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Clean catalysis with clean solvents – phosphonium tosylates for transfer hydrogenation reactions

Claire Comyns[a], Nazira Karodia[b], Serge Zeler[a] and Jo-Ann Andersen[a,*]

[a] *School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK*
[b] *Department of Chemical and Forensic Sciences, University of Bradford, Bradford, West Yorkshire BD7 1DP, UK*

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Molten salts have been applied for the first time as solvents in rhodium-catalysed transfer hydrogenation reactions. The salts are tetraalkyl/aryl phosphonium tosylates; they are liquid at the reaction temperature and solid at room temperature, thereby facilitating catalyst recovery. In certain cases they can give rise to favourable enantioselectivities.

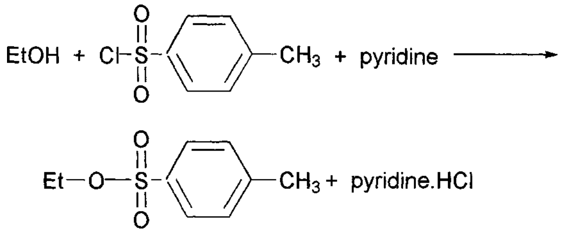
Keywords: catalyst, rhodium, asymmetric, hydrogenation, molten salts, catalyst recovery

Many organometallic and coordination compounds have been used successfully in homogeneous catalysis. Often these catalyst systems are highly selective and allow the use of mild reaction conditions. However, difficult separation of the catalyst from the reaction products or deactivation due to irreversible structural changes can compromise the benefits of homogeneous catalyst systems. Interest is thus now focusing on heterogenising homogeneous catalysts in order to combine the activity and selectivity of a homogeneous catalyst with the processing advantages of a heterogeneous catalyst [1].

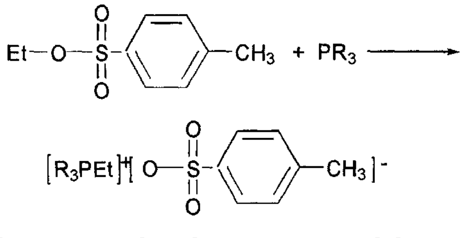
In today's environmentally conscious world, another problem with homogeneous catalysts has emerged, viz. many of the solvents traditionally used in transition metal catalysis, such as chlorinated hydrocarbons, acetonitrile and DMF to name but a few, are currently on the "environmental blacklist". It is rapidly becoming apparent that the way in which solvents are used in organic synthesis needs rethinking. The way forward may thus be to choose the solvent on environmental grounds and then optimise the reaction in that solvent [2]. In this respect, the use of high-melting ionic solvents (molten salts/ionic liquids) will be highly advantageous if the organic product(s) can readily be decanted from the stable catalyst system. The advantages of these systems will be manifold: in addition to facilitated catalyst recovery, they may exhibit low viscosity, high thermal and air stability, good electrical conductivity, low vapour pressure and they will readily solubilise the reagents and catalyst. They also exhibit a large "liquid range", thereby allowing for extensive kinetic control [3].

Room temperature ionic liquids have been developed by Seddon and others [3–7] and have been found to function as highly efficient catalyst systems for reactions such as dimerisation and alkylation. However, much less attention has been paid to higher melting ionic solvents such as tetraalkyl ammonium and phosphonium salts. These offer advantages over the room temperature systems in that (i) they are not corrosive (although not all room temperature systems are corrosive, many are), and (ii) being solid at room temperature, they are more easily manipulated and product separation is simple, being accomplished by decantation rather than by biphasic extraction. They are also stable to much higher conditions, thereby enabling more forcing reaction conditions to be used. We now report our results on the synthesis of tetraalkyl/aryl phosphonium tosylates and their application as solvents in transfer hydrogenation reactions.

Salts **I**–**III** were synthesised by reaction of the tosylate ester (equation (1)) with the appropriate tertiary phosphine (equation (2)).



(1)



(2)

where R = phenyl (**I**), R = p-tolyl (**II**) and R = n-octyl (**III**). All three salts were fully characterised; selected data are shown in table 1.

The salts were then applied as solvents for the rhodium-catalysed transfer hydrogenation of acetophenone to *sec*-

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[*] To whom correspondence should be addressed.

Table 1
Characterisation data.

Salt	Yield	$\nu_{P\text{–}C}$ (cm^{-1}) (alkyl, aryl)	Melting point (°C)	δ ^{31}P (ppm)
$Ph_3PEt^+OTs^-$ (**I**)	72	1460, 1380	94–95	26.6
(p-tolyl)$_3$PEt$^+$OTs$^-$ (**II**)	98	1450, 1390	148–152	25.6
(n-octyl)$_3$PEt$^+$OTs$^-$ (**III**)	90	1377	68–72	34.9

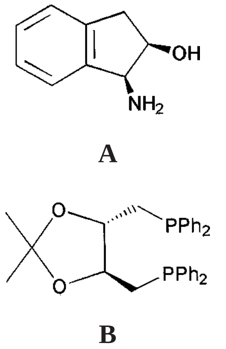
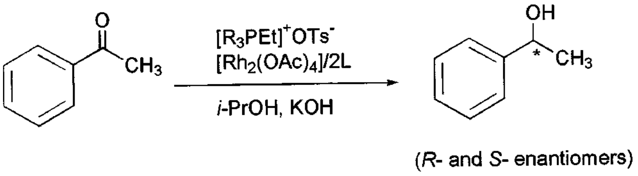


Figure 1. Structures of **A** ((1S, 2R)-*cis*-aminoindanol) and **B** ((−)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (DIOP)).

phenethyl alcohol using isopropanol as the hydrogen donor (Meerwein–Pondorf–Verley reduction, equation (3)).



(3)

In all cases the catalyst precursor used was dirhodium tetraacetate [$Rh_2(OAc)_4$] which was used either on its own or in the presence of the added ligands (1S, 2R)-*cis*-aminoindanol (**A**) or (–)-DIOP (**B**), the structures of which are shown in figure 1. The results are shown in table 2. After the reaction the system was cooled to room temperature and the products were decanted and characterised by ^{1}H NMR and GC analysis. The salt–catalyst mixture remained as a solid and could be re-used to give identical results. Analysis of the product mixture by UV-VIS spectroscopy showed that there were no rhodium species present (within detection limits).

The results show that the phosphonium tosylate salts **I–III** function as efficient solvents for the rhodium-catalysed transfer hydrogenation of acetophenone by KOH/i-PrOH and allow for a very facile catalyst/product separation. Varying the salts did not give greatly different results, although **III** did result in higher conversion (ca. 20% higher) to the phenethyl alcohol than **I**. In all cases, conversions were slightly higher in the presence of added ligand than with no ligand, which is as expected. The addition of ligand **A**, (1S, 2R)-*cis*-aminoindanol, resulted in only a minor increase in activity and a very small improvement to the enantioselectivity (ee) of the reaction. A reason for this could be that the ligand contains a primary amine (NH_2) group, resulting in a less basic and less sterically demanding ligand than substituted nitrogen, or phosphorus, ligands. When ligand **B**, (−)-DIOP, was used a marked improvement in catalytic activity was observed and the ee improved dramatically to 92%. The higher activity is presumably due to the increased basicity of the DIOP ligand (cf. aminoindanol) and the improvement in enantioselectivity will be due to the steric constraints imposed on the reaction centre by the chiral, more sterically demanding DIOP.

Table 2
Catalytic transfer hydrogenations using salts **I–III** as solvents.[a]

Salt	Temperature (°C)	Ligand (L)	Conversion (%)	ee (%)
I	120	–	28	0
		A	33	0
II	150	–	34	0
		A	41	5
III	120	–	30	0
		A	37	7
		B	50	92

[a] [$Rh_2(OAc)_4$] 5 mg, $R_3PEtOTs$ 1.5 g, KOH 7.2 mg, i-PrOH 5 ml, acetophenone 50 μl, Rh : L = 2 : 3, 16 h.

Although these results are far from being optimal in terms of catalyst activity and selectivity, they are extremely promising in the context of developing cleaner catalyst systems. Not only are these phosphonium salts air-stable, non-toxic and easy to store and handle, they also permit a rapid, easy and convenient product–catalyst separation. We have previously reported the application of similar systems for hydroformylation reactions [8] and found that they formed very active and selective catalytic systems. This is, as far as we are aware, the first report of the use of ionic solvents for transfer hydrogenation reactions. We thus believe that with further study, the correct combination of salt, catalyst, ligand and reaction conditions can be optimised to produce a system which will be at least comparable to analogous homogeneous catalysts in terms of activity and selectivity, but which will allow for more facile product/catalyst separation and will comprise a more environmentally compatible catalytic system.

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