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Hydrogenation Catalysis in Biobased Ionic Liquids

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Abstract

This chapter is dedicated to hydrogenation procedures of (poly)-alkenes or unsaturated ketones in various biobased and not-biobased ionic liquids. The first part of this chapter defines the concept of biobased ionic liquids and their preparation. In the second part, hydrogenation processes performed in non-biobased ionic liquids are described. Finally, in the last part, the two themes are mixed and recent examples of hydrogenation procedures of alkenes, polyalkenes or unsaturated ketones in biobased ionic liquids are developed.

Keywords: ionic liquids, biomass, hydrogenation, transition metal-based catalysts, alkenes, (poly)-unsaturated alkenes, α,β -unsaturated ketones, mild conditions

1. Introduction

Hydrogenation reactions of unsaturated compounds have been among the most extensively studied processes in catalysis for many years [1, 2]. To process, generally metallic catalysts are required. Nevertheless, one of the principal challenges facing the field of transition metal catalysis is the efficient recycling and the possibility to reuse the catalytic species.

Ionic liquids (ILs) were rapidly considered as very promising solvents for this purpose, due to their tunable physicochemical properties and capacity to immobilise catalysts. As their name indicates, ILs are ionic species containing an organic cation and presenting usually low melting points below 100°C [3, 4]. ILs have a negligible vapour pressure, are not so viscous over a wide temperature range and many are non-flammable [5]. Chemical and physical properties of ILs can be also refined through proper choice of cation and anion. For these reasons, ILs have been

intensively investigated for the last three decades as green alternatives to conventional organic solvents [6–8]. Indeed, their numerous properties confer to these compounds the opportunity to replace classical organic solvents and their fields of applications are numerous: electrochemistry, organic synthesis, catalysis, complexation, extraction, etc. [4]. However, their low biodegradability or the toxicity of their degradation products and their high (eco)toxicity led the scientific community to reduce their use or to find other greener alternatives [9–13]. Considering this aspect, biobased ionic liquids could be a good alternative to classical ionic liquids but their preparation remains relative long and costly [14].

This chapter will be dedicated to the description of hydrogenation procedures of (poly)-alkenes or unsaturated ketones in biobased ionic liquids (ILs). In order to present this specific topic, the first part of the chapter will present the preparation of various biobased ionic liquids. Next, general procedures of hydrogenation in “classical” ILs will be developed according to recently published reviews. Finally, we will show that hydrogenation processes could be performed in biobased ILs with few examples.

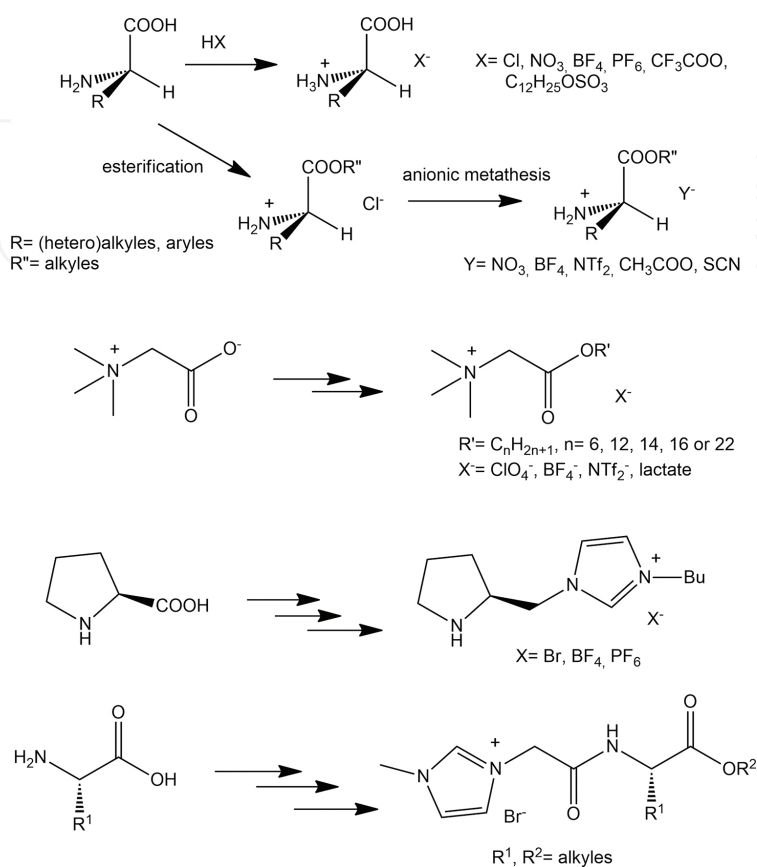
2. Biobased ionic liquids

Due to their biodegradability and non-toxicity, the use of renewable resources could improve the green character of ILs. Among biobased precursors, building blocks such as amino acids [15] and amino alcohols from proteins, sugars from cellulose, chitin, starch and other polysaccharides, aromatic aldehydes from lignin and other compounds like fatty acids from vegetable or algae-derived oils can be used.

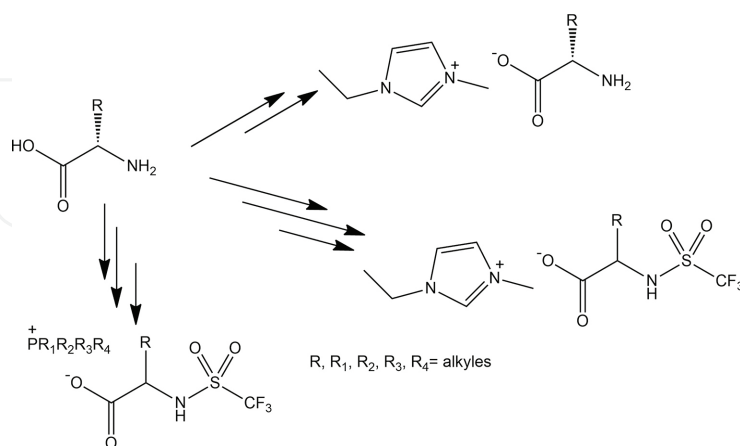
Amino acids or esters have been commonly used for the preparation of cations through classical acidification reaction or esterification/anionic metathesis sequences [16, 17]. The syntheses of all these ILs are summarised in **Scheme 1**. Protic or aprotic ILs could also be prepared, but their stability under acidic conditions was not suitable. One interesting example of such IL was presented by Trivedi et al. in which the counter anion was a sodium lauryl sulphate [18].

N-Heterocyclic amino acid-derived [19] chiral imidazolium based on valine, leucine and alanine [20], 4,5-dihydrothiazolium derived from biobased amino alcohol [21] and chiral pyrrolidine-based ILs from proline [22, 23] have been also prepared by synthetic ways involving more than four reaction steps. Gathergood et al. proposed some ILs with a neutral amino acid side chain that showed improvement on biodegradability [24]; they described also very recently L-phenylalanine ethyl ester ILs and non-ionic derivatives [25], and a series of amino acid derived ionic liquids showing microbial toxicity and biodegradation [26]. In addition, one of these last ILs presented the advantage to have antimicrobial properties. Betaine or betaine derivatives (**Scheme 2**) could be also transformed into ionic liquids, which can be used in extraction processes [27] or as herbicidal compounds [28]. Recently, de Almeida Meirelles et al. reviewed the use of ILs for food and bioproducts Industries; the authors suggested that biobased ILs could be use in food processes, especially when derived from

amino acids or choline, and that moreover, their biocompatibility could even improve the methods [29].



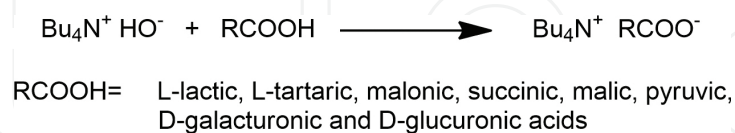
Scheme 1. Examples of aminoacids or esters-based as cations for ILs.



Scheme 2. Examples of aminoacids or esters-based as anions for ILs.

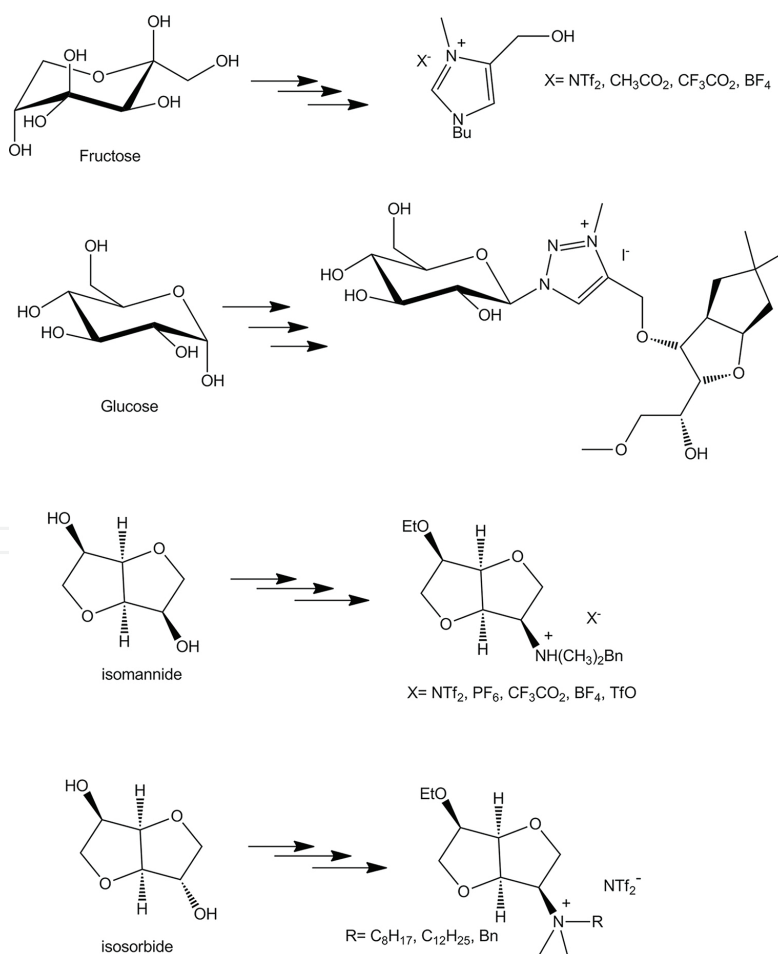
Aminoacids could as well be used to build the anionic part of the ILs. They are commonly associated with imidazolium, ammonium or phosphonium cations (**Scheme 2**) [30, 31].

In our group, an acido-basic method was used to form various ILs with anion from natural acids (L-lactic, L-tartaric, pyruvic, malic, malonic, succinic and osidic acids), but also L-proline and its derivatives. Even they were not readily biodegradable, these compounds showed in general lower toxicity towards various organisms than usual chlorinated and commercial ILs (**Scheme 3**) [32].



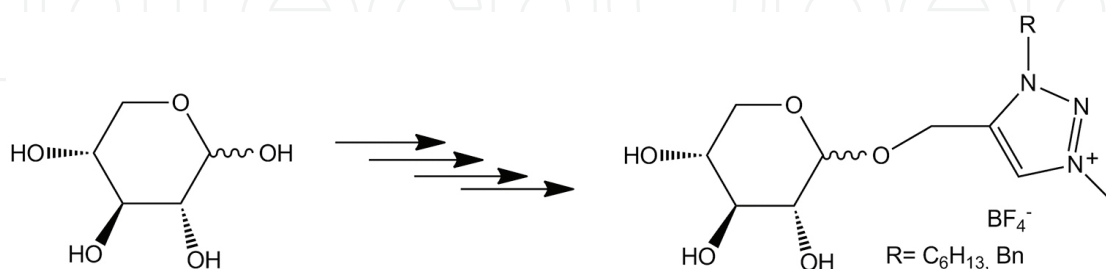
Scheme 3. Biomass-derived acid-based ILs.

Concerning the sugar family, these starting materials were essentially used to build cations. Fructose [33], glucose [34, 35], arabinose [36], isomannide [37] or isosorbide [38] have been transformed through multistep reactionnal pathways (**Scheme 4**). The resulting ILs were mainly used as chiral agents and presented in general low decomposition temperatures.



Scheme 4. Examples of sugar-based ILs.

Our group developed particularly xylose-derived ILs wearing a triazolium group. They were obtained by click chemistry between alcyated xylose and azido alkyls or benzyl, followed by methylation [39] (**Scheme 5**). Positive glass transition and low decomposition temperatures were observed, which seemed to be in relation with the presence of sugar moieties. Considering these temperatures, these ILs could only be used under mild conditions as solvents or chiral agents for chemical transformations or catalysis.



Scheme 5. Xylose-derived ILs.

Lipids represent also biosourced compounds, which could generate both cations and anions for ILs. Even if imidazolium-wearing oleic and stearic chain were easily prepared [40], the major utilisation of these lipids concerned the formation of anions, which were next associated with ammonium or phosphonium cations (**Figure 1**) [41].

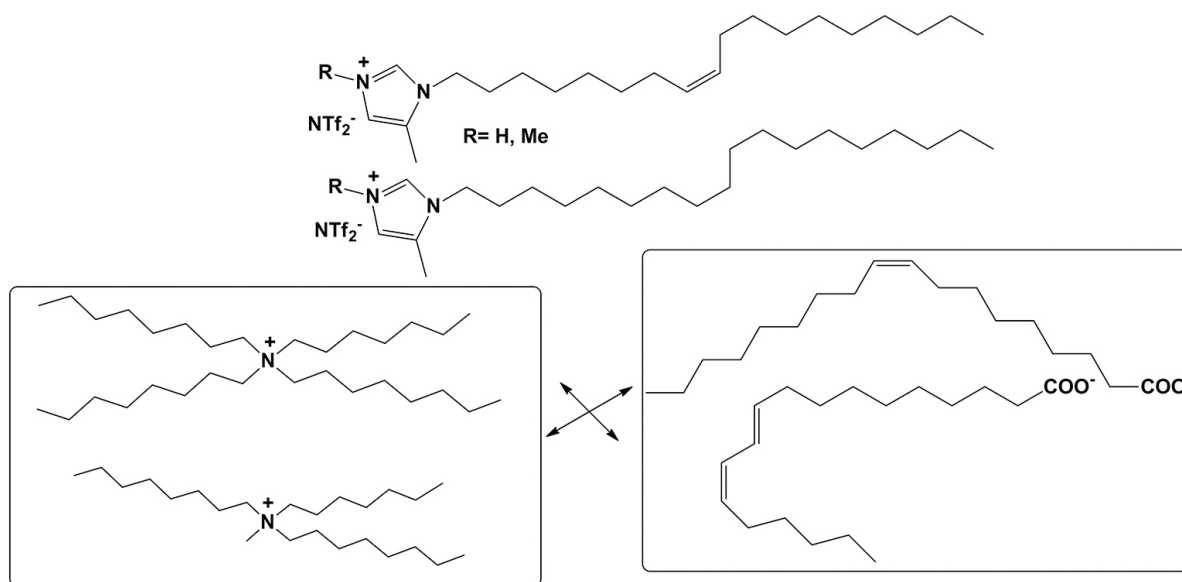
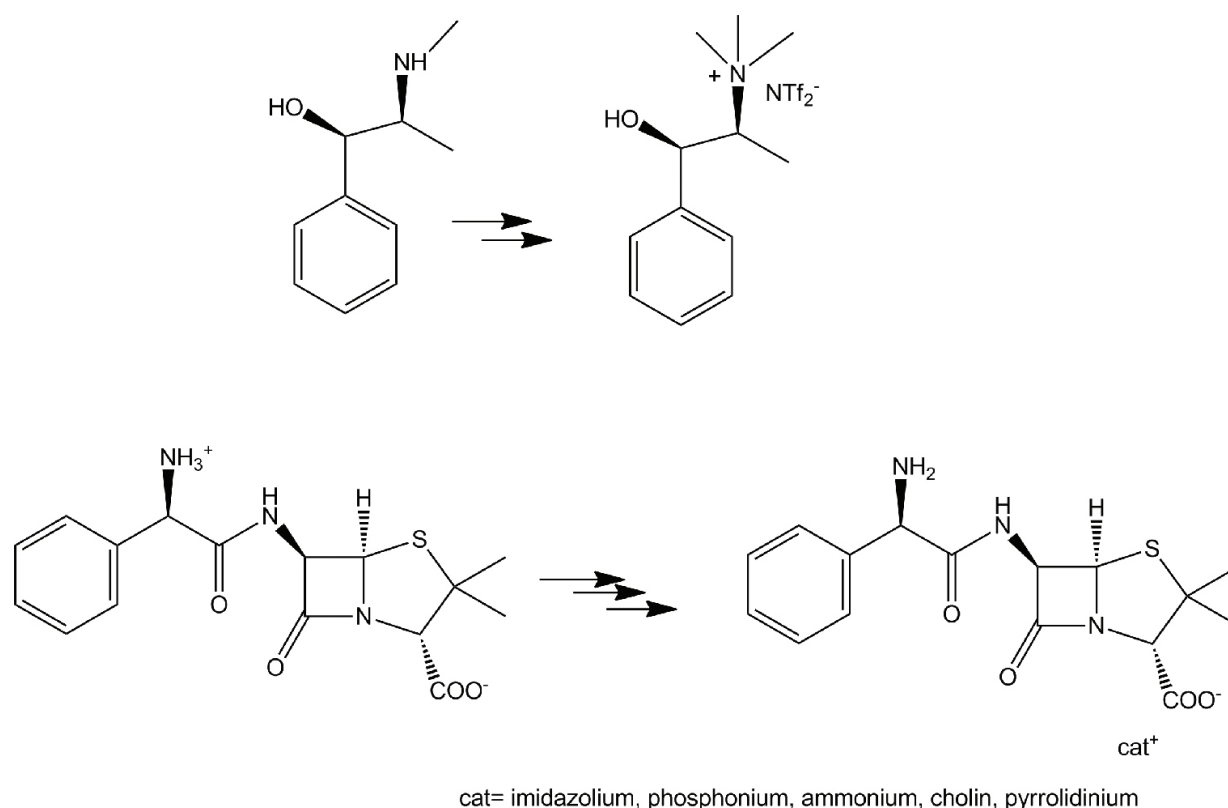


Figure 1. Lipids-based ILs.

Hulsbosch et al. described more exotic examples of bioresources for ILs as ephedrine or ampicillin in a recent and quite complete review dedicated to biobased ionic liquids for industry processing (**Scheme 6**) [14].



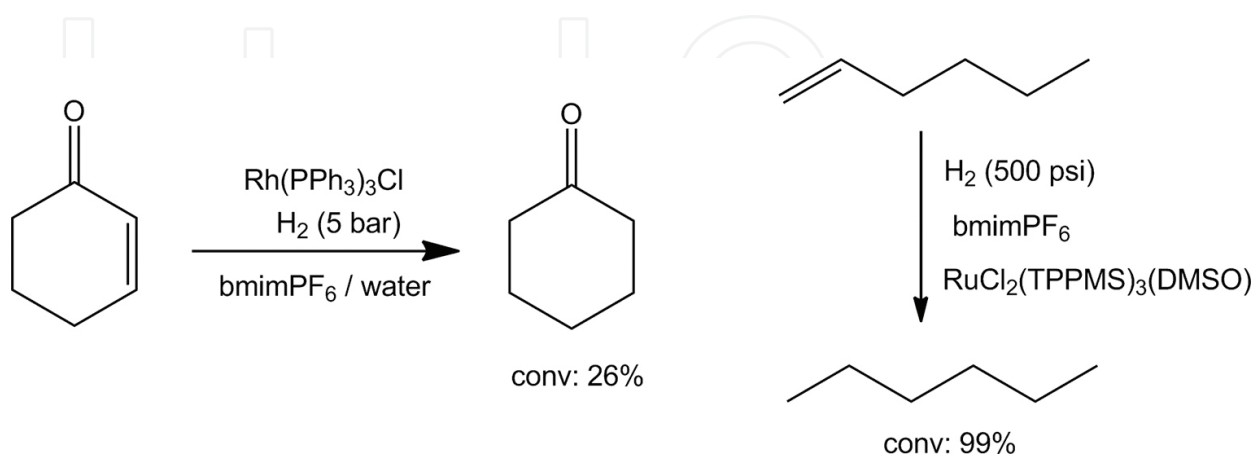
Scheme 6. Ephedrine- or ampicillin-based ILs.

3. Hydrogenation in ionic liquids

Research into catalytic hydrogenations in ILs began in 1995 with the almost simultaneous work of Chauvin [42] and Dupont [43]. Since, catalytic reactions involving metal complexes in ILs have been actively investigated. Around 300 ILs have been screened and have led to the production of useful products and intermediates [44–46]. The majority of these ILs contained heterocyclic cations, such as pyridinium, imidazolium and polyalkylammonium and recently, synthesized guanidinium, piperidinium, pyrrolium, pyrrolidinium, morpholinium, cholinium, piperazinium and thiazolium. Other ILs had bridged structures, binuclear or polynuclear, zwitterionic, hydrophobic (fluorinated) and chiral derivatives [47].

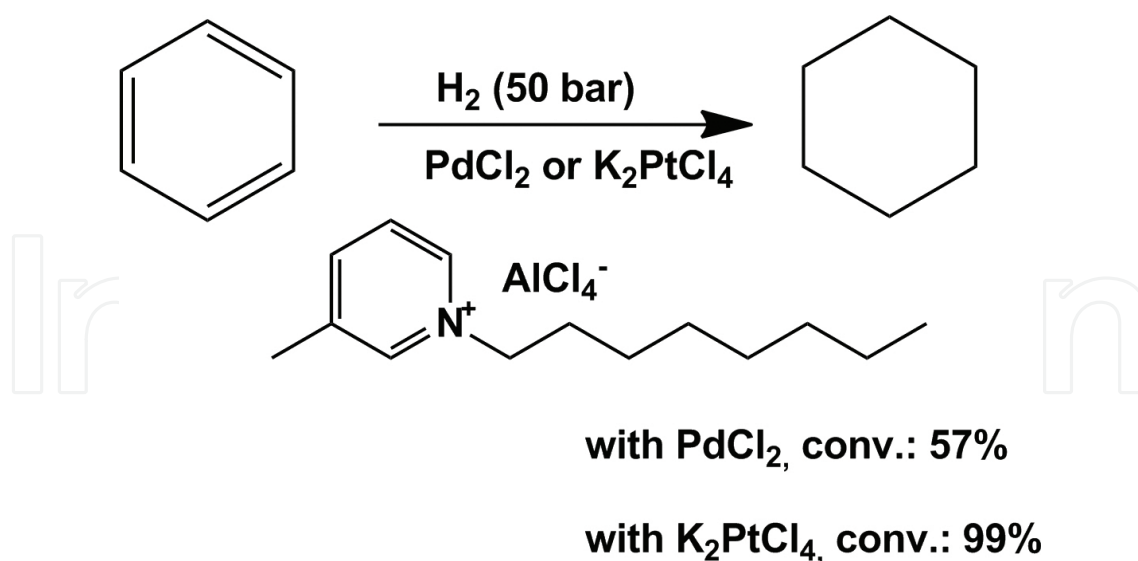
Gathergood et al. wrote, in 2011, a big chapter entirely dedicated to hydrogenation processes in ILs [48]. This chapter is quite complete. For each hydrogenation reaction reviewed, catalysts and ILs are noted, together associated with the nature of the substrate. A section describing kinetic and thermodynamic studies of hydrogenations in ILs is also presented, as well as the solubility of H₂ in many solvents and ILs under 1 atm. Some relevant examples have been identified from this chapter exclusively based on the use of H₂ and catalysts (metal complexes or nanoparticles) in ILs.

Concerning the use of transition metal-based catalyst, various Ru- or Rh-based catalysts were used for the hydrogenation of halonitrobenzenes [49], cinnamaldehyde [50], cyclohexanone [51] or hexene [52] in 1-butyl-3-methylimidazolium hexafluorophosphate (bmim PF₆) (Scheme 7).



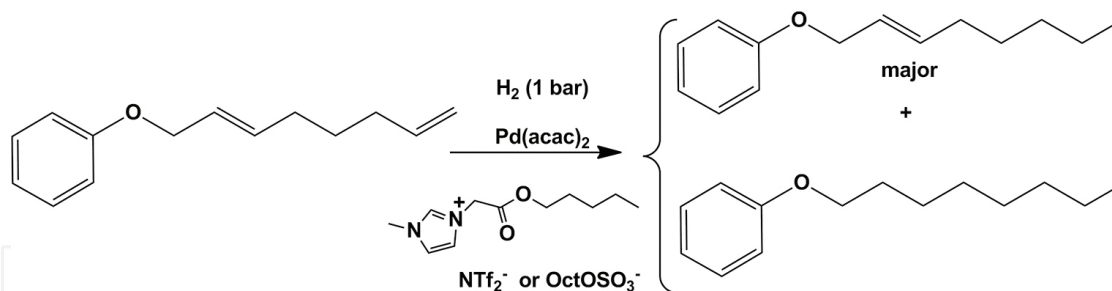
Scheme 7. Rh- or Ru-catalysed hydrogenations.

For these last compounds, Pt- or Pd-based complexes could also be used [53] as well as for the hydrogenation of benzene [54] or benzene derivatives [55] pyridinium ILs (Scheme 8).



Scheme 8. Pd- or Pt-catalysed hydrogenations of benzene.

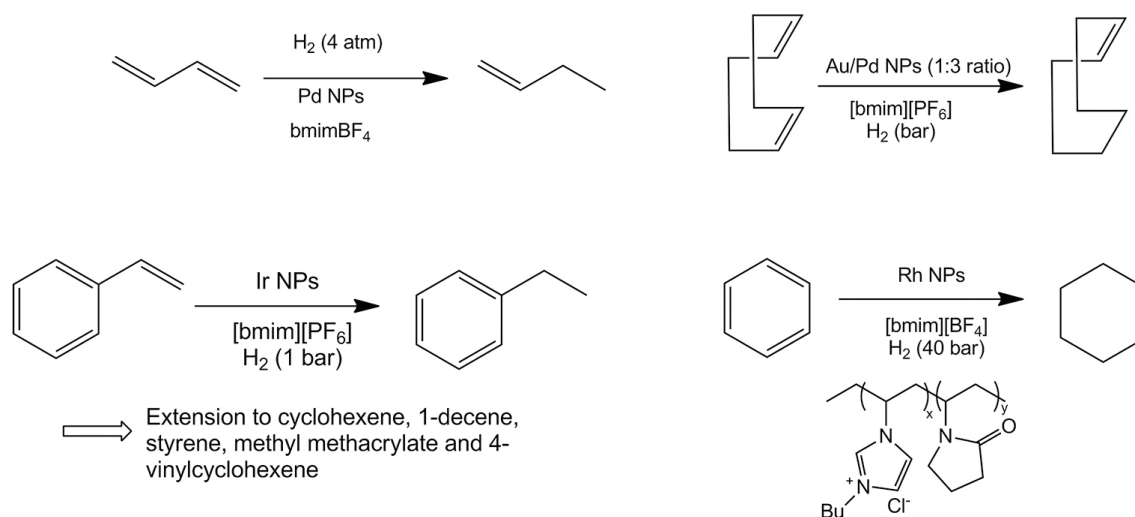
PdCl₂ was also used by Gathergood et al. [56] in imidazolium ILs, including a readily biodegradable IL [(3-methyl-1-pentoxycarbonylmethyl)imidazolium octylsulphate], for the selective hydrogenation of phenoxyocta-2,7-diene under mild conditions (Scheme 9).



Scheme 9. Pd-catalysed hydrogenation in the presence of ester-functionalised ILs.

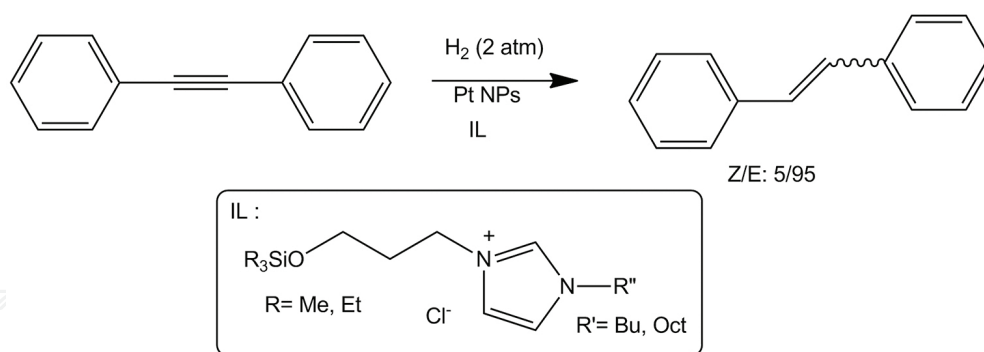
Concerning the asymmetric hydrogenation leading to enantiomerically pure products [57], the source of chiral induction was generally due to the presence of chiral ligands (BINAP or BINAP derivatives) coordinated to a metal catalyst [58–61], Rh- and Ru-based catalysts being generally the favourite candidates [48].

Metallic nanoparticles (NPs) could also be very useful for the hydrogenation processes. However, the knowledge about their formation and stabilisation for hydrogenation reactions in ILs is relatively new [62]. Pd [63, 64], Pt [65], Ir [66, 67], but also mixed Pd/Au NPs [68] were commonly used for (selective) hydrogenation of (poly)alkenes, while Ru-[69] and Ni-NPs [70] remained quite rare and were used for selective or complete hydrogenation of alkenes or arenes in imidazolium ILs (**Scheme 10**).



Scheme 10. NPs-assisted hydrogenations.

Scheeren et al. showed the formation of stable and isolable Pt(0)-NPs by reacting $\text{Pt}_2(\text{dba})_3$ in 1-n-butyl-3-methylimidazolium hexafluorophosphate Bmim PF_6 with molecular hydrogen (4 atm) at 75°C [65]. These NPs were very efficient for the hydrogenation of diphenylacetylene in Si-functionalised ILs (**Scheme 11**).



Scheme 11. Hydrogenation of diphenylacetylene in the presence of Pt NPs in Si-functionalised ILs.

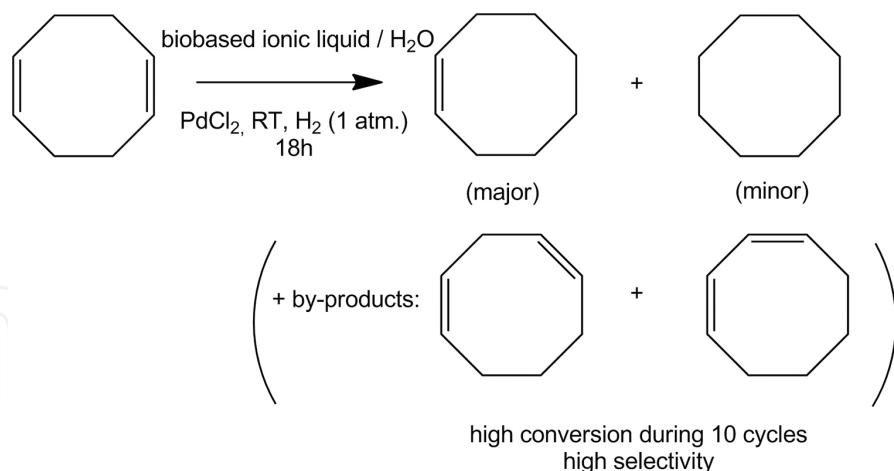
4. Hydrogenation in biobased ionic liquids

In 2013, Ferlin et al. prepared easily and with good yields, biobased ionic liquids from natural organic-derived anions (L-lactate, L-tartrate, malonate, succinate, L-malate, pyruvate, D-glucuronate and D-galacturonate) by reaction between tetrabutylammonium hydroxide (TBA·OH) and an excess of the corresponding acid (**Scheme 3**) [32]. Toxicity assays towards a large panel of bacterial and fungal strains were performed. ILs containing D-glucuronate or D-galacturonate anions were the less toxic whereas TBA L-tartrate and TBA L-malate were the most toxic biomass derivatives. All ILs were less toxic to *E. coli* than TBA Br. Unfortunately, none of the salt containing biomass-derived anions passes the closed bottle test, nor tetrabutylammonium, tetraethylammonium or tetramethylammonium bromide.

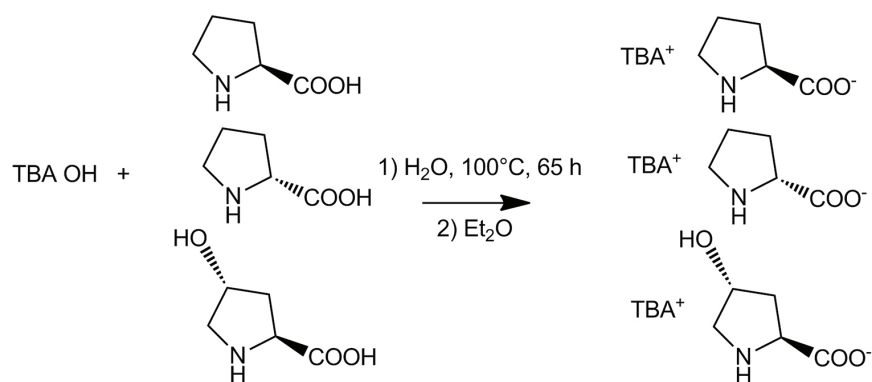
These biobased ILs showed good performance and recyclability (until 10 runs without loss of activity) in catalytic selective hydrogenation of 1,5-cyclooctadiene into cyclooctene at room temperature under atmospheric H₂ pressure. In these mild conditions, they were more suitable for selective hydrogenation than commercial imidazoliums or ammonium ILs, which gave cyclooctane as major product (**Scheme 12**) [32].

Proline was also used to prepare easily chiral ionic liquids (CILs) tetrabutylammonium-(S)-prolinate, tetrabutylammonium-(R)-prolinate and tetrabutylammonium trans-4-hydroxy-(S)-prolinate from amino acid, still by acid-base reaction with tetrabutylammonium hydroxide (TBA·OH). While all three CILs have low antimicrobial toxicity to a wide range of bacteria and fungi, they did not pass the closed Bottle biodegradation test (**Scheme 13**) [71].

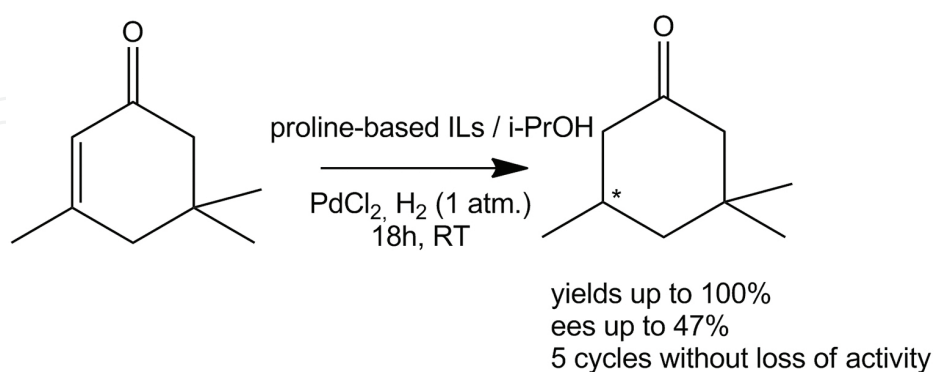
The hydrogenation of double carbon-carbon bonds of α,β -unsaturated ketones was processed under mild conditions with PdCl₂ as catalyst in the presence of a CIL and a co-solvent (**Scheme 14**) [71]. The best performance was achieved when isopropanol was used in a co-solvent/CIL ratio equal to 5. Total conversion of isophorone with an enantiomeric excess (ee) up to 47% was obtained, and recyclability of the system was observed for five cycles without loss of reactivity.



Scheme 12. Selective hydrogenation of 1,5-cyclooctadiene in the presence of ILs.



Scheme 13. Preparation of proline-based ILs.

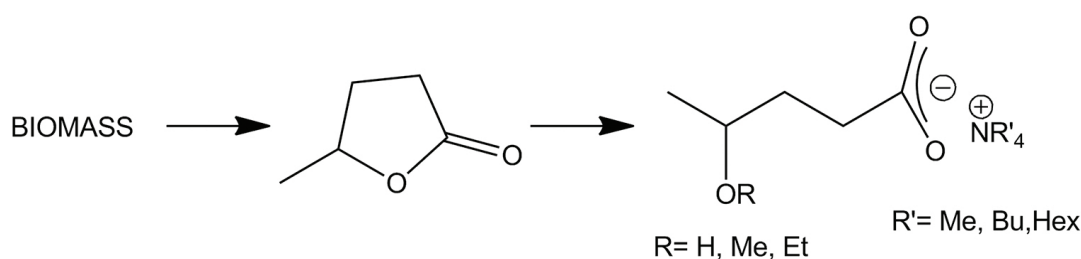


Scheme 14. Selective hydrogenation of α,β -unsaturated ketones under mild conditions in the presence of ILs.

Enantioselective hydrogenation of others α,β -unsaturated ketones was studied in the same mild conditions. Considering the particularly mild conditions, it was found that the method was very effective and competitive by comparison with previous works. Total conversion of

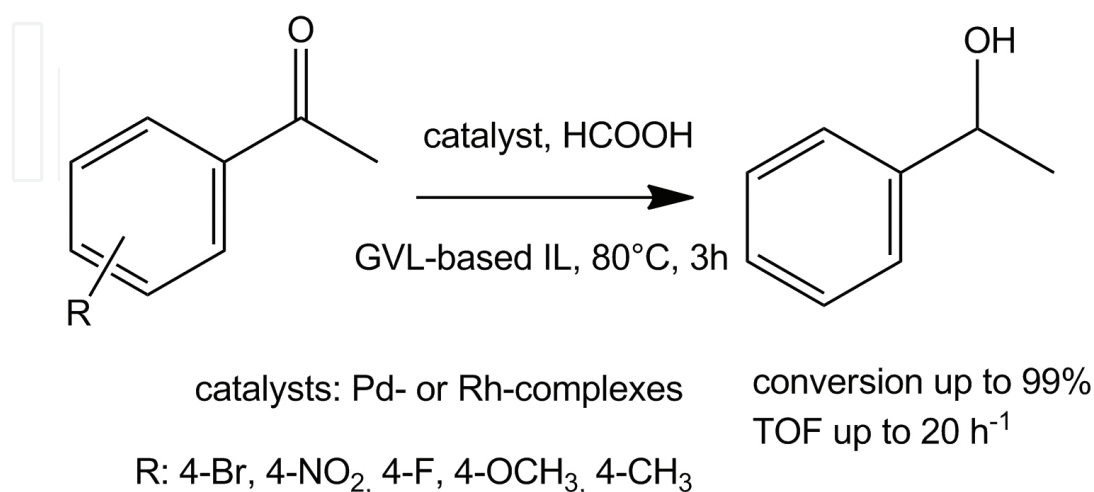
pulegone was obtained with a good diastereoisomeric excess (de). Conversion was also complete for (R)-carvone with a very high selectivity of 90%. Hydrogenation occurred in the two carbon-carbon double bonds and an important de of 73% was observed. In the case of progesterone and 4-cholest-3-one, reaction occurred with very good yields and de, especially for 4-cholest-3-one.

Finally, concerning the field of transfer hydrogenation (so without the use of metallic species), γ -valerolactone-based ionic liquids (GVL-ILs) containing hydroxyvalerate anion were prepared according acid base reaction (**Scheme 15**) [72]. These ILs were successfully applied as alternative solvents for homogenous catalytic transfer hydrogenation of acetophenone and its substituted forms, but also of functionalised ketones and alkenes.



Scheme 15. Preparation of γ -valerolactone-based ILs.

A series of GVL-based ILs associated with tetraalkylammonium cations were tested. Structure of the cation had negligible influence on the catalytic activity. The potential recyclability of the catalytic system was demonstrated in four consecutive cycles, especially for the reduction of acetophenone. The highest conversions were achieved by using $[\text{Rh}(\text{cod})_2]^+[\text{BF}_4]^-$ as catalyst precursor and formic acid as hydrogen donor. The optimal reaction conditions were 80°C and a molar ratio of HCOOH /substrate between 5:1 and 6:1 (**Scheme 16**) [73].



Scheme 16. Transfer hydrogenation of substituted acetophenones.

5. Conclusion

ILs are good solvents or co-solvent for metallic induced hydrogenation reactions. At first, their physical-chemical properties can be tunable depending on the anion-cation association. Consequently, the appropriate IL has to be simply chosen/found for the studied reaction. In addition, ILs are highly thermally stable, which is an advantage in the case of high-temperature hydrogenation reactions. The more important points are that they present good solubility of hydrogen and they are able to solubilise and stabilise metallic catalysts. As a consequence, they can promote hydrogenation reactions in mild conditions, sometimes the selectivity of the reaction, and/or they can allow the recyclability of the catalyst.

Hydrogenation in “usual” ILs has been performed on various unsaturated and aromatic substrates with various metallic catalysts or nanoparticles. In general, satisfying conversions and/or yields were observed. These reactions mainly used imidazolium derivatives. They are the more common ILs, but also present (eco)toxicity and are not biodegradable.

To contour this problem, biobased and green ILs can be used. These compounds can be easily obtained from different biomass, such as amino acid, acids from bioprocess, carbohydrates or fatty oils. Despite their low biodegradability at the moment, they present in general lower (eco)toxicity than the commercial ILs. Similar to the “usual” ILs, biobased ILs are ideal solvent for hydrogenation reaction and can even bring improvements. When used as co-solvent, ammonium biobased ILs showed better selectivity and recyclability for 1,5-cyclooctadiene hydrogenation into cyclooctene in mild conditions than commercial ILs. Also biobased ILs can be chiral, brought by the chirality of their biobased building blocks, and be used for enantioselective hydrogenation reactions. With proline ILs, isophorone and carvone were hydrogenated in mild conditions with a good enantiomeric and diastereoisomeric excess, respectively. Transfer hydrogenation reactions were also recently investigated with biobased ILs. High conversion of acetophenone was achieved in the presence of γ -valerolactone-derived ILs, and the systems were reused four times without loss of reactivity.

Even if improvement needs to be made, especially for biodegradability of the compounds and simplification of their synthesis, biobased ILs seem to be good solvents, not only for hydrogenation reaction, but also for a wide range of chemical transformations (coupling reactions, oxidation, etc.). Moreover, with the increasing interest of valorisation of the biomass and the need to replace compounds derived from oil, new structures and applications of biobased ILs are expected for a near future.

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