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New biobased Tetrabutylphosphonium ionic liquids: synthesis, characterization and use as solvent or co-solvent for mild and greener Pd-catalyzed hydrogenation processes

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ABSTRACT: Phosphonium-based Ionic Liquids (PhosILs) with natural organic derived anions (L-lactate, L-tartrate, malonate, succinate, L-malate, pyruvate, D-glucuronate, Dgalacturonate, ferulate, p-coumarate) were easily prepared by acid-base method from tetrabutylphosphonium hydroxide and an excess of the corresponding acid with good yields. Their characterization was realized through classical NMR, IR and elemental analysis techniques; their viscosity and ATG parameters were also determined. These ionic liquids showed good performance and recyclability in the selective Pd-catalyzed hydrogenation of alkenes, polyenes like linoleic acid and enantioselective hydrogenation of unsaturated ketones such as isophorone at room temperature under atmospheric H₂ pressure. Furthermore, NMR studies leading to computational calculations were performed to establish easily the composition of the resulting mixture obtained through the hydrogenation of linoleic acid.

Keywords: Ionic liquids, tetrabutylphosphonium, (di)acids, aminoacid, hydrogenation, palladium, linoleic acid, unsaturated ketones, enantioselectivity, recyclability.

Introduction

Ionic liquids (ILs) present a class of salts, usually characterized by low melting points below $100 \, {}^{\circ}\text{C}^{1}$ With their numerous properties, ILs qualify as a good candidate to replace classical organic solvents in many fields:^{1b} electrochemistry, organic synthesis, catalysis,

complexation, extraction, etc ...Compared to their ammonium analogues, ILs containing phosphonium cations are much rarer and studies involving quaternary phosphonium systems are scarce.² Indeed, ILs based on quaternary nitrogen cations such as imidazolium and pyridinium have been extensively investigated by comparison to phosphonium ILs which received scant attention; however, there is no predilection for either family as both have their own advantages and disadvantages.²

Typical phosphonium cations have the general formula $[R'PR_3]^+$, in which three of the alkyl groups are identical while the fourth is different. As well, asymmetric tertiary phosphines $(RR'_2P \text{ or } R_2R'P)$ could lead to $[RR'_2R''P]^+$ and $[R_2R'R''P]^+$ cations through free radical addition.³ These phosphonium salts associated to halides are commercially available. Through anion exchange reactions, a large variety of phosphonium-based ILs have been synthetized.⁴ Halogen free systems can be also produced by direct reaction of tertiary phosphines with alkylating agents such as benzenesulfonate, alkyltosylates, trialkylphosphates, and dialkylsulfates.⁵ Chiral,⁶ protic⁷ and cyclic⁸ phosphonium based ILs have also been prepared through classical methods used with ammonium analogues. Respective properties (stability, conductivity, self-diffusion) of both ILs families were also compared and revealed important influence of the nature of the cation.

However, classical ammonium or phosphonium based ILs present toxicity on diverse microbial strains and are low biodegradable,⁹ limiting their character of "green compounds or green solvents". Consequently, greener ILs have been then extensively investigated since 2010 essentially concerning ammonium, imidazolium, thiazolium, choline or betaine cations associated to aminoacids or esters as counter ions.¹⁰ Concerning phosphonium cations, alkyltrihexylphosphonium acesulfamates were obtained in high yields by a metathesis route, starting with alkyltrihexylphosphonium chlorides or bromides and the commercially available acesulfamate potassium salt considered as a nontoxic organoanion.¹¹ This IL was essentially used in electrochemistry. Ohno and coll. also described the synthesis of ILs with 20 natural aminoacids with ammonium¹² and phosphonium¹³ cations. However, in general, the phosphonium analogues showed relatively low levels of biodegradability, in contrast to dialkylimidazolium and alkylpridinium ILs with incorporated ester moieties and octylsulfate anions, as demonstrated by Scammells et al..¹⁴

For our part, we prepared a few years ago, ILs with a bioderivated anion, such as acids obtained from biomass (lactic, tartaric, malic... acids), osidic acids or amino acids like proline or derivatives (Figure 1).^{15a,b} These ILs derived from TBA (tetrabutylammonium) showed good performance and recyclability in catalytic selective hydrogenation of 1,5-cyclooctadiene

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(1,5-COD) into cyclooctene at room temperature under atmospheric H₂ pressure and were less toxic to E. coli than commercial TBABr. Our system was already largely competitive compared to other selective hydrogenation processes of 1,5-COD conducted under harsh conditions (5-50)bar, 50-100°C and 4-6 h) with different systems BMIM.PF₆/Na₂[Ru₆C(CO)₁₆],^{16a} Ni catalyst coated with BMIM.C₈H₁₇SO₄^{16b} and BMIM.BF₄/Pd(acac)₂.^{16c}



Figure 1 - Biobased TBA ionic liquids

In fact, catalytic hydrogenations in ILs have become the subject of extensive studies since 1995 triggered by the simultaneous work of Chauvin^{17a} and Dupont.^{17b} Ever 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.¹⁸ The majority of these ILs contained heterocyclic cations, such as pyridinium, imidazolium, polyalkylammonium and recently synthesized guanidinium, piperidinium, pyrrolium, pyrrolidinium, morpholinium, cholinium, piperazinium, thiazolium. Hydrogenation processes in ILs have been recently reviewed by Gathergood et al.¹⁹ in a quite complete book chapter.

Many organometallic catalytic systems were already described for the hydrogenation of isophorone, essentially based on palladium derivatives associated to chiral ligands. These systems consist on black palladium or palladium supported over Al₂O₃, MgO, BaCO₃, SrCO₃, CaCO₃ or modified silica, associated to proline,²⁰ proline-based chiral modifiers,^{20h,21} or (–)-dihydroapovincaminic acid ethyl ester in high pressure conditions.²² Other organometallic systems are used like Ru-²³ or Raney Ni-based²⁴ catalytic systems which preferentially lead to trimethylcyclohexanol (TMCH), wahile Cr-Ni-,²⁵ Zn²⁶- or Rh²⁷- based ones yield only the saturated ketone. In general, these catalytic systems are performed in harsh reaction conditions (very high pressure, toxic solvents).²⁰⁻²² scCO₂ as a reaction medium as a replacement for organic solvents for heterogeneously catalyzed hydrogenation of carvone was also highlighted by enhancing conversion.²⁸

Apart from our work with ILs or CILs (Chiral Ionic Liquids)^{15a,b}, to our knowledge only one work concerning hydrogenation process in biobased ILs has been reported.^{15c,29} It concerned γ -valerolactone-based ILs used for transfer hydrogenation, so without the use of metallic species. These ILs were successfully applied as alternative solvents for homogenous catalytic transfer hydrogenation of acetophenone and its substituted forms, as well as other functionalized ketones and alkenes.

Chiral ionic liquids (CILs) tetrabutylammonium-(*S*)-prolinate, tetrabutylammonium-(*R*)prolinate and tetrabutylammonium *trans*-4-hydroxy-(*S*)-prolinate were also easily prepared by our team in one step from the aminoacid and tetrabutylammonium hydroxide (TBAOH) and revealed interesting properties in ecotoxicity and in asymmetric catalysis of α , β -unsaturated ketones such as isophorone.^{15b}

Furthermore, as hydrogenation of vegetable oils represents a real challenge, we were interested to develop these hydrogenation processes in ILs. In 2012, Pagliaro and co-workers prepared some Pt(0) nanoparticles stabilized on silica which could lead in mild conditions (RT, 1 atm. H₂) to the complete hydrogenation of vegetal oils for many runs.³⁰ Electrochemical pathways were also performed using Pd/Al₂O₃ and Pd-Co/Al₂O₃ as catalysts in various pH conditions: oleic acid was obtained with 80% yield at pH equal to 13.^{31a} The partial hydrogenation of this polyunsaturated acid was also performed by Pd/Al₂O₃ doped with various thiolate self-assembled monolayers under high H₂ pressure and at high temperature.^{31b}

So, this paper covers a detailed description of tetrabutylphosphonium based ionic liquids (PhosILs) and their major influence on hydrogenation catalysis especially their contribution to selective mild hydrogenation procedures of fatty acids or to asymmetric catalysis of α , β -unsaturated ketones.

Results and Discussion

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Synthesis of phosphonium-based ionic liquids (PhosILs) with tetrabutylphosphonium (TBP) as cation:

As previously described for ammonium based ILs,^{15a} **PhosILs** were prepared from tetrabutylphosphonium hydroxide (TBPOH) and an acid following an acid-base method developed by Ohno and co-workers.¹² The acids issued from the biomass were L-lactic, L-tartaric, malonic, succinic, L-malic, pyruvic, D-glucuronic, D-galacturonic acids and S-proline (Scheme 1). Three different pathways were improved considering the different physical properties (solubility, melting points, etc..) of the employed acids. All pathways were simple and efficient, as corresponding ILs were obtained with high yields and most of them were liquid at room temperature.

		Pathway A : 1) H ₂ O, 100°C, 24h	
		2) Et ₂ O	
		Pathway B : 1) EtOH, 75°C, 24h	
		2) Et ₂ O	
TBPOH	+ R-COOH		→ TBP R-COO
(1 eq.)	(1.2 eq.)	Pathway C : 1) H ₂ O, RT, 24h	
	, I <i>I</i>	2) Et ₂ O	

R-COOH	Pathway / Yield (%)/ aspect (at RT)	PhosILs
L-Lactic acid	A / 87/ oil	^{TBP} → COO [☉] 1
L-tartaric acid	A / 81/ wax	TBP [⊕] OOC OOC COOH 2 OH
L-malonic acid	A / 92/ Solid	⊕ ⊖ твр ООС СООН 3
L-succinic acid	A / 91/ viscous oil	TBP OOC COOH 4
L-malic acid	A / 92/ oil	TBP HOOC COO HO 5
Pyruvic acid	B / 87/ oil	$TBP^{\oplus} \xrightarrow[]{O}_{O} \bigoplus_{O} $



Table 1 - Phosphonium-based ionic liquids with biomass based carboxylates

These PhosILs have been characterized by usual analytical methods involving NMR, IR and elemental analysis. Thermogravimetric and DSC analyses were also performed and allowed respectively the determination of the decomposition and glass transition temperatures.

Decomposition temperatures were relatively high, up to 315°C and furthermore higher than ammonium analogs^{15a} except for osidic acid derivatives (7, 8). These sugar derivatives generally present low thermal stability limited by the strength of heteroatom/heteroatom associations and carbon/hydrogen bonds.^{32a} The higher thermal stability of the synthesized PhosILs was expected, as phosphoniums ILs are generally described in the literature as having better thermal stability than imidazolium or ammonium ILs.^{32b} Therefore, PhosILs **1-6** could play an important role as solvent for different chemical reactions.

The glass transition temperature (Tg) values were all under 0°C. A negative Tg is classical for ionic liquids. But the fact that negative Tgs were observed with osidic carboxylates

derivatives **7** and **8** was different from what was previously found with ammonium analogs, which presented Tgs above 0° C.^{15a}

Finally, the viscosity was following the relationship between the number of carbon and/or hydrogen bonds as described in the literature^{32c} and it was also influenced by the nature of the anions. Values at 80°C were in general quite low, except for compounds **2** and **8**, which values were 268 cP and 617 cP respectively and lower than their TBA analogues (Figure 2). ILs with low viscosity are expected, to avoid difficulties of mixing homogeneously or dispersing reactants during reaction

PhosILs	Viscosity (cP) at 80°C	Tg (°C)	Tdec (°C)
1	21	-	314
2	268	-20	167
3	-	-9.8	288
4	125	-49.3	277
5	105	-40.2	203
6	16	-59.3	315
7	-	-8.7	130
8	617	-22.5	142
9	47	-56.8	301
10	-	-	241
11	-	-	278

Table 2 - Glass transition temperature, decomposition temperature and viscosity values of phosphonium-based ionic liquids



Figure 2 - Viscosity (cP) of TBA and TBP ionic liquids at 80°C

Other biobased acids were also employed, as *p*-coumaric or ferulic acids. *p*-Coumaric can be found in a wide variety of edible plants such as peanuts or vegetables (navy beans, tomatoes and carrots), wine and also barley grain.²³ Ferulic acid (FA), an ubiquitous natural phenolic phytochemical is present in seeds, leaves, both in its free form and covalently conjugated to the plant cell wall polysaccharides, glycoproteins, polyamines, lignin and hydroxy fatty acids.³⁴

The experimental pathway had to be modified taking in account the physical properties of the phenolic acids (scheme 2) and the synthesis was extended to tetrabutylammonium (TBA) salts to complete the preliminary study.^{15a}



Scheme 2 - Synthesis of ILs with *p*-coumarate and ferulate anions

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The respective salts were obtained with good yields and were all solid at room temperature. But it is more adequate to consider them as molten salts due to their high melting point which is higher than 100°C. Their decomposition temperatures were also relatively low fluctuating between 132 to 181°C. As a result, they won't be considered for the hydrogenation studies.

ILs	Yield %	Aspect Melting point	Tdec (°C)
$H_{3}CO \xrightarrow{H} O \xrightarrow{\oplus} TBP^{\oplus}$ $HO \xrightarrow{H} H$ $HO \xrightarrow{H} O \xrightarrow{\oplus} TBP^{\oplus}$ $HO \xrightarrow{H} O \xrightarrow{H} O \xrightarrow{\oplus} TBP^{\oplus}$ $HO \xrightarrow{H} O H$	86	White solid 115°C	132
$H_{3}CO \rightarrow H_{13}CO \rightarrow$	89	White solid 119°C	157
HO O TBP HO HO 14	89	White solid 145°C	156
HO =	93	White solid 150°C	181



Catalytic hydrogenation Hydrogenation of 1,5-cyclooctadiene (1,5-COD)

For the study, the selective hydrogenation of the 1,5-cyclooctadiene (1,5-COD) was chosen as a model reaction to improve the ability of our ionic liquids to be 'selective' co-solvents and appropriate for the recycling process.



Scheme 3 - Hydrogenation of 1,5-COD in PhosIL/water

In the absence of an IL, complete conversion of 1,5-COD into COA was obtained in water in the first run. Recycling the Pd catalyst led to the formation of COE until 90% with conversion attained at the eight run (Figure 3a).



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Figure 3 - Pd-catalyzed Hydrogenation of COD in water (a) and in TBABr/H₂O (b)

Similar results were obtained in commercial TBPOH, while hydrogenation reactions in TBPBr (Figure 3b) led also to COE but with lower conversions each run after the other and generation of isomerization compounds. This phenomenon was already observed in presence of other copper or zinc-based catalysts (CuO-Al₂O₃, CuO-SiO₂ or ZnO-Al₂O₃) *via* water gas shift reaction.³⁵ These results confirmed the importance of the nature of the counter anion on the hydrogenation mechanism.

Next, in the presence of PhosILs 2-7, the results were close to those obtained with water as solvent. But improvements were observed as no isomerization compounds traces were present, as shown in Figures 4a with compound 3/water system.



Figure 4 - Pd-catalyzed Hydrogenation of COD in TBP malonate $3/H_2O$ (a) and in TBP lactate $1/H_2O$ (b)

On the contrary, with PhosIL $1/H_2O$, COA was mainly obtained for all cycles (Figures 4b). This result was probably due to the low viscosity of TBP L-lactate 1 with regard to the other ILs tested. Indeed, even if few data in the literature are available on the solubility of H₂ in ILs, the diffusion of gases depends generally on the viscosity of the environment.³⁶

Hydrogenation of linoleic acid

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Linoleic acid is being a growing subject of interest in chemistry and biology. This polyunsaturated fatty acid can be found in large amounts in vegetable oils. Its hydrogenation could lead to saturated stearic acid (C18:0) and mono-unsaturated acids cis-12-octadecenoic acid (C18:1-12) and oleic acid (C18:1-9), and their isomerization products (Scheme 4). Our goal was to produce mainly a mono-unsaturated compound (C18:1) without formation of isomers and furthermore without changing the *cis* configuration.

The focus of our laboratory was to develop a simple and mild process using the synthesized biosourced PhosILs with water as co-solvent to induce partial hydrogenation and recycling (Scheme 4).



Scheme 4 - Hydrogenation of linoleic acid in H₂O / PhosIL

The identification of the composition of the resulting mixture, was assured using gas chromatography (GC), completed by NMR techniques. By GC, after post-hydrogenation esterification of the acids,³⁷ various columns (Column TR-1 : 100% Dimethyl Polysiloxane, Column TR-5: 5% phenyl methyl polysiloxane, INNOWAX (PEG)) and conditions³⁸ were

tested without success to separate and quantify specifically mono and poly-unsaturated isomers presented in the resulting mixture. To solve this problem, a NMR method was developed in our laboratory inspired from reported works concerning the determination of the composition of plant oils.³⁹ Mixtures obtained after hydrogenation were then analyzed by ¹H NMR without preliminary separation of constituents.

Assignment of proton signals:

The products of linoleic acid hydrogenation in ILs were saturated acid (X), mono-unsaturated acid (Y) and poly-unsaturated acid (Z).

The ¹H NMR spectrum of linoleic acid hydrogenation product in ILs is shown in figure 5. The spectrum signals are annotated from a to g.^{39b} These groups are assigned as follows: a, olefenic protons; b, divinyl methylene protons; c, α -methylene protons adjacent to carbonyl carbon; d, allyl methylene protons; e, β -methylene protons adjacent to carbonyl carbon; f, methylene protons on saturated carbon atoms; g, terminal methyl protons of saturated, monounsaturated and polyunsaturated acids; g', terminal methyl protons of residual PhosIL traces.





Figure 5 - ¹H NMR spectrum in CDCl₃ of the mixture obtained after hydrogenation of linoleic acid in TBP lactate 1/H₂O

In the divinyl methylene protons chemical shift, there were three signals (Figure 6). The triplet at 2.77 ppm corresponded to linoleic acid divinyl methylene protons and was confirmed by NMR spectrum of linoleic acid. The other signals were attributed to isomer product of linoleic acid divinyl methylene protons.



Figure 6 - Divinyl methylene ¹H NMR spectrum in CDCl₃ of hydrogenation product in PhosILs/H₂O.

(triplet at 2.77ppm corresponded to linoleic acid divinyl methylene protons)

After calculations (see ESI), composition of hydrogenated products could be determined. The analytical results for the hydrogenation of linoleic acid in TBP malonate $3/H_2O$ can be summarized on the following graph (Figure 7). Selective hydrogenation towards monounsaturated compounds Y was observed with almost complete conversion of the linoleic acid. The selective hydrogenation was also realized without formation of compounds presenting a *trans* configuration as observed with NMR coupling constants. Moreover, catalytic system was could be easily recycled and reused without changes in reactivity for 6 cycles. Results were strongly similar regardless of the nature of the used PhosILs. Contrary to what was previously observed with 1,5-COD, it seemed there was no effect of neither the anion nor the viscosity of the used PhosILs for hydrogenation of linoleic acid.



Figure 7 - Hydrogenation of linoleic acid in TBP malonate $3 / H_2O$

The results obtained during our study in soft conditions (RT, atmospheric pressure, water) were quite near to those obtained by Suarez and coll. in 2011 for the selective hydrogenation of biodiesel, however a drastic system (Pd(OAc)₂/[BMIM] [BF₄], H₂ (5-75 bar) and 80°C) was used.⁴⁰

As a fair assessment, it is safe to say that our system of hydrogenation was very competitive towards all systems of hydrogenation described until today in the literature for such compounds. It was realized under 1 atm. of H_2 at room temperature and did not require preliminary preparation of catalysts. The selective hydrogenation of the linoleic acid towards

mono-unsaturated compounds was also realized without formation of compounds presenting a *trans* configuration as observed with NMR coupling constants.

Hydrogenation of α , β -unsaturated ketones

Previous work concerning tetrabutylammonium based CILs (TBA (R) – or (S)- prolinate and TBA 4-hydroxy-S-prolinate) showed that these ILs were good chiral modifiers for the hydrogenation of carbon-carbon double bond of α , β -unsaturated ketones in isopropanol (*i*-PrOH) under mild conditions.^{15b} Consequently, we tested our CPhosILs **9-11** (chiral phosphonium ionic liquids) in such enantioselective hydrogenation process.

Isophorone was chosen as model substrate to define the best conditions. The conversion and the selectivity were determined by GC; the determination of the enantiomeric excess (ee) requiring the use of a β -cyclodextrine chiral column.

First of all, the influence of the CPhosILs ratio CPhosIL/substrate was studied. Results are summarized in Table 4 and best conditions were met with 0.5 eq. of CPhosIL 9. Indeed, good conversion of isophore was observed with high selectivity for trimethylcyclohexanone (TMCH) and with an important ee of 40% in favour of the isomer S. It also proved that CPhosIIs were suitable solvents to induce good conversion, high selectivity and good ee for such mild process compared to other harder processes.⁴¹



Scheme 5 - Hydrogenation of isophorone in CPhosIL 9

Equivalent of 9	Conv. (%)	Select. (%)	e.e. (%)
1	7	93	32 (<i>S</i>)
0.5	60	95	40 (<i>S</i>)

Table 4 - Influence of the ratio of CPhosIL 9 for the hydrogenation of isophorone

Recycling of the catalytic system led unfortunately to by-products as for example trimethylcyclohexanol by reduction of the C=O bond.

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Next, to envisage the recycling of the catalytic species, we tested several polar co-solvents which could facilitate the adsorption of the substrate on the catalyst and also participate to the solubilization of the hydrogen (H₂) in the medium.⁴²



Solvent	Conv. (%)	Select. (%)	e.e. (%)
H ₂ O	96	95	5
<i>i</i> -PrOH	100	90	37 (<i>S</i>)
МеОН	70	98	6
H ₂ O / MeOH (1/1)	52	95	13
Acetonitrile	54	96	34 (<i>S</i>)
<i>i</i> -PrOH/ H ₂ O (2/1)	17	67	11
<i>i</i> -PrOH/ H ₂ O (3 /1)	43	93	2

Scheme 6 - Hydrogenation of isophorone in CPhosIL 9/solvent

Table 5 - Influence of co-solvent for the hydrogenation of isophorone with CPhosIL 9

The best ee (37%) was obtained using 9 /*i*-PrOH as solvents. It also gave total conversion of isophorone with high selectivity for TMCH. Other co-solvents were tested as MeOH or mixtures $H_2O/MeOH$ or H_2O/i -PrOH but led to lower conversions, selectivity and ee. Acetonitrile, a non-polar solvent gave similar ee than *i*-PrOH but with lower conversion, probably due to the weak solubility of H_2 . However, the recycling remained difficult as *i*-PrOH was miscible to diethylether. To conclude, no improvement of ee was observed using co-solvent.

The enantioselective hydrogenation was then performed on other α , β -unsaturated ketones using respectively TBP *S*-prolinate **9** or TBP trans-hydroxy-*S*- prolinate **11** as solvents.

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Substrate	CPhosIL	Runs	Conv. (%) ^a	Select. (%)	de (%) ^b	Products
P corvona	9	1	100	98	69 (3 <i>R</i> , 6 <i>S</i>)	
N-carvone O	,	2	52	84	10 (3 <i>R</i> , 6 <i>S</i>)	
	11	1	33	29	36 (3 <i>R</i> , 6 <i>S</i>)	<u>*</u>
	11	2	27	27	28 (3 <i>R</i> , 6 <i>S</i>)	
D 1	9	1	100	100	40 (2 <i>S</i> , 5 <i>R</i>)	1
<i>R</i> -pulegone	,	2	57	79	44 (2 <i>S</i> , 5 <i>R</i>)	menthone O
	11	1	39	77	40 (2 <i>S</i> , 5 <i>R</i>)	-*
	11	2	16	64	38 (2 <i>S</i> , 5 <i>R</i>)	
β -ionone		1	70	88	-	Q
	9	2	36	86	-	
trans-Chalcone	9	1*	100	100	-	O

*In the presence of 1 mL of *i*-PrOH to facilitate the solubilization of the chalcone.

^a: Determined by GC ; ^b: Determined by GC using a chiral colum

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Scheme 7 - Hydrogenation of \alpha,\beta-unsaturated ketones with TBP S-prolinate 9 or TBP trans-
hydroxy-S-prolinate 11 as solvents
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We observed complete conversions and good diastereoisomeric excess (de) for the hydrogenation of *R*-carvone and *R*-pulegone in presence of **9**. These results were excellent in comparison to literature data obtained with high pressure of H₂ (5-10 bar) and/or high temperatures (40-100°C).⁴³ After a first run, the catalytic system had unfortunately lost some

crucial activity and the use of **9** led generally to lower conversion for all ketones. The anion had an important effect on the reactivity. With PhosILs **11**, both conversion and selectivity were significantly lowered; de was maintained with *R*-pulegone, but a drastic decreased was observed with *R*-carvone. The presence of the alcohol function on the chiral anion might cause steric hindrance or/and change H₂ solubility of the CPhosILs. As a consequence, other substrate hydrogenations were pursued with only CPhosIL **9**. Good conversion of β -ionone was measured with a good selectivity, the double carbon bond of the chain being preferentially hydrogenated compared to the cyclic one. Total conversion of *trans*-Chalcone was observed with only formation of 3-phenylpropiophenone, as system was too soft to attack the aromatic double carbon bonds.

Experimental

All reagents were commercially available and used as received (TBPOH.30H₂O, acids or diacids from Sigma-Aldrich). NMR spectra were recorded at 298 K at 500 MHz for ¹H and at 63 MHz for ¹³C and 202 MHz for ³¹P on an Avance III Bruker spectrometer in CDCl₃ as solvent with TMS or phosphoric acid as references.

Concerning the quantification of the hydrogenation of linoleic acid, NMR spectroscopy was performed at 500MHz with Bruker Avance III spectrometer equipped with a BBFO+ probe and at 600MHz with Bruker Avance III spectrometer equipped with a CPTCI cryoprobe. The sample was dissolved in CDCl₃ or in MeOD-d₄ and the resulting solution was placed in a 5 mm diameter NMR tube. ¹H NMR spectra were taken with 30 degree pulse angle, 10s relaxation delay and 16 scans.

IR spectra were recorded on a NICOLET IMPACT 400 spectrometer (KBr pellets or films).

Elemental analysis (C, H, N, S) were realized on a Flash EA-1112 Series.

GC analyses were recorded on a Hewlett–Packard HP-6890 gas chromatograph, fitted with DB-1 capillary column (25 m, 0.32 mm), a flame ionization detector and HP-3395 integrator under the following conditions: helium as vector gas (5.10^4 Pa), temperature of injector: 250 °C, temperature of the oven: isotherm 150 °C, 5 min, then 150-300 °C (10 °C/min) and isotherm 300 °C, 5 min.

GC/MS analyses were recorded on a THERMOQUEST Draw GC on 2000 Series by using the techniques of chemical ionization under the following conditions: capillary column DB1 (length: 25 m, diameter: 0.32 mm), vector gas: helium (0.5 bar), temperature injector: 250°C. ee were determined with a β -cyclodextrines-based chiral gas chromatography column and byprodutes by GC/MS.

Thermogravimetric analyses coupled with a mass spectrometer were performed between 30 °C and 500 °C under a constant flow of dry argon (50 mL/min) using a Simultaneous Thermal Analyzer STA 449C Jupiter from Netzsch, and a heating rate of 10 K/min. The isothermal drift and sensitivity values are 0.6 μ g/h and 0.1 μ g, respectively. Alumina crucibles were loaded with 10-20 mg of sample powder.

The mass spectrometer was a quadrupole QMS 403 Aëolos® with a stainless steel capillary and a SEV detector (Channeltron). The counting time for mass spectrometer is of 20 ms per m/z values (scanning width: m/z = 10-150 amu) with a resting time of 1 s.

The DSC experiments were carried out on a Netzsch DSC 204F1 heat flux differential calorimeter at a heating/cooling rate of 10 K/min under a constant argon flow with 200 mL/min. The crucibles were loaded with 10-20 mg of sample powder/liquid. Samples were weighed in aluminium sample pans covered with a pierced lid. An empty aluminium sample pan with a pierced lid was used as a reference.

The viscosities measurements in cP (or mPa.s) were performed with a Brookfield LV-DVII+ PRO viscometer using a CP51 cone spindle. The instrument was connected to a HUBERministat circulation-type thermo-regulated water bath, and measures were realized between 298.15 and 353.15 K. The repeatability of the viscometer was of 0.20 % with an uncertainty in the viscosity measurements of 1.00 % of the full scale range, declared by the manufacturer.

General procedure for the synthesis of PhosILs 1-3

Pathway A

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In a 250 mL round-bottom flask, a 40% wt aqueous solution of TBPOH (7 mL, 10 mmol) was diluted in distilled water (100 mL). The acid (6 mmol, 1.2 eq.) was then added and the

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mixture was stirred and refluxed during 24h. After evaporation of the solvent under reduced pressure, the excess of acid was precipitated by addition of Et_20 (3 x 50 mL) and removed by filtration. The resulting product was dried *in vacuo* at 50°C during 24h.

Pathway **B**

In a 250 mL round-bottom flask, a 40% wt aqueous solution of TBPOH (7 mL, 10 mmol) was diluted in EtOH (100 mL). Pyruvic acid (6 mmol, 1.2 eq.) was then added and mixture was stirred and refluxed during 24h. After evaporation of the solvent under reduced pressure, the excess of acid was precipitated by addition of Et_2O (3 x 50 mL) and removed by filtration. The resulting product was dried *in vacuo* at 50°C during 24h.

Pathway C

In a 250 mL round-bottom flask, a 40% wt aqueous solution of TBPOH (7 mL, 10 mmol) was diluted in distilled water (100 mL). The osidic acid (12 mmol, 1.2 eq.) was then added and the mixture was stirred during 24h at room temperature. After evaporation of the solvent under reduced pressure, excess of acid was precipitated by addition of EtOH or MeOH (3 x 50 mL) and removed by filtration. The resulting product was dried *in vacuo* at 50°C during 24h.

Pathway **D**

In a 250 mL round-bottom flask, phenolic acid was dissolved (1.2 eq.) in 100 mL EtOH 99%. A 40% wt aqueous solution of TBPOH (7 mL, 10 mmol) was then added and the mixture was stirred during 24h at room temperature. After evaporation of the solvent under reduced pressure, the excess of acid was removed by washing with Et_2O or by filtration after precipitation following the addition of distilled water (3 x 50 mL). The resulting product was dried *in vacuo* at 50°C during 24h.

Pathway D'

In a 250 mL round-bottom flask, TBAOH (8 g, 10 mmol) was dissolved in EtOH 99% (100 mL). The phenolic acid (12 mmol, 1.2 eq.) was then added and the mixture stirred during 24h at room temperature. After evaporation of the solvent under reduced pressure, the excess of acid was removed by washing with Et_2O or by filtration after precipitation following the addition of distilled water (3 x 50 mL). The resulting product was dried *in vacuo* at 50°C during 24h.

General procedure for hydrogenation

Hydrogenation of alkenes:

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A Schlenk tube was charged with the ionic liquid (c.a. 400 mg) and the catalyst (3.5 mg, 0.02 mmol, 0.01 equiv/substrate) and left for 10 min under vacuum. Next, the substrate (2 mmol, 1 equiv) and solvent (2 mL) were added under argon. The argon atmosphere was then replaced by hydrogen through a gas bag and the mixture was vigorously stirred for 18 h at room temperature. The aqueous phase was next extracted with Et₂O (3x5 mL); the combined organic layers were dried over MgSO₄ and then filtered through cotton (1 μ L was injected into GC to evaluate the conversion). The aqueous phase was kept in the Schlenk tube to be reused.

Recycling experiments: After a short vacuum/argon sequence (three times), the substrate (2 mmol, 1 equiv) was added, and the mixture was stirred vigorously for 18 h at room temperature under a hydrogen atmosphere (gas bag). Product isolation and characterization is the same as described above.

Hydrogenation of unsaturated ketone:

In a schlenk tube, ionic liquid (400 mg) and PdCl₂ (3.5 mg, 0.02 mmol, 0.01 eq.) were introduced. After 10 minutes under vacuum, isophorone (300 μ L, 2 mmol, 1 eq.) in 2 g of solvent was added under argon. A hydrogen atmosphere was filled into the reactor with the help of a gas bag and the mixture was stirred at room temperature during the required time. Then, distillated water (2 mL) was introduced and the aqueous layer was extracted three times with 5 mL of diethyl ether. The organic layers were gathered, dried over MgSO₄ and filtered through cotton. 1 μ L of the organic phase was injected in a gas chromatography to determine the conversion. Enantiomeric excesses (*ee*) were determined with a β -cyclodextrine-based chiral gas chromatography column and by-products by GC/MS.

Conclusions

Phosphonium ionic liquids (PhosILs) with natural organic acid derived anions (L-lactate,Ltartrate, malonate, succinate, L-malate, pyruvate, D-glucuronate, D-galacturonate, S-prolinate,

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p-coumarate and ferulate) were easily prepared from tetrabutylphosphonium hydroxide and an excess of the corresponding acid with good yields. Their characterization was realized through routine NMR, IR, elemental analysis, viscosity, and ATG techniques. These PhosILs as co-solvents showed good performance, recyclability and better efficiency than commercial ILs in catalytic selective hydrogenation of 1,5-cyclooctadiene (1,5-COD) into cyclooctene at room temperature under atmospheric H₂ pressure. Interesting extension of this hydrogenation process has been performed on unsaturated fatty acids, like linoleic acid. Fine NMR investigations proved the performance essentially concerning the selectivity of the catalytic system towards mono-insaturated acids in the presence of PhosILs under mild conditions. Furthermore, enantioselective hydrogenation of α , β -unsaturated ketones in mild conditions was performed in pure chiral PhosILs. Very good conversion of substrates, combined with high selectivity and good enantiomeric or diastereoisomeric excesses revealed the high potentialities of our PhosILs for such processes compared to literature data.

On-going investigations will deal with the evaluation of the biodegradability and/or (eco)toxicity of these new PhosILs in order to used them in other catalytic processes or extraction procedures.

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