mixture of *Selectfluor*™ (**1**) (Air Products and Chemicals, Inc., Allentown, PA, USA) and quaternary phosphonium salt, which react to provide the active fluorination catalyst.

All these applications act as a brief introduction to the potential of PTC. PTC protocols remain a hot topic in chemical research, and the importance of such transformations cannot be overstated. In diverse applications, PTC follows multiple green chemistry principles [72,73]. In particular, the ease of product isolation via extraction or/and decantation along with the minimization of specialized additives satisfy the use of less hazardous materials and safer chemical synthetic pathways. Additionally, byproduct formation is limited, and the necessity for extreme temperatures is circumvented. It is evident that the benefits that PTC offers can be further enhanced when it is applied in conjunction with other promising materials such as ionic liquids.



Scheme 5. (**a**) Application of PTC in the synthesis of substituted indoles. (**b**) Synthetic route to alkaloid scaffolds.

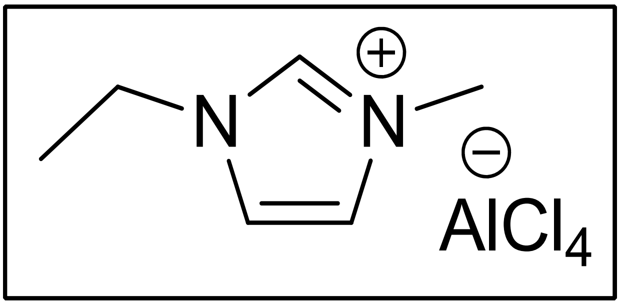


Scheme 6. Enantioselective tandem fluorocyclization PTC protocol.

3. Ionic Liquids: A Brief History and Applications

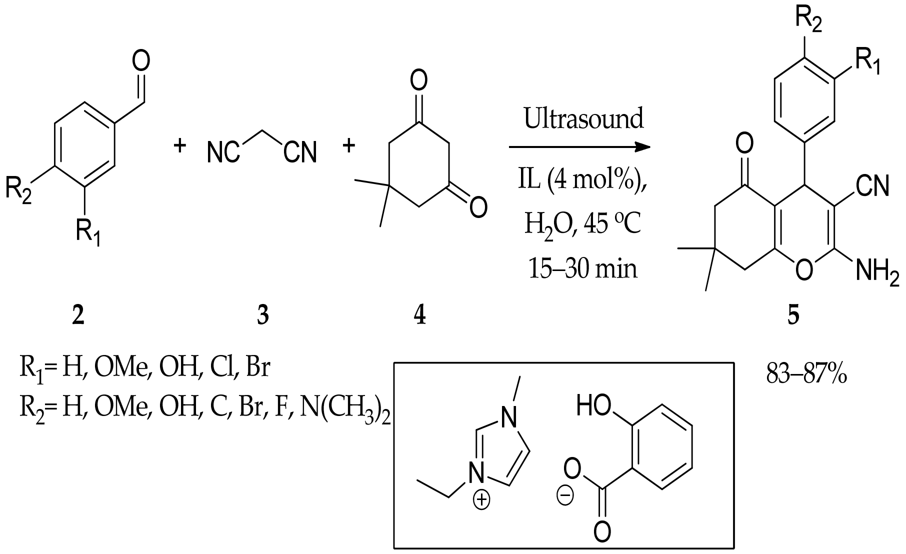
Ionic liquids (ILs) are a family of materials with exceptional physical and chemical properties. They are comprised entirely (or at least an extensive part of their bulk is) of ions. ILs have melting points below 100 °C and in some cases, even at −96 °C [6,12,74]. Especially, room temperature ILs are a widely investigated type of ionic liquid that could provide a green alternative to the usage of typical organic solvents [6,14,75]. Additionally, the complexity of both cationic and anionic species can be modified for the targeted synthesis of task-specific solvents [3,14,76–78]. Properties such as viscosity, thermal stability, and vapor pressure can be altered along with the lipophilicity of these materials providing innovative materials for various chemical processes [79]. Such properties are also linked to catalytic activity in PTC protocols. Additionally, the introduction of protic ionic liquids (PILs) as a subcategory of ILs attracted the interest of the scientific community [80]. The existence of protic hydrogens in the molecular scaffold of these compounds generates a vast network of hydrogen bonds, a beneficial factor in numerous applications [81]. Further investigation in PILs generated a new family of choline-based PILs, which enhance the green aspect of these molecules allowing for successful esterification under PTC conditions [82].

The first reported study on ionic liquids was conducted on a protic ionic liquid ethylammonium nitrate (EAN) by P. Walden in 1914 [83]. Unfortunately, this discovery had largely been neglected by chemists until the rediscovery of ILs in the late 1970s by the exceptional work of John Nardi et al., for possible military applications on behalf of the US Air Force [84]. This patent paved the way for one of the most prominent figures in the history of ionic liquids, John Wilkes, to develop dialkylimidazolium aluminum chloride salts (Scheme 7) [85]. In this pivotal paper, the synthesis, properties, and applications of ILs were methodically studied, and the difference from previous high temperature molten salts was reported. Over the next years, new papers focused on the study of ILs [1] and the nuclear magnetic resonance (NMR) properties of these materials [86]. Further independent investigations on the thermal properties were conducted in the following years on imidazolium-based ILs, and interesting results were collected regarding density, vapor pressure, decomposition, and glass transition temperature [87–89]. Additionally, the composition and physical description of such neoteric materials remains an exciting concept, prompting further investigation, which is reflected in various papers [90–93]. Likewise, the investigation of the hydrophilic and hydrophobic nature of ILs [5] is elemental for the discovery of the potential applications of PTC in biphasic environments; thus, a wide range of reports focus on that subject [94].



Scheme 7. 3-ethyl-1-methyl-imidazolium tetrachloroaluminate, the first reported ionic liquid by Wilkes.

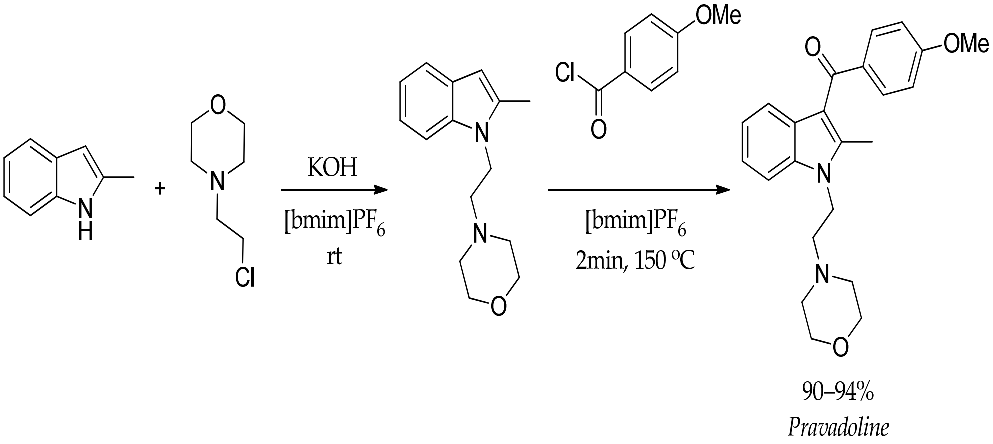
The behavior and interaction of ionic liquids in different solvents is a concept that is significant and correlated with hydrophilicity. In 2000, the effect of water and chloride on ionic liquids was explored [95,96]. It is evident that the presence of moisture alters the physical characteristics of ILs since it effectively creates a solution, whereas chloride generally increases the viscosity of ILs. Elaborating on these ideas, Cammarate et al., revealed that water interacts with the anionic part of ILs in an array of hydrogen bonds [97]. Additionally, in 2008, the collaboration of several research teams provided further insight into the properties of ILs in aqueous solutions, which is vital in the development of PTC protocols based on ILs [98]. More specifically, it was revealed that imidazolium-based ILs act as amphiphilic compounds, and the length of the alkyl chains greatly affects the interface organization parameters. The effects of amphiphilicity were also examined in papers that studied the interaction of several solvents with ILs. It was determined that ILs are an excellent solvent for organic substrates in a variety of multiphase catalytic systems [99]. Additionally, active metal catalytic complexes can effortlessly be immobilized in ILs, presenting a unique synthetic alternative to traditional solvents in multiple industrial processes [99]. Furthermore, supramolecular formations are observed by specialized ILs in an aqueous medium, and the catalytic capabilities of ILs in Michael and Knoevenagel tandem multicomponent reactions for tetrahydrobenzo[b]pyran derivative (**5**) production are exceptional (Scheme 8) [100]. The interaction of ILs with hydrocarbons has also been investigated for potential use in hydrogenation and other related reactions [99]. Recently, a study of n-butane/IL interactions was conducted, and the effect of the alkyl chain length was once more the greatest parameter regarding the solubility of hydrocarbons in ILs [101].



Scheme 8. Ultrasound-assisted multicomponent reaction using an IL as a catalyst.

In the dawn of the millennium, an upsurge in the applications of ILs can be observed. It is worth noting that the developers of these materials mentioned the potential applications that could emerge, exploiting the electrochemical properties of ILs [84,85]. Such properties were highlighted in the potential development of electrodes as early as 1996 [102]. The trend of green chemistry and the consequential need for ideal materials resulted in the development of novel IL-based electrolytes for potential solar energy generation by dye-sensitized solar cells (DSSCs) [9]. An overview of the potential IL applications in energy generation is developed in the review by MacFarlane et al. [103]. Among these applications, fuel cells based on ionic liquids [104] and the generation of hydrogen gas from water [105] are especially promising in terms of sustainability. In accordance with the previous reports, the industrial desulfurization of diesel was achieved at a 99% rate at 30 °C in less than 20 min using an ionic liquid catalyst, thus emphasizing the green potential of such applications [106].

The synthetic applications of ionic liquids cannot be overshadowed [107]. As early as 2000, the successful synthesis of the anti-inflammatory and analgesic drug pravadoline was achieved using a two-step reaction conducted in IL with a 94% overall yield (Scheme 9) [108]. Additionally, the recoverability and reusability of the IL were possible [108]. A multitude of different reactions have been investigated employing ILs in the epoxidation of α,β-unsaturated carbonyl moieties and alkenes [109,110], the intramolecular cyclization for N-alkynyl heterocyclic compounds [111], the generation of isoxazolines using cycloaddition of nitrile oxides [112], and the formation of carbenes [13]. Similarly, the production of cyclopropane derivatives was successful in tetraalkylammonium-based ILs [113].



Scheme 9. Total synthesis of pravadoline in IL.

In 2007, an explosion of review articles highlighting the potential application of ILs was reported. Specifically, applications of ILs in separations [114], biocatalytic protocols [19,115], synthetic pathways [2,18,116], and general catalytic protocols [7,8,16,17,117–119] were presented in a series of reviews. Moreover, ILs present an exciting alternative in various asymmetric catalytic protocols [120–122].

The research on nanomaterials based on ILs or on the generation of nanomaterials in ILs is a novel concept [123]. Hybrid materials of IL–graphene have been developed for the specific and chemoselective oxidation of alcohols [124]. Likewise, poly-ionic liquids offer a unique pathway for the promotion of radical polymerization reactions and fuel cell applications [104,125]. Supported ionic liquids can potentially act as catalysts for a multitude of different reactions [126,127]. A neoteric category of hybrid materials was investigated by Campisciano et al. [128]. In their research, the development of a fullerene/IL composite material was generated and studied for its promising properties.

One of the most intriguing properties of ILs is the interaction of these materials with gases and especially with CO_2. The potential applications in CO_2 traps [104,129–131] led to extensive studies of these interactions [11,132,133]. An early example of CO_2 entrapment by a task-specific IL was reported in 2002 by Betes et al. In their study, the development of an alkylamine chain connected to the imidazolium scaffold reacted with CO_2, resulting in absorption and stabilization of the gas [11]. This system also drew attention for its potential in CO_2 transfer technologies. Additionally, such technologies allow for the chemical transformation of CO_2 into valuable fuels [134,135], which correlate with policies of CO_2 emission minimization. An interesting property of the majority of ionic liquids is the immiscibility with supercritical CO_2, which is highly useful in many catalytic applications and extractions [136,137].

In accordance with the "Green Chemistry" guidelines [138,139], a recent trend is the development of novel ILs formed by naturally occurring molecules. This family of bio-ILs has been developed using various natural products and their synthetic analogues and/or active pharmaceutical ingredients (APIs) [140]. It is evident that such materials contain intriguing properties regarding biodegradability and can be unique sustainable alternatives across a wide range of chemical procedures and industrial applications.

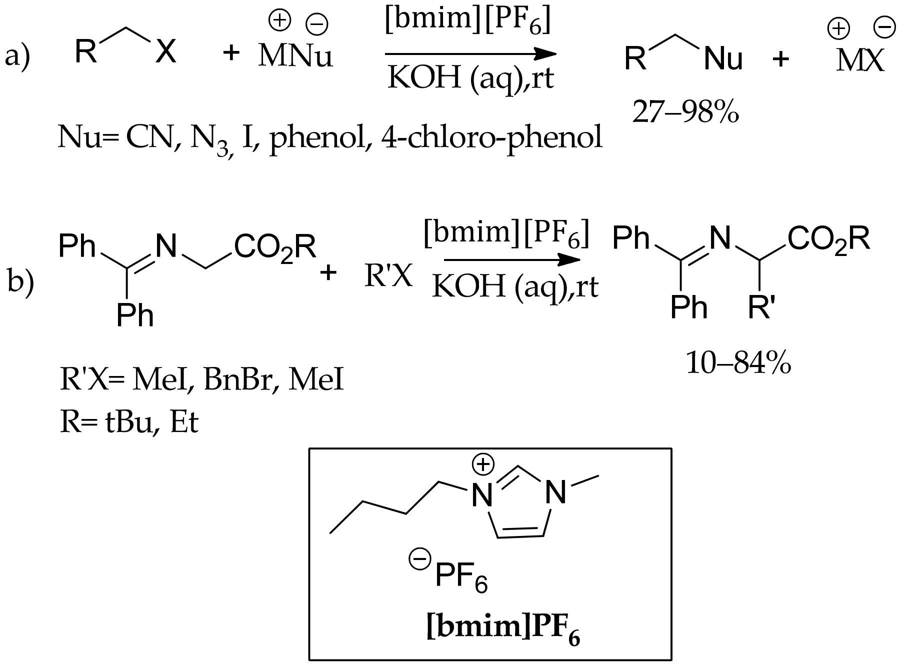
A rather recent implementation of ILs was reported for the exfoliation of different layer materials, thus complementing the dissolution capabilities of ILs. Specifically, in 2022, Yang Zhao et al., developed a strategy for the successful production of a two-dimensional porphyrin-based covalent organic framework from the respective powder using ILs as both stabilizers and intercalators. The resulting product was utilized for the photocatalytic CO_2 reduction in the gaseous phase [141]. Similarly, in the same year, the delamination of layered double hydroxides (LDH) was efficacious in IL as a dissolution medium; thus, stable and uniform dispersions of LDHs were obtained in one step and facile methodology [142]. Such properties could be described as the possible phase transfer from the solid to liquid phase in which the corresponding ionic liquids act both as catalysts as well as solvents.

4. Application of Ionic Liquids in Phase Transfer Catalysis

As has already been mentioned, ionic liquids can be used in a variety of chemical transformations [4,6,10,15,16,18,19,77,116,143]. The use of ILs in catalytic applications is apparent and is considered an interesting option in chemical synthetic methodology [3,8,115,144–148]. In the next paragraphs, applications regarding the use of ILs in PTC protocols are presented and discussed.

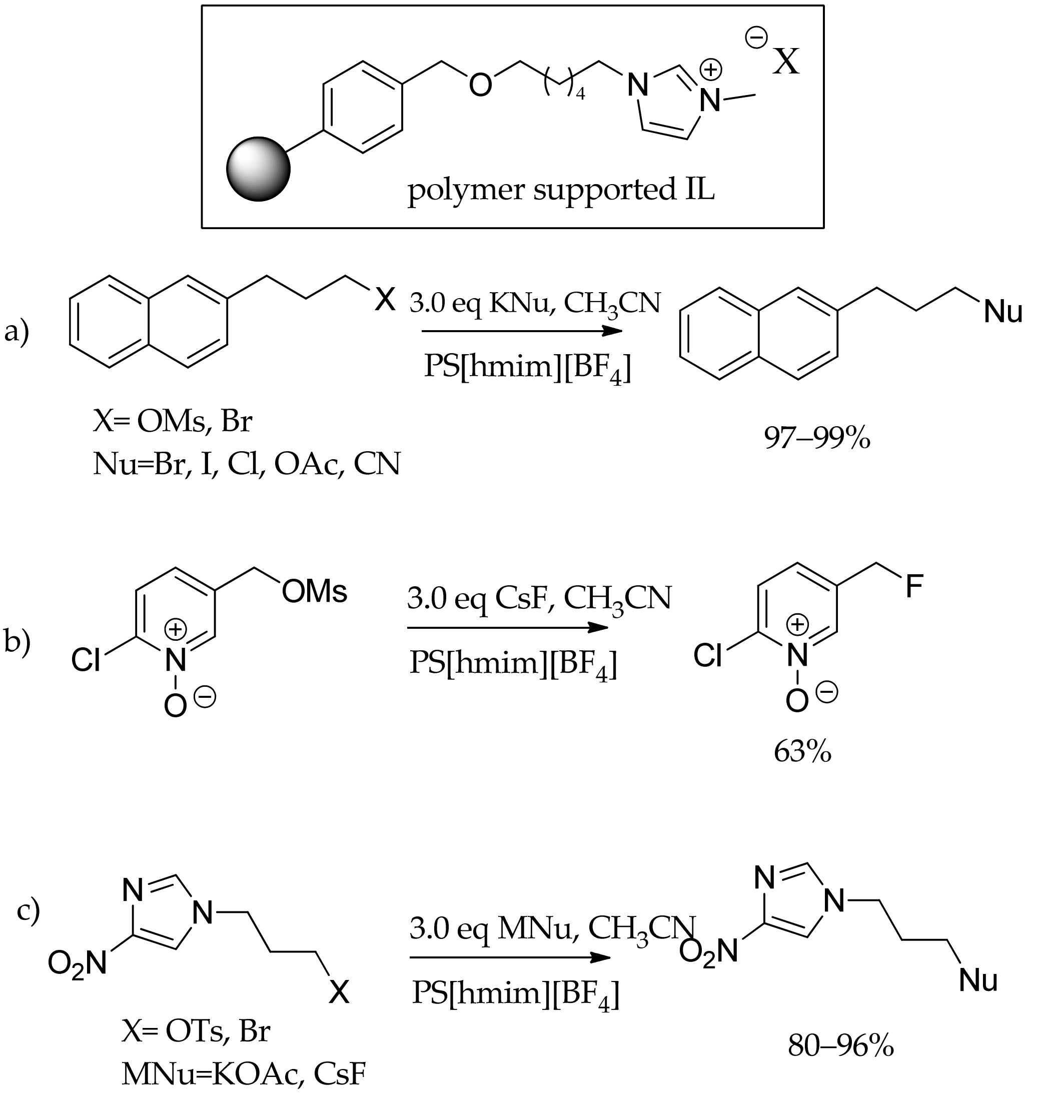
4.1. SN Displacement Reactions

The connection between the characteristics of N-imidazolium salts and the possible PTC activity has been early recognized [149]. This basic molecular scaffold is present in ILs of the first generation. As expected, the most practical application of early PTCs is in displacement reactions; thus, ILs were also used to promote such reactions. Lourenço et al., explored and first mentioned the ability of ILs to catalyze multiple reactions [150]. Specifically, using 1-n-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF_6] as a reaction medium, along with an aqueous phase at room temperature, the desired substitution product was received in high yields, contrary to the reactions where no ILs were used. Thus, it was evident that ILs possess phase transfer catalytic capabilities, providing a unique alternative for PTC without the need for any volatile organic solvents (VOS) and the use of an additional catalyst (Scheme 10a). Additionally, the reusability of these ILs was proved by the same group. In the same work, the catalyst allowed for the effective alkylation of Schiff bases at room temperature (Scheme 10b).



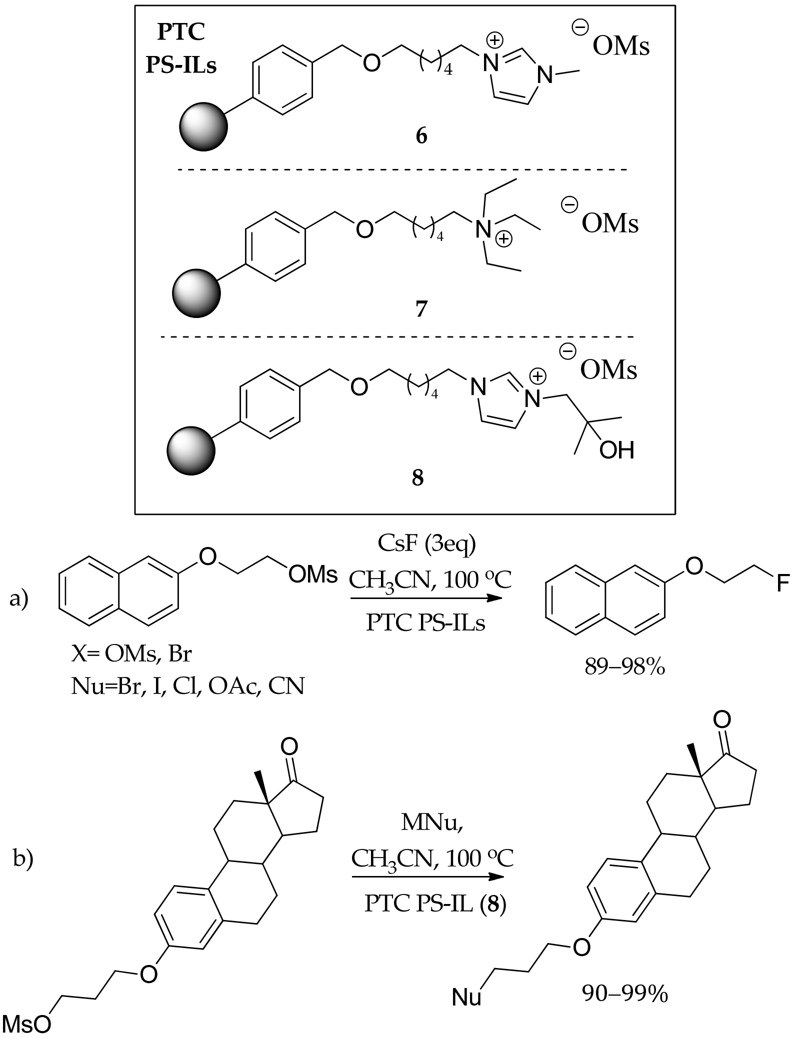
Scheme 10. (**a**) Nucleophilic substitution and (**b**) Schiff base alkylation using [bmim][PF_6] ILs.

The next year, the research team of Kim D. et al., modified an ionic liquid and created a polymer-supported (PS) efficient catalyst for nucleophilic substitutions, including the demanding fluorination [151]. Such catalysts are considered three-phase catalysts and offer unique benefits in chemical synthesis. Reusability, higher catalytic activity, and facile product recovery are some of the aspects that highlight the importance of these catalysts. The substrates that were converted successfully using this protocol included several sulfonyloxyalkanes and haloalkenes with demanding structural complexities (Scheme 11). The same team, two years later, investigated the structural modifications of this supported IL catalyst [152]. Different possible anionic structures were introduced along with the use of different organic solvents for successful alkoxylation and fluorination reactions, significantly expanding the scope of these catalysts. Elaborating on that scheme, in 2008, the same group used tert-amyl alcohol for a highly efficient fluorination protocol of interesting substrates based on the previously created supported catalyst [153].



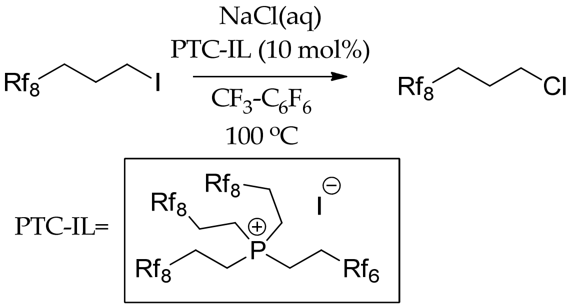
Scheme 11. Nucleophilic substitutions using a polymer-supported IL in a PTC protocol. (**a**) Nucleofilic substitution of alkyl-napthalenes. (**b**) Nucleophilic fluorination. (**c**) Nucleophilic substitutions of alkyl-imidazoles.

In the same year, this group presented a set of PS-protic ILs. More specifically, PS-[hmim][OMs] (**6**), PS-[hNEt$_3$][OMs] (**7**), and PS-[him-^{t}BuOH][OMs] (**8**) [154] were synthetized and used as PT catalysts for various nucleophilic substitutions (Scheme 12). Furthermore, the reusability of the catalysts was possible after filtration of the reaction mixture without diminishing the catalytic activity.



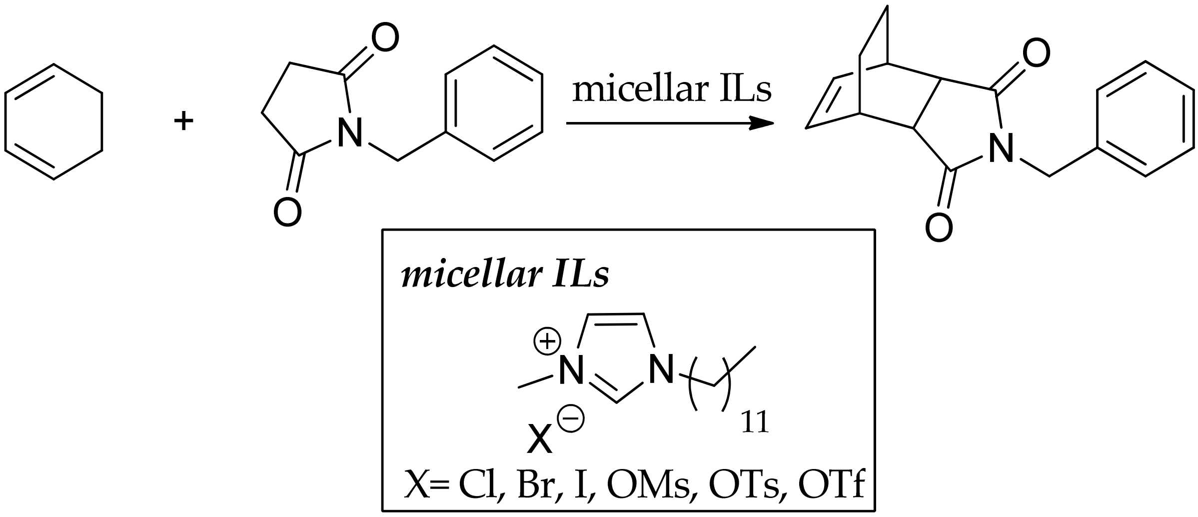
Scheme 12. Polymer-supported catalysts and applications. (**a**) Nucleophilic fluorination of naphthol derivatives. (**b**) Nucleophilic substitution of steroid derivatives.

In 2006, Ch. Emnet et al., reported the creation of a novel family of fluorous quaternary ions that could form ionic liquids which in turn bear phase transfer catalytic activity regarding substitution reactions [155]. Under this protocol, the successful transformation of fluorous alkyl iodine to the corresponding chloride was achieved. The reaction was performed in a two-phase system of a NaCl aqueous phase and a $CF_3C_6F_6$ organic phase (Scheme 13), exploiting the use of the developed IL as an effective PT catalyst [155].



Scheme 13. Fluorous ionic liquids in PTC displacement reactions.

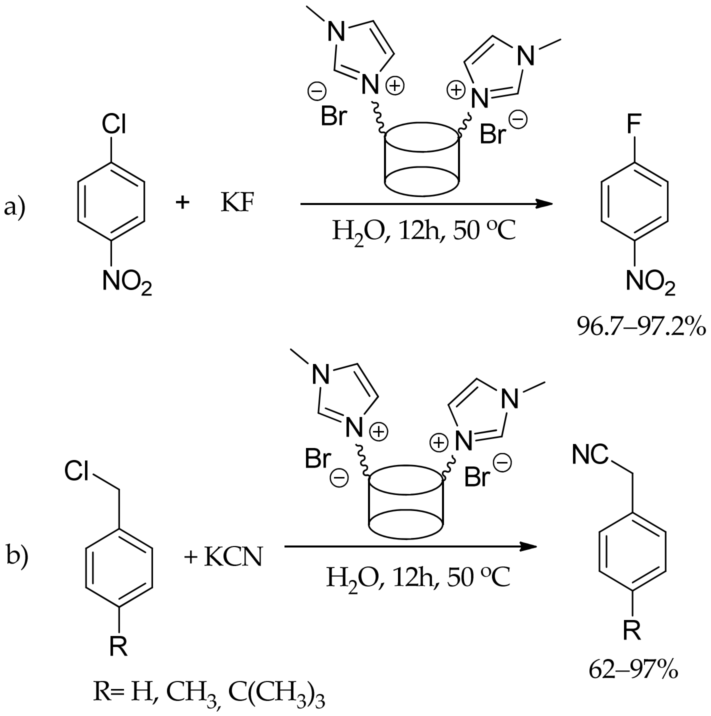
Ionic liquids and water micellar mixtures have been studied for their thermodynamic behavior [156]. These mixtures provide an interesting alternative instead of sole IL solutions in the Diels–Alder reaction, leading to higher yields (Scheme 14) [157]. Specifically, in this study, 1-alkyl-3-methylimidazolium ILs with Br^-, Cl^-, and PF_6^- as anionic counterparts were used for the generation of micelles that presented remarkable catalytic activity. This group also reported that such catalysts greatly enhanced the reaction rate in comparison with water or neat ILs as reaction media, and the reaction time was reduced significantly. It is worth noting that in 2016, Alice Cognigni et al., reported that the anionic counterpart in micellar–IL systems of dodecyl-3-methylimidazolium impacted greatly the reaction rate and catalytic capabilities of these surface-active ionic liquids [158].



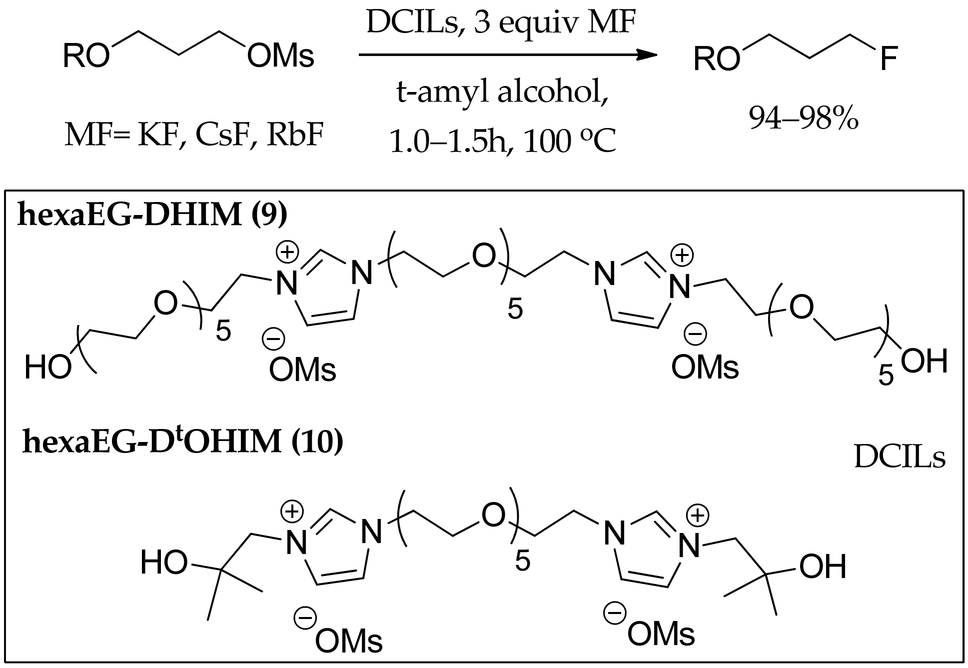
Scheme 14. Micellar ionic liquids in the Diels–Alder reaction.

The versatility and tunability of ILs were also exploited for the formation of hybrid calixarene–ionic liquid molecules with remarkable phase transfer catalytic activities regarding displacement reactions in water [159]. Specifically, the nucleophilic aromatic substitution of chlorine with fluorine was achieved using this neoteric material at the relatively low temperature of 50 °C for 12 h. When the research group tried using solely an ionic liquid as a catalytic medium, the product yield was 10%, and without the use of any catalyst, trace amounts of the desired product were formed. Nonetheless, the use of the hybrid material allowed for the production of the desired product at a 97–99% yield (Scheme 15a). In addition, these hybrid materials achieved the successful benzylic substitution of chlorine by CN moiety in water at an 84.5–95.1% yield (Scheme 15b). The phase transfer catalytic properties of these molecules stem from the synergistic effect of ionic liquids as the solvent and the lipophilic cavity that the calixarene skeleton creates. These molecular scaffolds allow for the effective binding of the substrate as well as the emergence of the observed catalytic activity.

In 2017, the group of Dong Wook Kim developed di-cationic ionic liquids (DCILs) and used them as phase transfer catalysts in a series of fluorination reactions with various substrates with tert-amyl alcohol as the solvent [160] (Scheme 16). This study also provided useful insight into the possible formation of the β-elimination byproduct, which is a challenge of typical PTC systems. Additionally, it is worth noting that an excellent chemoselectivity along with higher yields were observed using hexa-EG-DHIM (**9**) as a catalyst. Thus, the same group reported the importance of this protocol regarding the fluorination reaction, which could be utilized industrially, for the formation of labeled fluorinated pharmaceuticals [160].

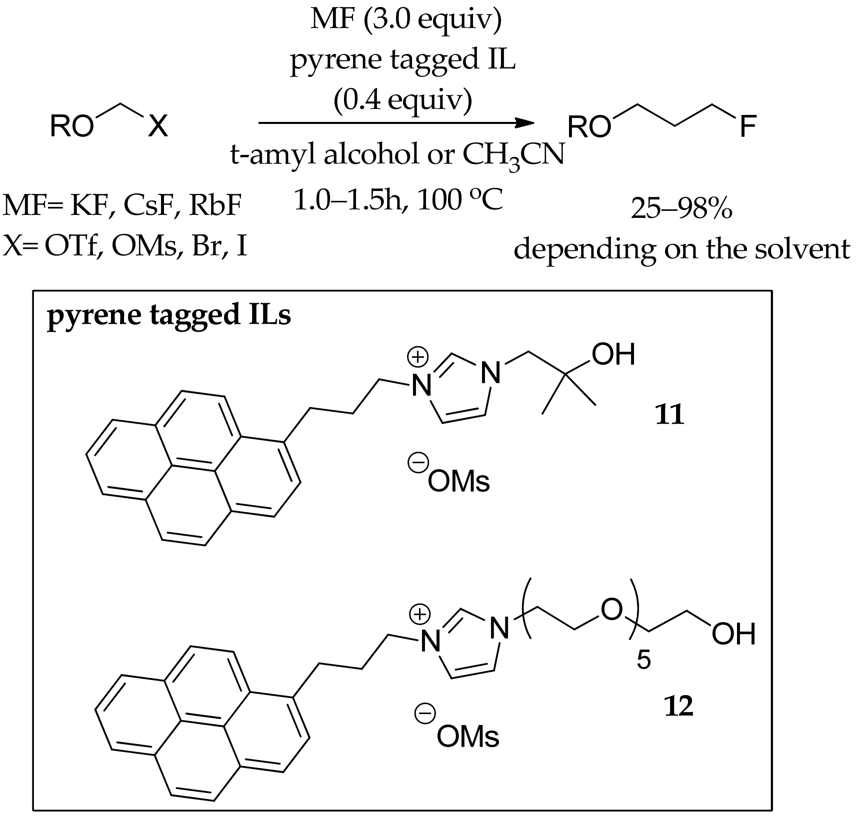


Scheme 15. Calixarene and ionic hybrids, a novel phase transfer catalyst in (**a**) aromatic nucleophilic fluorination and (**b**) benzylic substitutions.



Scheme 16. Application of di-cationic ionic liquids in a fluorination protocol.

The most recent example of ILs exercised in PTC for various nucleophilic displacement reactions was reported in 2020. In their work, Abu Taher and Dong Wook Kim formulated a hybrid material connecting ILs with a pyrene moiety [161]. Thus, a set of catalysts for fluorination reactions was created (**11**,**12**). Additionally, a unique separation methodology was introduced, taking advantage of the noncovalent bonding (NCB) effect between the pyrene moiety and commercially available graphene oxide. The S_N2 substitution reactions were performed both in tert-amyl alcohol and CH_3CN, but in the presence of the protic solvent, higher yields and an enhanced chemoselectivity were achieved (Scheme 17).

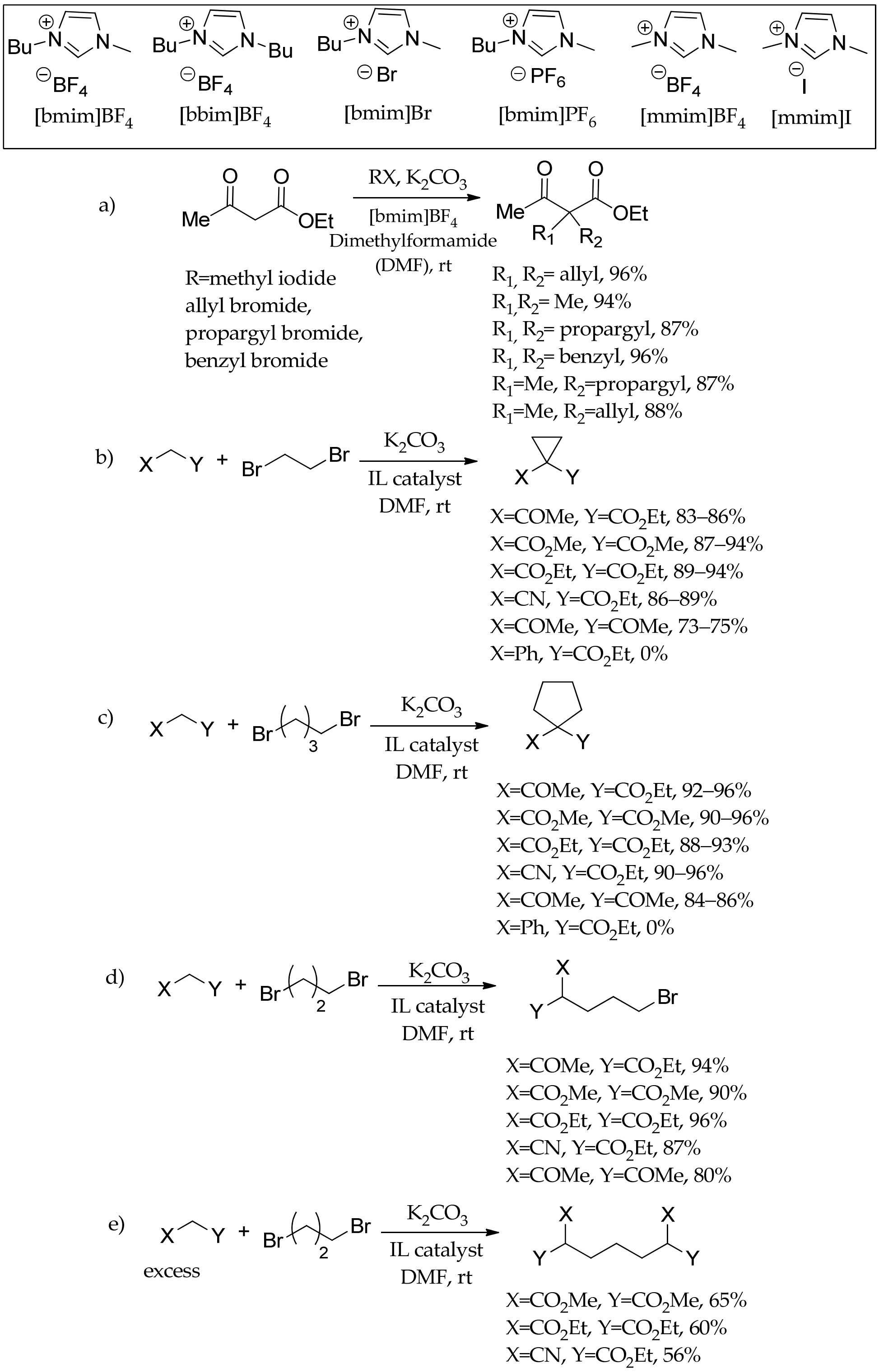


Scheme 17. Pyrene-tagged ionic liquids as a promising PTC for fluorinations.

A special type of displacement reaction is the glycosidation reaction, which allows for the synthesis of natural products, interesting pharmaceutical precursors, and even biologically active compounds [162]. In 2011, a PTC protocol enabled the production of such synthons using a biphasic mixture of imidazolium-based ionic liquids and an organic solvent. Extensive screening of several ILs resulted in the choice of lipophilic $[Hxim]PF_6$ as the ideal phase transfer catalyst for the glycosidation of 2,3,4,6-tetra-O-acetyl-a-D-galactopyranosyl bromide by various phenols and thiophenols with very good yields. Interestingly, the reaction was tested using a system of IL/chloroform/aqueous NaOH as well as a system without the use of an organic solvent. Surprisingly, no serious detriment regarding the yield was observed. This fact, along with the proven recyclability of the ILs, greatly highlighted the application of ILs as both solvents and PTC promoters for several environmentally benevolent applications.

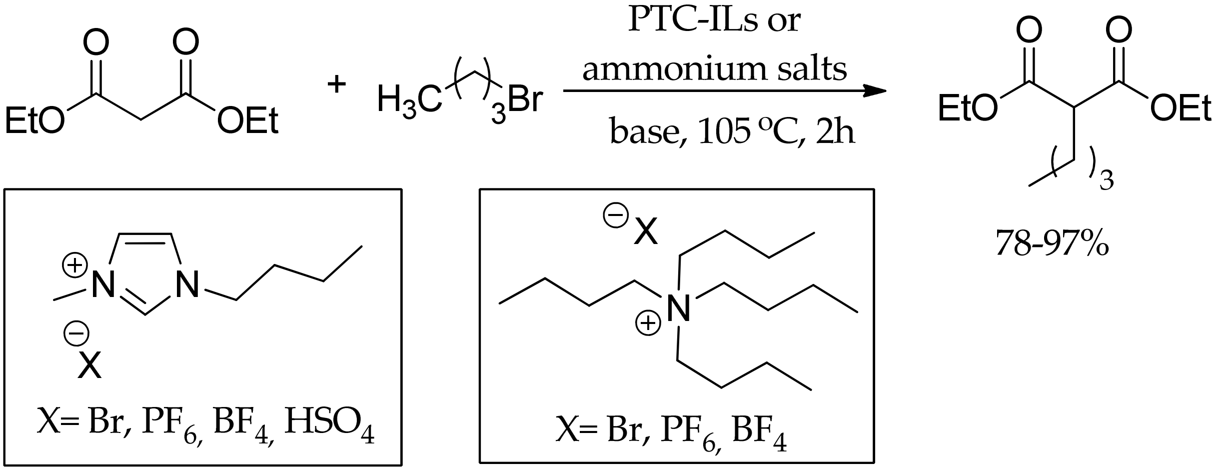
4.2. Alkylation Reactions

An important family of reactions in organic chemistry is alkylation, which can increase the length of the carbon skeleton of different molecules. The known activity of classic quaternary ammonium salts as phase transfer catalysts for alkylations was the linchpin for the development of various IL catalysts for successful PTC alkylations. Specifically, Sengodagounder Muthusamy and Boopathy Gnanaprakasam reported that ionic liquids based on N-methylimidazolium ion can be employed as phase transfer catalysts for the alkylation of active methylene compounds under mild conditions and room temperature (Scheme 18a). In their work, cyclopropane and cyclopentane formations (Scheme 18b,c) were attained, but surprisingly, only monoalkylation (Scheme 18d) occurred when cyclobutene formation experiments were conducted [163]. Intriguingly, in their work, the researchers reported that intramolecular dialkylation reactions (Scheme 18e) occurred under the same conditions [163].



Scheme 18. Alkylation reactions using ILs as phase transfer catalysts. (**a**) Active methylene compounds alkylation. (**b**) Cyclopropane addition. (**c**) Cyclopentane addition. (**d**) Monoalkylation reactions. (**e**) Di-alkylation reactions.

Hui Sun et al., in 2007, examined the effect of a series of 1-N-butyl-3-methylimidazolium (bmim)-based ionic liquids on the monoalkylation of diethyl malonate [164]. The catalytic protocol that was developed was solvent-free and provided great yields and relatively low reaction times (Scheme 19). Interestingly, this group compared the catalytic activity of ILs as phase transfer catalysts along with classic phase transfer catalysts based on quaternary ammonium salts. From this study, it was evident that the anionic part of both these catalysts noticeably affected the catalytic activity. Namely, regarding the ILs that were utilized, the order of the catalytic activity increased based on the anions: $PF_6^- > H_2PO_4^-, BF_4^-, Br^- > HSO_4^-$. In the case of the classic PTCs, the order of the catalytic activity based on the anions was $BF_4^- > PF_6^- > Br$ [164]. Additionally, the effect of different bases was investigated, and Cs_2CO_3 was reported to provide the highest yields. It is worth noting that the absence of harmful solvents, ease of product recovery, and PTC–ILs' recyclability accentuate the environmentally benign nature of this protocol.

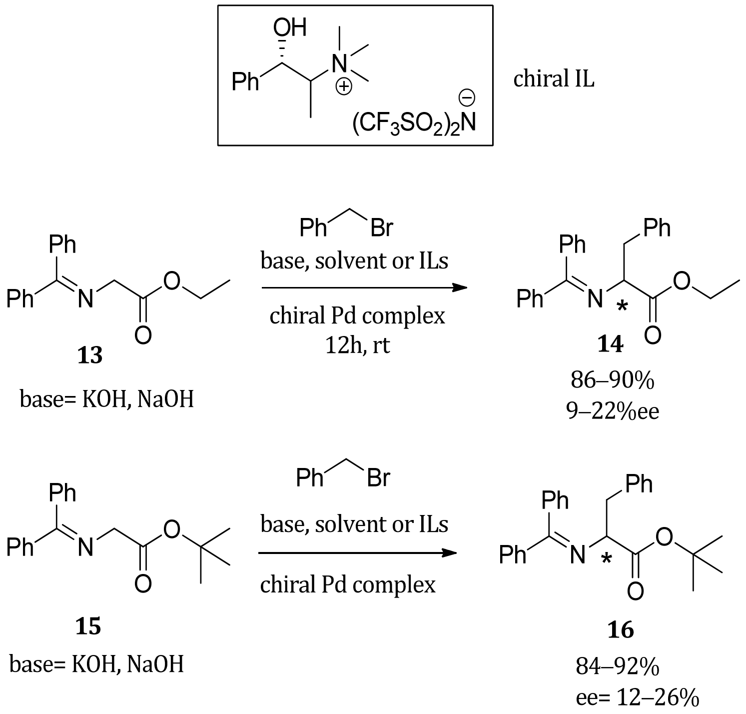


Scheme 19. Diethyl malonate monoalkylation based on a PTC–IL system.

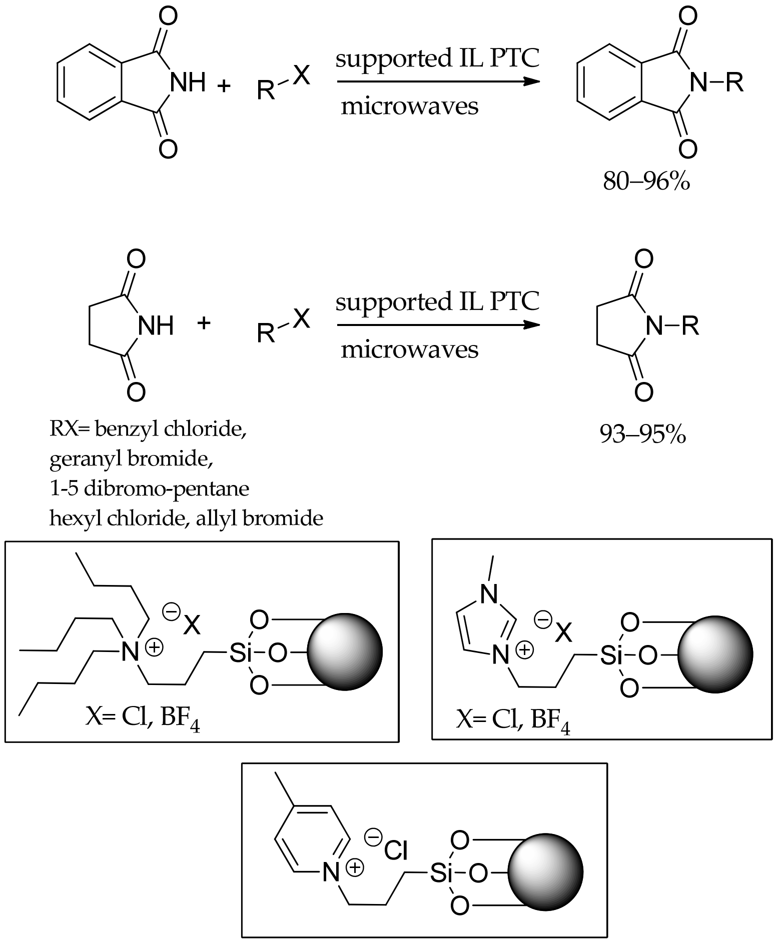
A unique methodology was established in 2007 by Deb Kumar Mukherjee and Nripendranath Ghosh [165]. In their work, a chiral ionic liquid along with a chiral di-palladium acetato-bridged complex successfully co-catalyzed the asymmetric benzylation of ethyl-N-diphenylmethyleneglycinate (**13**) and tert-Butyl-N-(diphenyl-ethylene) glycinate (**15**) (Scheme 20). Furthermore, the researchers observed that the application of solely the ionic liquid catalyst did not offer any enantiomeric excess, and the use of the Pd complex also provided limited enantiomeric excess. Instead, only the simultaneous use of these catalysts acts as a chiral booster for any significant enantiomeric excess to be observed, but with limited success regarding the enantiomeric purity of the product.

More recently, in 2015, Shallu Dogra et al., examined the effects of conventional and immobilized ILs for microwave-assisted *N*-alkylation (Scheme 21) on a variety of heterocyclic substrates [166]. Additionally, the comparison between heterogeneous solid–liquid PTCs and homogeneous PTCs was accomplished, which indicated the superiority of the immobilized ILs regarding the N-benzylation of phthalimide. An obvious advantage of these catalysts is the ease of separation and recyclability, which are both key aspects of the "Green Chemistry" trend.

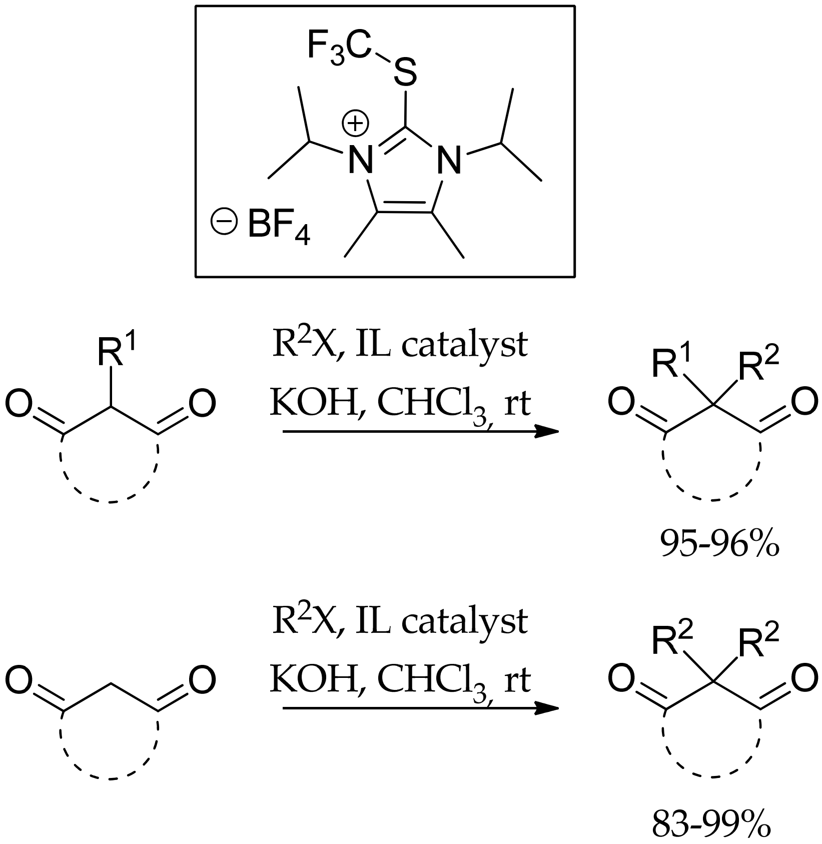
The exploitation of ILs as phase transfer catalysts was performed by Satoshi Mizuta et al., for the alkylation of activated methylene substrates [167]. The ILs that were used in this study contained a CF_3S moiety, which offered increased lipophilicity and electronegativity that greatly favored the desired product's formation. The reaction allowed for mono- and dialkylation depending on the molecular structure of the substrate (Scheme 22). As mentioned, the tunability of these catalysts and the ease of operation for these transformations emphasize the sustainability that ILs offer as phase transfer catalysts.



Scheme 20. Chiral ionic liquids in asymmetric alkylations.



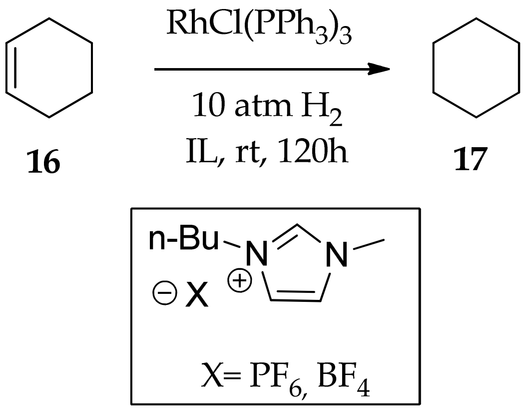
Scheme 21. Microwave-assisted *N*-alkylations based on a supported IL phase transfer protocol.



Scheme 22. Active methylene compound PTC alkylation by a novel CF_3-based IL catalyst.

4.3. Hydrogenation

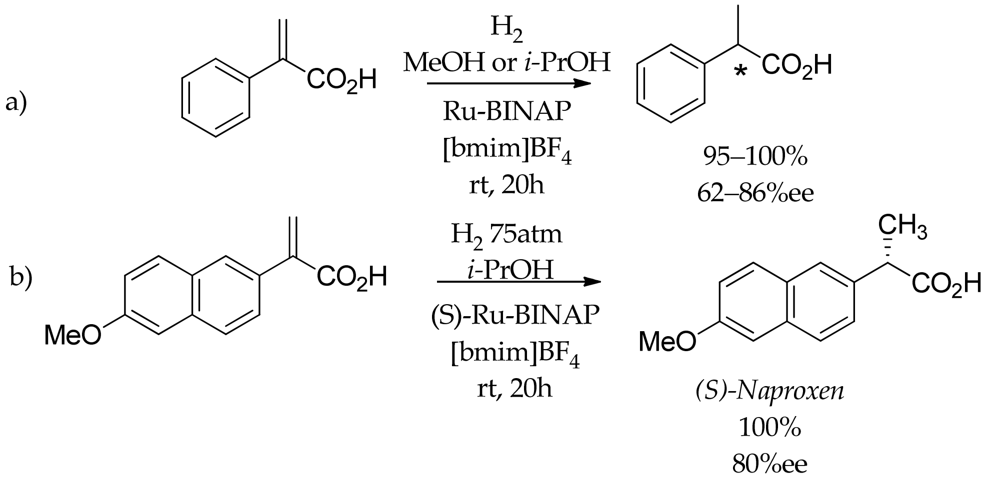
The importance of hydrogenation reactions cannot be overstated and is a category of reactions where ILs have been used extensively. Paulo Suarez et al., in 1996, proved that bmim-based ILs are air and water stable and can operate as solvents of Rh catalysts for the hydrogenation of cyclohexene (**16**) (Scheme 23) [168]. It was observed that the use of strong acids such as organo-aluminate ILs significantly favored the polymerization of the substrate, but the employment of less-acidic ILs favored exclusively the hydrogenation reaction. The reaction is a gas–liquid biphasic reaction, and the mechanism probably involves an interface phase transfer catalytic cycle. Possibly, the hydrogen gas is dissolved in the ionic liquids where it reacts with the substrate in the presence of the Rh catalytic complex.



Scheme 23. Hydrogenation of cyclohexane based on IL catalysts.

In the same year, the use of ILs as a solvent and booster for the catalytic activity of a Ph complex was described for both symmetric and asymmetric hydrogenation applications [169]. It was observed that, for the hydrogenation of pent-1-ene, the use of [bmim]SbF_6 as a solvent enhanced the catalytic activity in comparison with the reaction performed in acetone. When [bmim]PF_6 was used, a lower turnover frequency (TOF) than the previous IL was observed. That observation strongly indicated that the anionic part of the IL affects the reaction and possibly implied PTC, which stems from the differences in solubility. Furthermore, the hydrogenation of different species of conjugated diolefins was performed [169]. Interestingly, these olefins were more miscible in the ILs and were successfully transformed into the corresponding alkanes with excellent yields. Additionally, the use of a dissolved chiral Rh complex in [bmim]SbF_6 allowed for the fruitful asymmetric hydrogenation of α-acetamidocinnamic acid to (*S*)-phenylalanine in 64% ee. The substrate of this reaction was dissolved in isopropanol; thus, a phase transfer catalytic activity could be suggested. Noticeably, in their study, this group also reported the successful two-phase hydroformylation of targeted olefins in a heptanal/IL system by a modified Rh complex. Specifically, the solubility of the Rh catalyst in the organic phase implied the necessity for a chemical "immobilization" of the Rh complex in the IL phase via polar phosphine ligands.

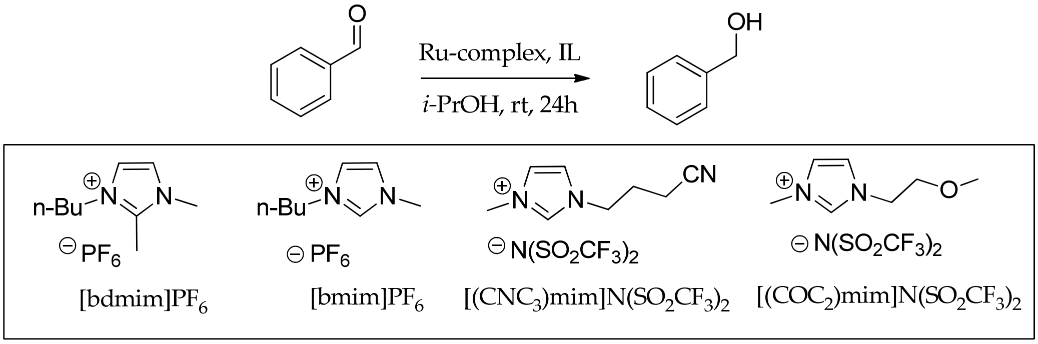
An asymmetric two-phase hydrogenation protocol based on a Ru–BINAP complex in ionic liquid was reported in 1997 by Adriano Monteiro et al. [170]. In their work, a chiral Ru complex catalyst immobilized on [bmim]BF_4 was used for the asymmetric hydrogenation of several 2-arylacrylic acids. The reaction was performed in a [bmim]BF_4–organic solvent biphasic system, and the use of various asymmetric catalysts for the hydrogenation of 2-phenylpropionic acid was implemented. Interestingly, when methanol was used, a homogeneous one-phase system was formed which obstructed the isolation of the desired product. The best results were obtained with the use of isopropanol as an organic solvent since two phases were present at the end of the reaction, and the desired product was obtained from the organic phase via simple decantation with a 99% yield and 72% ee (Scheme 24a). Additionally, the recycling of the catalytic system was possible without any detrimental effect on the catalytic activity or the enantioselectivity [170]. Moreover, the same catalytic protocol was used to produce the active pharmaceutical ingredient (S)-naproxen quantitatively in 80% ee (Scheme 24b).



Scheme 24. (**a**) Asymmetric hydrogenation of 2-phenylpropionic acid based on a Ru–BINAP/ionic liquid PTC protocol. (**b**) Naproxen production via asymmetric hydrogenation based on a Ru–BINAP/ionic liquid PTC protocol.

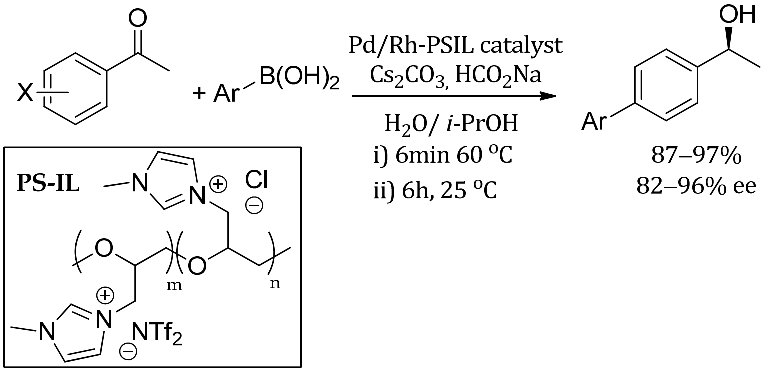
Elaborating on previous knowledge, Paul Dyson et al., highlighted the importance of [bmim]BF_4 ionic liquids in two-phase IL–arene systems as ideal solvents for catalytic species. In a series of hydrogenations of benzene, toluene, and cumene, the catalytic activity of $[H_4Ru_4(\eta^6\text{-}C_6H6)_4][BF_4]$ catalyst in ILs was comparable and even greater than the one observed in water [171]. Additionally, the low vapor pressure of the ionic liquids allowed for ease of separation from the product via simple vacuum evaporation, which simplified the product's purification. The increased lipophilicity of these ILs implies a phase transfer catalytic protocol and a possible interface mechanism in which the catalyst along with the substrate are dissolved in an interface layer between the organic and IL phase.

An interesting approach regarding the usage of ILs in biphasic hydrogenation was reported in 2017 by Francisco Sepúlveda et al. [172]. In their research, the biphasic system of various ILs in isopropanol was used for the hydrogenation of benzaldehyde (Scheme 25). The novelty of this approach was the utilization of isopropanol as the only hydrogen donor in this system, the absence of a base, and the in situ generation of the Ru catalytic species. The generation of the active catalytic species involves the phase transfer of a hydrogen into the IL phase via a unique phase transfer mechanism. The product could easily be obtained from isopropanol, and the addition of extra isopropanol allowed for continuous catalytic cycles without affecting the catalyst which was "immobilized" in the IL layer. This methodology stands as both environmentally benign and user friendly since no use of specialized equipment is needed for high-pressure hydrogen gas containment nor is there the presence of strong bases.



Scheme 25. Reduction of ketones based on a PTC ionic liquid biphasic system.

An interesting example showing the versatility of ILs in various PTC applications in chemical synthesis is the study of Xinjuan Li et al. [173]. In this pioneer work, the lipophilicity and the inherent thermal properties of ILs were applied in the synthesis of a composite cross-linked catalyst of chiral Ru-supported active species and polymer-supported ILs in the core of this system. Additionally, the chemical immobilization of $Pd(OAc)_2$ was achieved on the polymer's surface, thus creating a bifunctional catalyst able to perform the Suzuki coupling reaction and asymmetric hydrogenation in water through the formation of nanomicelles. Interestingly, the produced catalysts possessed temperature-sensitive properties. Specifically, at higher temperatures than the lower critical solution temperature (LCST) of this system, the catalyst seemed to catalyze only the cross-coupling reaction of ketones, whereas below that temperature, only the reduction of the ketones was observed. This indicated that, at lower temperatures, the chiral Ru active centers are available to the substrate; thus, asymmetric hydrogenation is greatly favored. On the other hand, at higher temperatures, more compact and regular structures are prevalent; thus, the Ru center is inaccessible to the substrate. Subsequently, the exposed Pd centers catalyze the Suzuki cross-coupling reaction of the ketones. These behaviors allowed for a one-pot two-step synthetic pathway for arylation and the asymmetric reduction of a substrate performed by a tailor-made thermally enantioselective bifunctional catalyst (Scheme 26) [173].

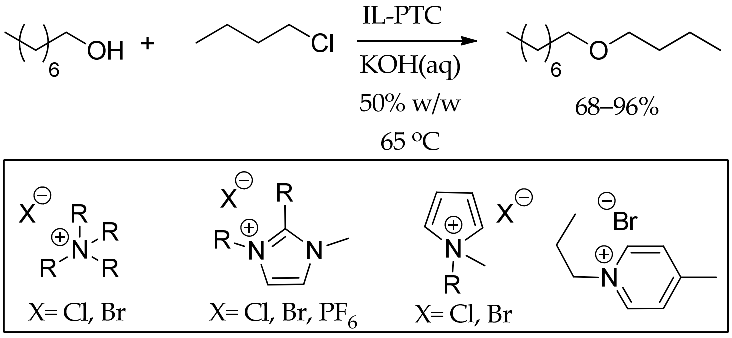


Scheme 26. Novel thermoregulation-controlled two-step one-pot reaction based on polymer-supported ionic liquid–Pd/Ru nanoparticles.

Likewise, the next year, a thermoregulated system based on a chiral Pt complex achieved the asymmetric hydrogenation of α-ketoesters [174]. The reaction was performed in a biphasic water/1-pentanol system using a chiral ionic liquid as a co-catalyst and immobilizer of the PT complex, and the formation of the desired products was achieved with excellent yields and with enantiomeric excess greater than 99%.

4.4. Etherification

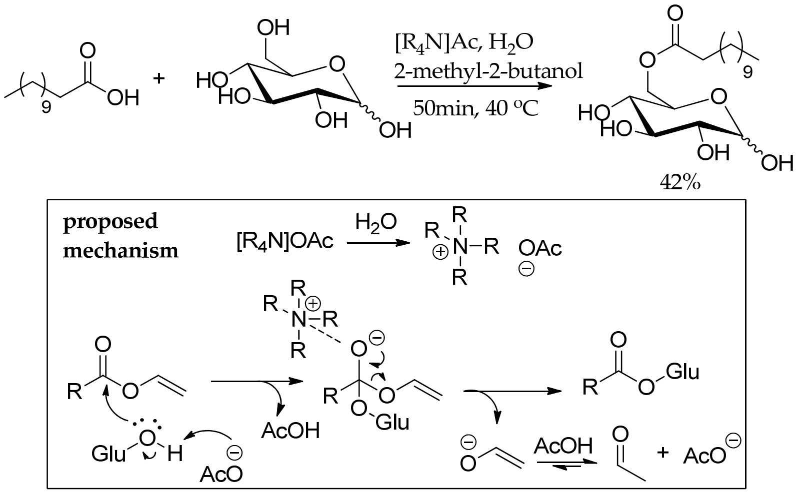
Etherification can be considered an interesting field of ionic liquid applications in phase transfer catalysis, but only one paper could be identified regarding such applications. In 2010, Jack Berden et al., reported the PTC etherification of 1-octanol with 1-chlorobutane in various ILs (Scheme 27) [175]. In this study, the structure of the ionic liquid greatly affected the reaction. It was determined that higher yields were observed when nonaromatic pyrrolidinium salts and Aliquat-type ILs were used. Surprisingly, imidazolium- and pyridinium-based ILs performed poorly under these conditions.



Scheme 27. Etherification under ionic liquid-phase transfer catalysis.

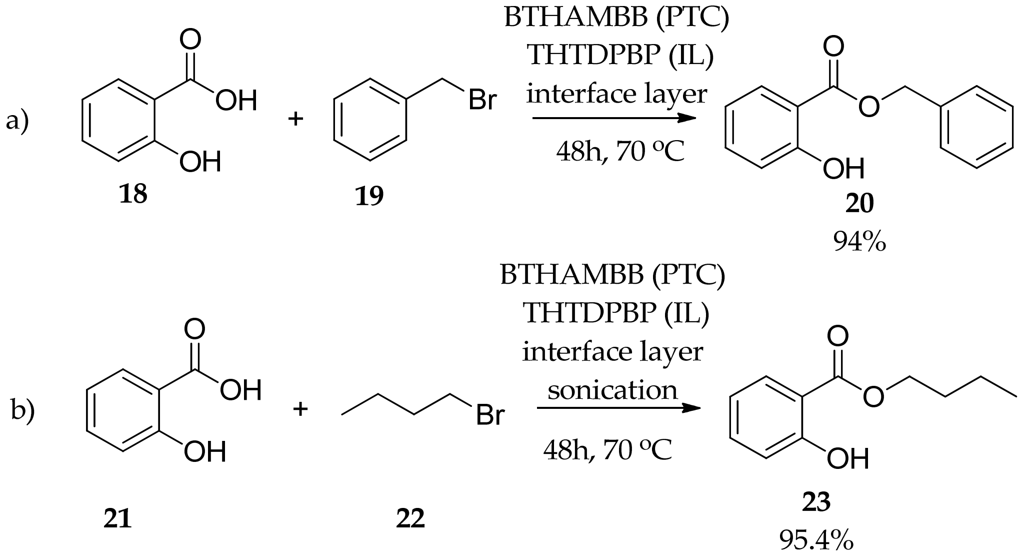
4.5. Esterification

The esterification reaction between water-soluble sugar and fatty acids to produce sugar fatty acid esters is a challenging endeavor due to the difference in polarity and lipophilicity of these molecules. Xiao-Sheng Lin et al., reported, in 2016, the esterification of glucose and vinyl laurate to provide glucose laurate ester in a biphasic IL–water system [176]. PTC was reported to be the possible reaction mechanism for the completion of this reaction. Specifically, various ILs based on quaternary ammonium ions were used, and the length of the alkyl chains greatly affected the rate of the reaction. It was proposed that these chains associate with glucose, making it more miscible in the interface layer between the two phases, and subsequently, they facilitate the interaction between the fatty acid substrate and glucose via stabilization of the anionic intermediate of the transesterification mechanism (Scheme 28).



Scheme 28. PTC esterification of glucose using IL as the catalytic medium and proposed mechanism.

A novel approach for the synthesis of different salicylate esters was introduced in 2014. The successful triphasic synthesis of benzyl salicylate was achieved using a PTC protocol. A third interface liquid phase was formed when 4,4′-bis(tripropylammonium methyl)-1,1′-biphenyl dichloride (BTPAMBC) as a phase transfer catalyst and the ionic liquid tributyl(tetradecyl)phosphonium methanesulfonate (TBTDPMS) were mixed. This co-catalytic system provided the desired product (**20**) with a 94% yield in 15 min. Additionally, a meticulous examination of the factors that possibly affect the creation of the third interface layer was performed (Scheme 29a) [177]. The same group reported the sonication-assisted PTC triphasic synthesis of butyl salicylate. The reaction was performed in a third interface layer that was formed by mixing 1,4-bis(trihexylammoniomethyl)-benzenedibromide (BTHAMBB) and the ionic liquid trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phoshinate (THTDPBP) as a co-catalyst. Product 23 was formed with a 95.4% yield in 48 h at 70 °C (Scheme 29b) [178].

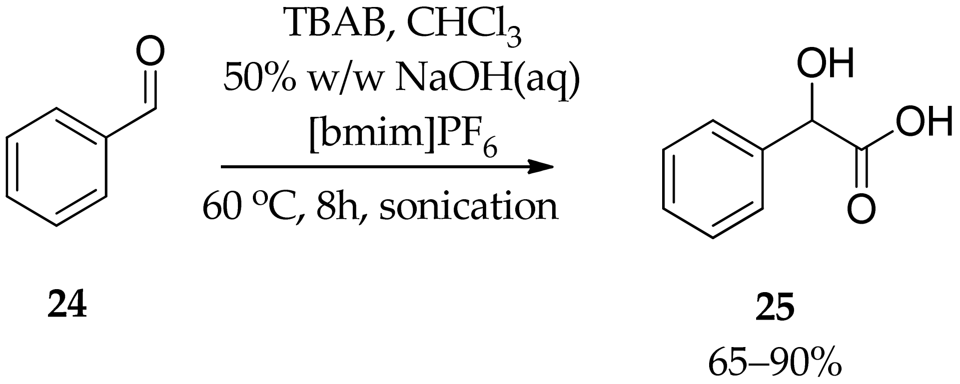


Scheme 29. Synthesis of (**a**) salicylate benzyl ester, (**b**) salicylate *n*-butyl ester using a triphasic PTC protocol in ionic liquids.

4.6. Carboxylic Acid Synthesis

The previously mentioned esterification reaction via sonication [178] was conceptualized based on the work of ultrasound-promoted synthesis of mandelic acid (**25**) by Qian Hua et al. [179]. The sonochemical approach in the formation of mandelic acid in

[bmim]PF_6 was achieved with the implementation of a PT catalyst in a biphasic organic solvent–IL system (Scheme 30). The desired product was obtained in 8 h at 60 °C. Various phase transfer catalysts were tested, with tert-butylammonium bromide (TBAB) providing the best results. Additionally, the reusability of the IL phase was successfully proved with the continuous use of the ionic liquid up to five times without detrimental effects on the observed yield.



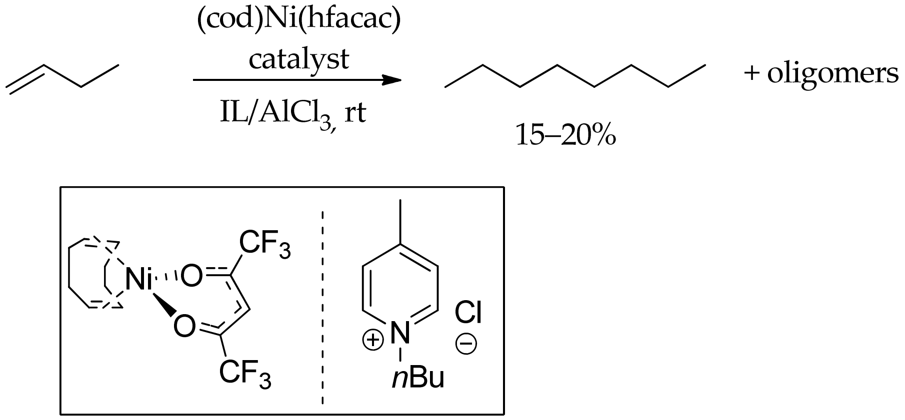
Scheme 30. Sonication-assisted synthesis of carboxylic acids based on PTC ionic liquids.

4.7. Olefin Dimerization

One of the first reported applications of ILs was their use in biphasic systems for olefin dimerization. As early as 1996, Chauvin Y. et al., reported the use of an immobilized Ni–phosphine catalytic complex in an ionic liquid phase of [bmim]Cl and a mixture of $AlCl_3/AlEtCl_2$ for the dimerization of propene [180]. The lipophilicity of the ionic liquid allowed for the olefins to interact with the catalyst in the polar environment and successfully dimerize. Preferably, the $[NiCl_2(P(Bu)_3)]$ complex was used as a catalytic precursor which quantitatively produced dimerization products with various octane numbers, which are highly useful hydrocarbon fuels. It was observed that the reaction proceeded slowly at temperatures under −15 °C and was greatly affected by the different ligands of the catalytic complex.

Sandra Einloft et al., reported the successful dimerization of ethylene in 1997 [181]. Notably, the reaction was highly exothermic, and cooling of the reaction vessel was necessary to ensure control over the products' selective synthesis. Additionally, the use of $[Ni(MeCN)_6][BF_4]_2$ as catalyst produced alkenes quantitatively with 83% selectivity of 1-butene at −10 °C and a continuous feed of ethene for 90 min [181].

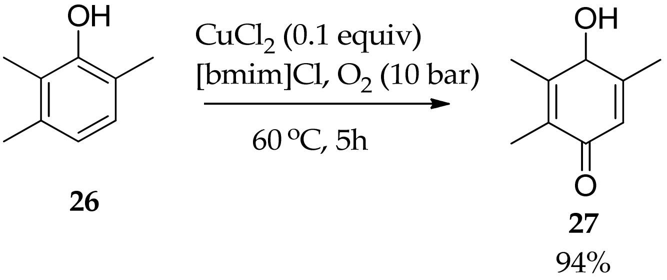
The implementation of ionic liquids has been also described [182] by Keim, W. et al., the first research group that used a Ni complex catalyst for the dimerization of alkenes in 1979 [183]. Specifically, the dimerization of 1-butane by the (cod)Ni(hfacac) complex was performed in a mixture of 1-butyl-4-methylpyridinium chloride ionic liquid and $AlCl_3$ (Scheme 31). The catalytic activity requires the dissolution of alkene in the polar IL phase by the lipophilic nature of this ionic liquid, which implies phase transfer catalysis. Additionally, the in situ formation of $AlCl_4^-$ anions, which react with 1-butyl-4-methylpyridinium cations, was reported with the addition of trace amounts of an organic base [182]. This addition significantly enhanced the catalytic activity and facilitated the use of ionic liquids as a solvent. This protocol allowed for the poor conversion of 1-butene to linear dimers and generally oligomeric and nonlinear products were observed. The novelty of these systems lies in the use of higher temperatures of 25 °C and the absence of alkylaluminium species, which do not favor reduction-sensitive organometallic complexes [182].



Scheme 31. Ionic liquids in a biphasic dimerization reaction.

4.8. Oxidation

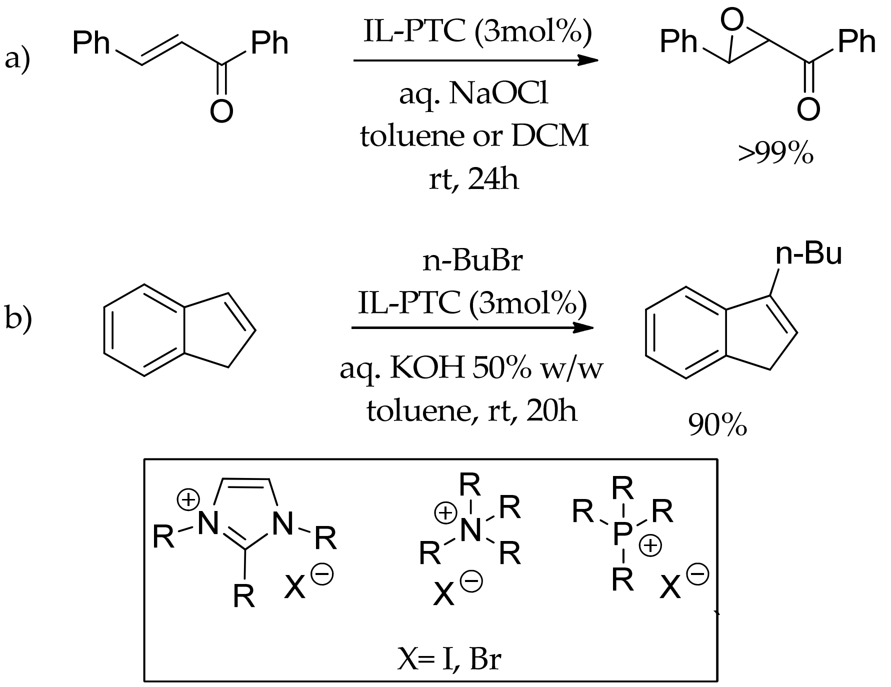
Oxidation reactions are a type of reaction in which ILs have found great applications, and possible PTC activity is suggested [184]. An interesting example is the study of Hongjian Sun et al., in which trimethyl-1,4-benzoquinone was obtained quantitatively from the $CuCl_2$ catalytic oxidation of 2,3,6-trimethyl-phenol (**26**) with oxygen in the presence of [bmim]Cl and butanol (Scheme 32). In this study, the isolation of an active catalytic species, in which the incorporation of the imidazolium cation occurred, was successful. Additionally, the best results were obtained from equimolar amounts of $CuCl_2$ and ionic liquid. These results possibly indicate the phase transfer catalytic activity of the IL. The active catalytic species is possibly dissolved in the interface layer between butanol and [bmim]Cl; thus, the IL acts as a co-catalyst and a solvent [184,185].



Scheme 32. Phenol oxidation via an ionic liquid/copper catalyst.

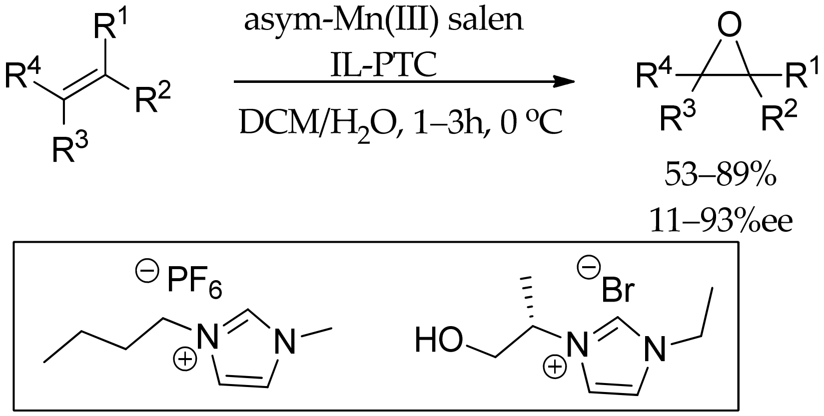
4.8.1. Epoxidation

Sentaro Okamoto et al., in 2006, also noted the phase transfer catalytic activity of imidazolium-based ILs in nucleophilic epoxidation reactions along with SN displacement [186]. In this study, a wide range of catalysts were used for the epoxidation of (*E*)-chalcone, and the desired product was obtained with a 99% yield at room temperature in 24 h (Scheme 33). Moreover, the β-elimination reaction allowed for the total conversion of the haloalkane substrate to the desired alkene. Additionally, when this catalyst was tested for the biphasic alkylation of indene under basic conditions, the desired product was produced with a 90% yield. Intriguingly, NMR analysis of deuterated indene reaction revealed that the catalyst acts possibly via the formation of an ylidene species as an intermediate, which had never been reported before. As mentioned by the group, the great efficiency of ionic liquids as phase transfer catalysts for a multitude of reactions was proved.



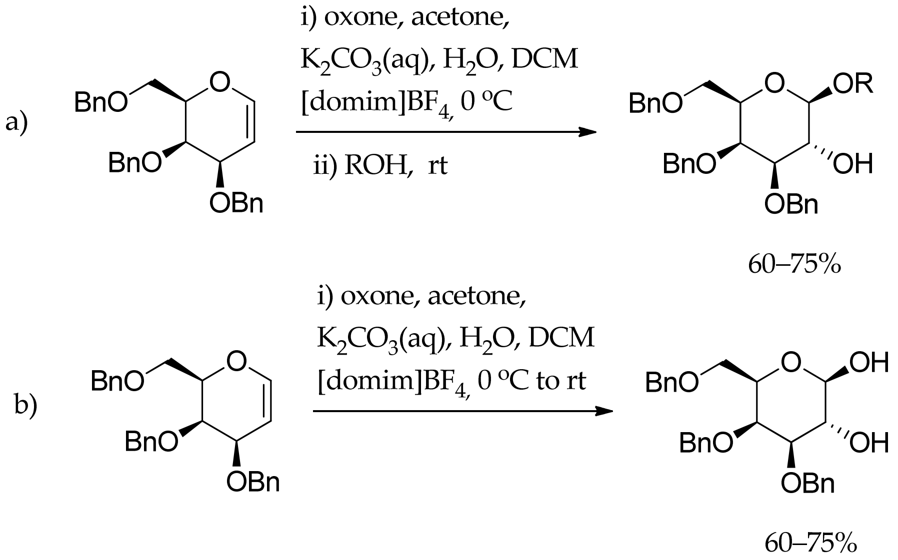
Scheme 33. (**a**) Phase transfer epoxidation of olefins using an ionic liquid. (**b**) Alkylation of indene based on PTC.

The use of epoxides as useful synthons for asymmetric ring-opening applications led to the development of asymmetric PTC protocols based on ionic liquids [187]. This protocol was based on the synergistic phase transfer effect of an immobilized asymmetric dinuclear Mn(III)-based salen complex and imidazolium-based ionic liquids. The resulting products were obtained with very good yields and in moderate-to-excellent enantioselective excess (Scheme 34). The unique structure of these complexes allowed for weak interactions with water, which highlighted the PTC role of the ionic liquids. Additionally, the reusability of these salen complexes was possible up to six times without any significant loss of the catalytic activity.



Scheme 34. Asymmetric epoxidation of olefins through a PTC protocol based on Mn–salen.

In the same manner, Cintia C. Santiago et al. [188], in 2017, reported the ring-opening reaction of various epoxides in a two-step tandem synthetic route to biologically active β-O-glycosides using ILs as effective phase transfer catalysts. Researching the scope of the imidazolium-based ILs as PTCs for the epoxidation of 3,4,6-tri-O-benzyl-D-glucal, the superiority of 1-dodecyl-3-methylimidazolium tetrafluoroborate ([domim]BF_4) was apparent since, in just 3 h, the desired product was obtained with a 70% yield. The second-best result was obtained in 12 h with a 40% yield using 1-hexyl-3-methyl-imidazolium-hexafluorophosphate ([hmim]PF_6). In the presence of acetone and aqueous $NaHCO_3$, Oxone reagent (potassium peroxymonosulfate) produced in situ dimethyl-dioxirane which, in turn, generated the desired epoxide under phase transfer conditions induced by [domim]BF_4 at 0 °C. In the second step of the reaction, the epoxide ring opening by a selected alcohol afforded the production of the final product at room temperature (Scheme 35a). Additionally, the production of the 1,2 diols was possible from the epoxides when the reaction temperature was slowly raised from 0 °C to room temperature (Scheme 35b).



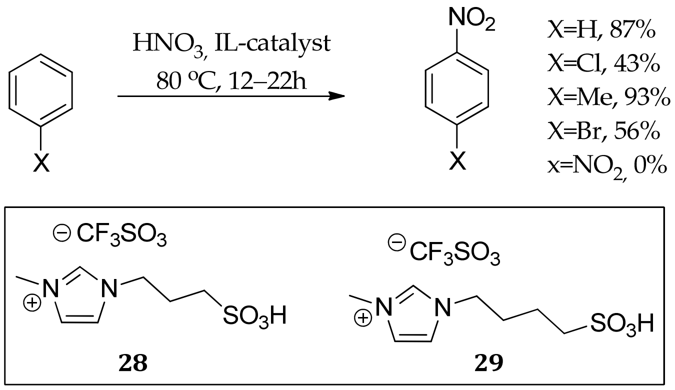
Scheme 35. Tandem phase transfer IL-assisted epoxide generation and ring-opening nucleophilic substitution by (**a**) alcohols and (**b**) water.

4.8.2. Desulfurization

An interesting work was published in 2008 in which an ionic liquid-phase transfer protocol was used for the desulfurization of mineral oils [189]. In this process, tetraethylammonium fluoride was used as a phase transfer catalyst in the presence of trifluoracetic acid, 30% H_2O_2, and the crude mixture of natural oils. Then, the biphasic mixture was heated at 50 °C for 170 min under sonication, which oxidized the organic sulfur compounds into sulfones which were dissolved in the IL phase. Further purification of the mixture was achieved by solvent extraction with acetonitrile, and the concentration of sulfur was under the detection limit. Such applications generally highlight the importance and adaptability of ILs in significant industrial procedures and future perspectives.

4.9. Nitration

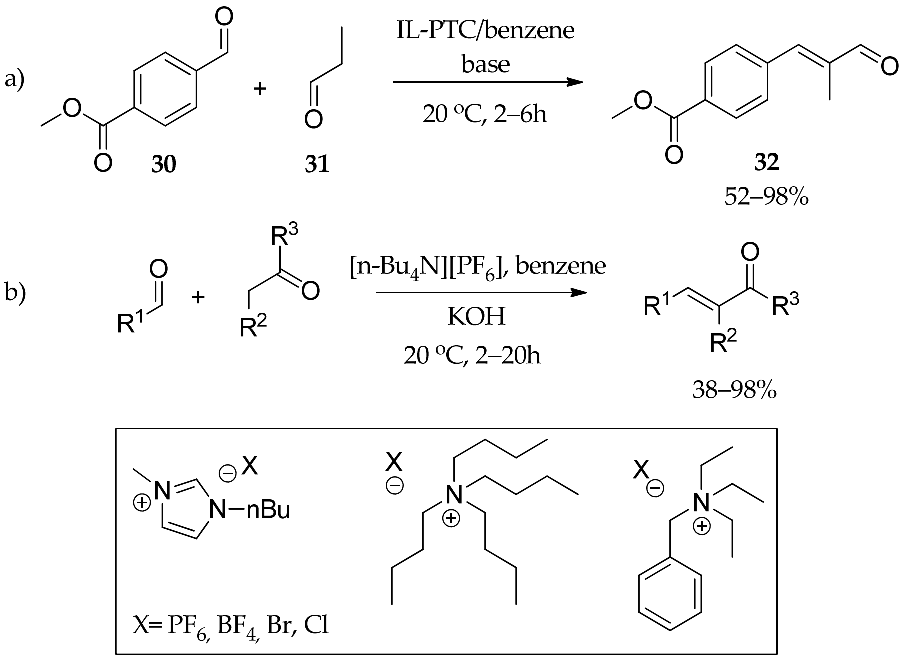
In 2004, biphasic nitration using ILs as catalysts without the need for extra organic solvents was reported [190]. The imidazolium-based IL that was used contained a terminal SO_3H moiety (**28**,**29**); thus, it was recognized as a Bronsted acid (Scheme 36). The biphasic nature of this reaction strongly implied a phase transfer catalytic mechanism, which is favored by the amphiphilicity of the IL. The nitration of various aromatic compounds followed a predictable pattern based on the type of the substituents present on the aromatic scaffold. In this regard, the deactivated nitrobenzene was not converted at all by this protocol, whilst other aromatic compounds formed the nitration products with good-to-great yields. Additionally, the reusability of the IL was proven experimentally, which indicated the possibility for more practical applications.



Scheme 36. Ionic liquids for arene catalytic nitration.

4.10. Aldol Condensation

Galina V. Kryshtal et al., in 2005, reported the cross-aldol condensation under a biphasic PTC system of benzene and [bmim]-, [BuEt$_4$N]-, and [n-Bu$_4$N]-based ionic liquids [191]. The reaction between methyl 4-formylbenzoate (**30**) and propanal (**31**) formed the condensation product (**32**) with great-to-excellent yields (Scheme 37a). Additionally, [nBu$_4$N][PF$_6$] was used as an aldol condensation catalyst of various aldehydes and carbonyl compounds for the production of the respective products with up to a 98% yield (Scheme 37). Furthermore, this catalyst was repetitively used, and no significant alteration in catalytic activity was observed, even at the fifth cycle of recycling. In comparison with this catalyst, the catalytic activity and recyclability of [bmim][PF$_6$], [nBuN][BF$_6$], and [BnEt$_3$N][PF$_6$] were notably lower [191].



Scheme 37. Biphasic PTC protocol based on ionic liquids for aldol coupling reactions. (**a**) Aldol condensation of methyl 4-formylbenzoate and propanal. (**b**) Aldol condensations using ([n-Bu$_4$N][PF$_6$]) as a phase transfer catalyst.

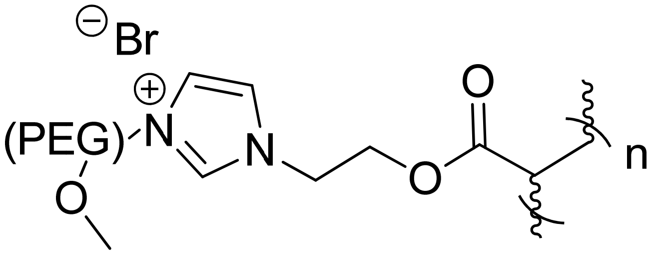
4.11. Dichlorocarbene Formation

A useful application of ILs was reported in 2008 by Galina V. Kryshtal et al., for the formation of dichlorocarbenes and trichloromethyl anion insertion using alkenes as substrates [192]. These reactions were performed using a PTC protocol based on quaternary ammonium salt ionic liquids, benzene, and chloroform and aqueous KOH as a base. The reaction yielded the best results when the [n-Bu$_4$N]PF$_6$ IL was applied. Under this protocol, a wide array of alkenes allowed for the production of the respective dichlorocyclopropane products with great-to-excellent yields of up to 98% conversion. Under the same conditions, the reaction of acrylic acid, aldehyde, and vinyl acetate derivatives resulted in the formation of the Cl$_3$C moiety insertion due to the in situ generation of trichloromethyl anion, which favorably reacts with the electrophile substrate to generate the final product [113]. The ease of ionic liquid separation and the reusability were studied, whereas a PTC interface mechanism was proposed.

4.12. Polymerization

The application of thermoregulated ionic liquids to radical polymerization reactions was reported in 2014 [193]. The reaction was controlled with the use of a [(CH$_3$(OCH$_2$CH$_2$)$_{16}$) NEt$_3$][CH$_3$SO$_3$] ionic liquid which offered thermoregulation properties and readily acted as a solvent for the Cu-mediated polymerization of styrene. Generally, at room temperature, the selected IL is immiscible in heptane–toluene solvents in which the monomer and the resulting polymer are highly soluble. When the temperature reached 100 °C, the solubility of the ionic liquid increased and allowed for the formation of a homogeneous phase in which the reaction proceeded smoothly. Under these conditions, the catalyst–IL system could easily be retrieved and recycled without loss of the catalytic activity. Such behavior could imply the formation of phase transfer ionic liquid micelles, which enable the catalytic activity to emerge in higher temperatures as observed.

An evolution of this methodology is the creation of thermoregulated poly-ionic liquids (**33**) (Scheme 38) which dissolve the active Cu(II) catalytic species and the AIBN reducing agent [194]. The ionic liquid is miscible with the benzene organic layer only at higher temperatures and also affords the polymerization of methylacrylate. After cooling, the active catalytic layer is immiscible with the benzene layer; thus, the resulting polymer can effortlessly be isolated from the reaction mixture. A similar tri-co-polymer ionic liquid was employed for the thermoregulated polymerization of methylacrylate [125]. An attractive aspect of this protocol is the repetitively high conversion rates of over 92%, even after ten catalytic cycles and the reusability of the tri-co-poly-ionic liquid/immobilized Cu species catalytically active phase. Additionally, efficient control over the polymerization reaction was achieved, and only trace amounts of the copper catalyst were detected in the polymer product.



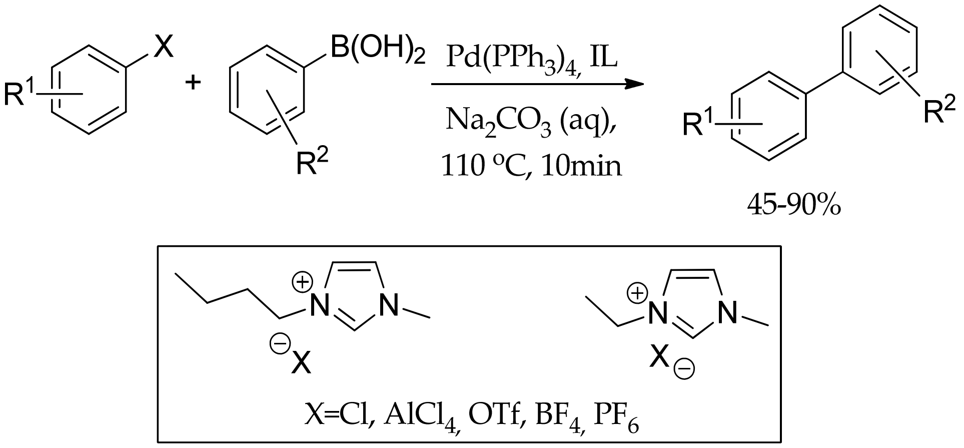
33

poly-ionic liquid

Scheme 38. Poly-ionic liquid scaffold.

4.13. Organometallic Coupling Reactions

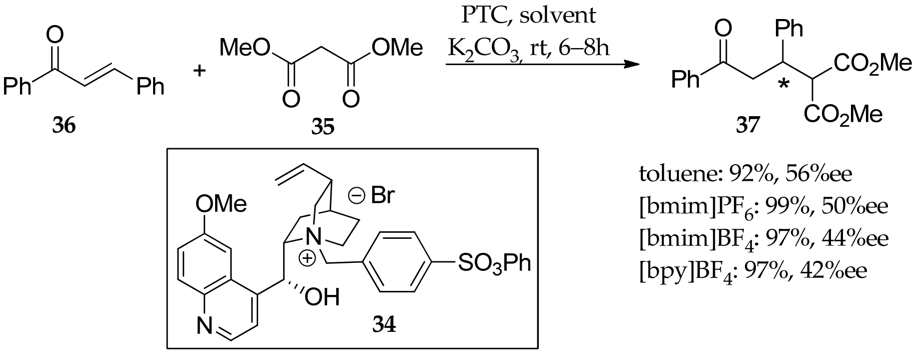
It has been mentioned that ILs can be employed for cross-coupling reactions via the immobilization of active catalytic species [173]. These types of reactions proceed probably through phase transfer catalysis in biphasic systems. Christopher J. Mathews et al., as early as 2000, reported the development of a Pd-catalyzed Suzuki coupling in the presence of [bmim]- and [emim]-based ionic liquid and aqueous phase [195]. As had been reported, the water miscibility of these ionic liquids could be finely tuned for greater efficiency, thus implying a possible PTC reaction mechanism. The reaction was able to perform aryl coupling for a wide scope of arylboronic acids and arylbromides in 10 min at 110 °C. Surprisingly, the reaction was tolerant to the presence of air, and the isolation of the desired products was performed using precipitation via water addition or diethyl ether extraction, greatly simplifying the protocol (Scheme 39).



Scheme 39. Ionic liquids in a possible PTC Suzuki reaction.

4.14. Michael Coupling Reaction

As has been noted, the importance of asymmetric PTC protocols cannot be overstated [196]. In 2003, Dere R. et al., reported the development of an asymmetric phase transfer protocol for enantioselective Michael reactions. Specifically, the use of a phase transfer catalyst based on quininium bromide (**34**) in ionic liquids and other solvents resulted in the Michael reaction between dimethyl malonate (**35**) and chalcone (**36**) [197]. The reaction occurred at room temperature and was completed in a short time interval (Scheme 40).

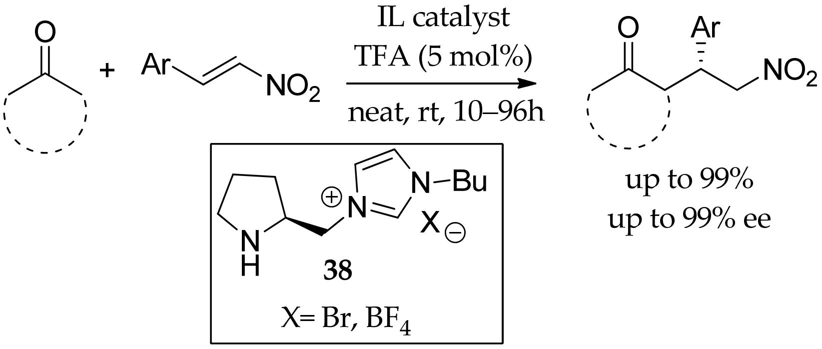


toluene: 92%, 56%ee
[bmim]PF_6: 99%, 50%ee
[bmim]BF_4: 97%, 44%ee
[bpy]BF_4: 97%, 42%ee

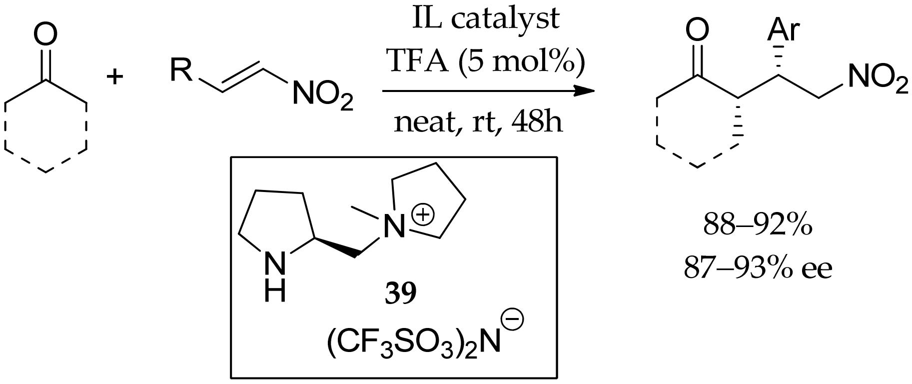
Scheme 40. Quinine-based ionic liquid as a chiral phase transfer catalyst for asymmetric Michael coupling reactions.

In an analogous approach, chiral proline-based ILs were developed for the enantioselective Michael reaction [198]. Under this reaction protocol, the formation of the product was feasible with excellent yields and enantiomeric excess (Scheme 41). These organocatalytic methodologies promote the importance of ionic liquids in chemical applications but are generally underexplored. Only one similar protocol of (*S*)-proline-based ionic liquids (**38**) was reported in 2014 [199]. In this work, the Michael reaction was achieved using a chiral catalyst with a unique structure of pyrrolidinium cation (**39**) (Scheme 42). The reaction between different ketones with nitroalkanes generated the desired produces with excellent yields and great enantiomeric excess, as implied by the chirality of the catalytic species. Additionally, the possible formation of an enamine intermediate was proposed.

A phase transfer catalytic mechanism is also plausible due to the excess of ketone, which could act as a solvent.



Scheme 41. Proline-based ionic liquids in a controled asymmetric Michael reaction.

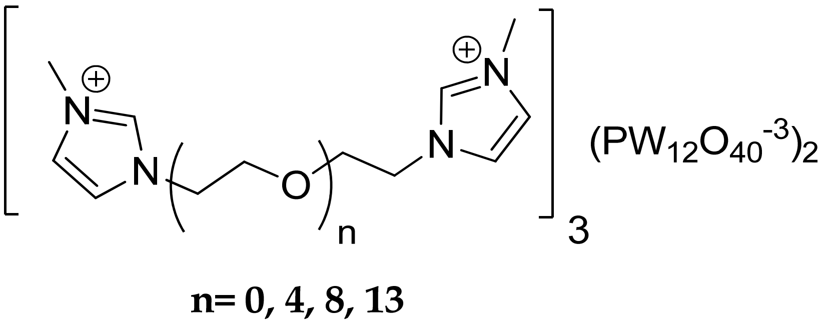


Scheme 42. Novel proline-based ionic liquid in a Michael coupling protocol.

4.15. Polyoxometalate-Based Ionic Liquids

Polyoxometalates (POMs) comprise a broad family of metal oxides with a unique and tunable morphology which have attracted scientific attention due to the various and adjustable properties, which can be exploited in a multitude of chemical applications [200]. Interestingly, hybrid materials of ILs and POMs have been developed in recent years, attempting to exploit the smelting of benefits, which both these materials possess.

Applications of these hybrid materials include the selective catalytic oxidation of sulfur-containing compounds and alcohols in diesel using H_2O_2 as oxidant. These hybrid catalysts acted as surfactants and homogeneous catalysts when a uniform distribution was achieved in water/oil emulsions. Moreover, the recovery of these catalytic species was possible with simple de/re-emulsification of the bulk mixture [201]. In a similar approach, Dan Liu et al., reported the efficient oxidation of alcohols using a composite IL–POM. In this work, a 1-butyl-3-methylimidazolium decatungstate $[\mathrm{bmim}]_4W_{10}O_{32}$ was synthetized and used as a recyclable catalyst for the chemical transformation at the relatively low temperature of 60 °C and without using organic solvents. The resulting catalyst bears thermo-regulative properties since it only generates a homogeneous system at the temperature of 60 °C, and after the completion of the reaction, it precipitates at room temperature [202]. Another practical application of similar systems was developed for the selective oxidation of benzyl alcohol to the corresponding benzaldehyde. The novel catalytic system implemented the use of a polyethylene glycol (PEG)-bridged bi-imidazolium IL and the tungsten-based POM $H_3PW_{12}O_{40}$. The resulting catalysts (Scheme 43) could provide the desired product in 30 wt% H_2O_2 aqueous solutions [203].



Scheme 43. Hybrid catalyst of POM and ILs.

All these applications that emerged from the use of POM–IL hybrid materials highlight the importance of such catalytic systems. It is expected that further developments in similar methodologies will be promoted in the future in accordance with the sustainability goals.

5. Conclusions and Perspectives

In the light of an ever-demanding need for environmentally benign alternatives, ionic liquids are a promising neoteric family of materials with unique capabilities with a wide range of applications that could potentially offer new solutions for specific problems. In this review, we inspected the use of these unique materials in the generally acknowledged, but often neglected, field of phase transfer catalysis. Unfortunately, whilst such materials could be ideal catalysts in such protocols, surprisingly, in our literature search, only a modest number of reports was found. However, the discovery of new applications of such materials in PTC protocols could boost their wide acceptance as ideal alternatives in green chemical applications. This trend can be traced systematically, especially considering the rising number of papers regarding the development of such molecules. It is our belief that the aforementioned necessity for more sustainable materials will result in an upsurge of catalytic protocols based on ionic liquids. As a result, the standardization of their use in PTC could effectively minimize the use of classic organic solvents [14,75] as ionic liquids can be effective catalysts and solvents in various reactions. Additionally, ionic liquids based on natural substances, such as choline and amino acids, are a relatively new class of IL, usually mentioned as biocompatible ILs, and a plethora of new applications will eventfully arise from their utilization [140,204]; therefore, superfluous labor must be invested in that direction. Furthermore, it can be expected that a wider use of PTC in the chemical industry may receive a severe blow regarding the serious environmental considerations in the implementation of organic solvents. As discussed, ionic liquids could act as a much-needed replacement. Characteristics such as low vapor pressure, combustion resistance, and production from natural precursors are considered vital in industry [103,143]. This could be a historic turning point for ILs since their implementation in industrial applications will, in essence, allow for their mass production. As a result, the cost of production will plunge due to factors which govern economies of scale, thus effectively eliminating cost-related deliberations, which are the major deterrent in the widespread adoption of ILs in industrial processes.

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