Clean catalysis with ionic solvents—phosphonium tosylates for hydroformylation

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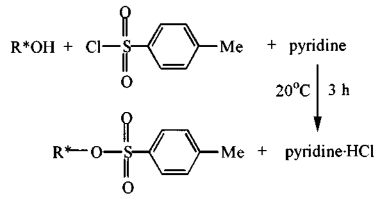
High-melting phosphonium tosylates are synthesised and applied for the first time as solvents in catalytic hydroformylation reactions; variation in the substituents attached to phosphorus can lead to markedly different results; the catalyst systems are non-corrosive, easily manipulated and can readily be recovered and reused.

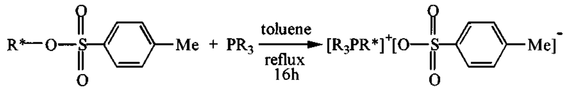
One of the major problems associated with homogeneous catalysts is that they are difficult to recover at the end of the reaction. Frequently distillation is used as a separation technique, but this is a very energy-intensive process. High-boiling products can remain with the catalyst and lead to catalyst deactivation or product contamination. This problem, especially for expensive and/or toxic precious metal catalyst systems, has precluded their more widespread application in the catalysis industry.

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, 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.[1] In this respect, the use of high-melting ionic solvents (molten salts/ionic liquids) will be highly advantageous if the product(s) can readily be decanted off 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', allowing for extensive kinetic control.[2] Room temperature ionic liquids such as alkylimidazolium chloride/$AlCl_3$ have been developed by Seddon and others[2,3] and have been found to function as highly efficient catalytic 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 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 temperatures, thereby enabling more forcing reaction conditions to be applied. We now report our results on the synthesis of tetraalkyl/aryl phosphonium tosylates and their application as solvents in hydroformylation reactions.

Salts **1–4** were synthesised by reaction of the tosylate esters [eqn. (1)] with the appropriate tertiary phosphine [eqn. (2)].



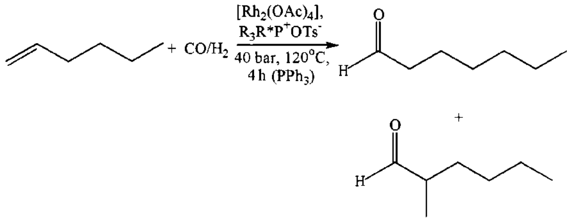
(1)



(2)

	R	R*
1	Ph	Et
2	Ph	Bu
3	Ph	Octyl
4	Bu	Et

All four salts were fully characterised; selected data are shown in Table 1. They were then applied as solvents in the hydroformylation of hex-1-ene to heptanal (**A**) and 2-methylhexanal (**B**) [eqn. (3)] in the presence of $[Rh_2(OAc)_4]$, both with and without added phosphine ligand. Selected results are shown in Table 2.



(3)

In some instances, trace amounts (*ca*. 1–2%) of additional reaction products were observed. The isomerisation products 2-methylhexanal (**B**) and 2-ethylpentanal (**C**) (derived from the isomerisation of hex-1-ene to hex-2-ene and subsequent hydroformylation) were typically present in small amounts. In the case of $Ph_3PBu^+OTs^-$ and $Ph_3POc^+OTs^-$, the corresponding C_5 aldehyde and C_9 aldehyde were observed, respectively. These are most likely to derive from elimination of the bulky alkyl moiety (butyl or octyl) to form the corresponding alkene, analogous to Hoffmann eliminations in ammonium salts. The alkene is then hydroformylated to the corresponding aldehydes (**F–J**; see Scheme 1). This elimination process does not occur with $Bu_3PEt^+OTs^-$ or with $Ph_3PEt^+OTs^-$; presumably, in these cases, the ethyl group is small enough to remain bound to the P atom and does not eliminate.

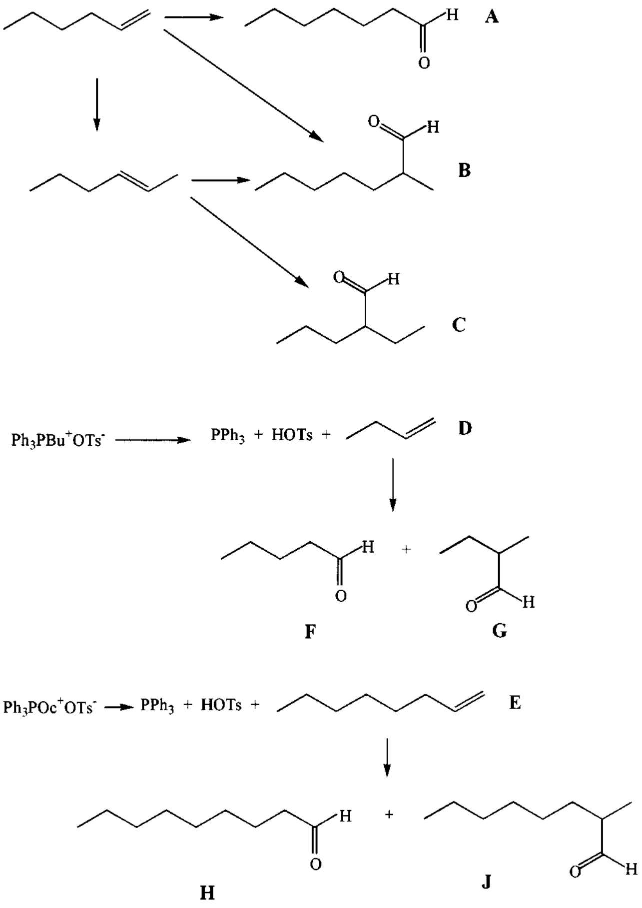
Table 1 Characterisation of phosphonium salts

Salt	Melting point/°C [literature value]	Yield (%)	$\delta(^{31}P)$	ν(P–C)/cm^{-1}
$Ph_3PEt^+OTs^-$; **1**	94–95 [93–94][4]	98	26.6	1460 ($P–C_{aryl}$); 1380 ($P–C_{alkyl}$)
$Ph_3PBu^+OTs^-$; **2**	116–117 [139–140][4]	98	24.8	1470 ($P–C_{aryl}$); 1380 ($P–C_{alkyl}$)
$Ph_3POc^+OTs^-$; **3**	70–71	95	26.7	1450 ($P–C_{aryl}$); 1390 ($P–C_{alkyl}$)
$Bu_3PEt^+OTs^-$; **4**	81–83 [70–78][4]	94	24.6	1380 ($P–C_{alkyl}$)

Table 2 Hydroformylation of hex-1-ene in the presence of phosphonium salts as solvents[a]

Salt	PPh_3	Conversion (%)	Yield (%) A	B	C	Product n : iso ratio (A : [B + C])
1	No	80	29.4	36.0	14.6	1 : 1.3
	Yes	95	55.7	29.8	9.5	1.5 : 1
2	No	96	18.4	34.1	32.3[b]	1 : 4
	Yes	99	20.8	30.2	37.7[b]	1 : 3.2
3	No	49	18.9	22.5	7.6[b]	1 : 1.7
	Yes	100	69.1	25.0	4.9[b]	2.2 : 1
4	No	90	62.6	22.5	4.9	2.5 : 1
	Yes	100	69.3	22.7	7.0	2.2 : 1
1	No[c]	100	65.2	27.4	7.4	1.9 : 1

[a] $[Rh_2(OAc)_4]$, 0.02 g (0.045 mmol); $R_3PR^{*+}OTs^-$, 1.0 g; PPh_3, 0.1 g (0.38 mmol); hex-1-ene, 1.5 ml (12 mmol); 40 bar, 120 °C, 4 h. [b] Trace amounts of elimination products observed. [c] $(Ph_3P)_3Rh(CO)(H)$, 0.085 g (0.093 mmol) added to reaction mixture in place of $[Rh_2(OAc)_4]$.



Scheme 1 Hydroformylation of hex-1-ene.

The results in Table 2 indicate that the substituents attached to the central phosphorus atom of the phoshonium salt exert a significant effect on the catalyst performance. With no added phosphine ligand, the conversions range from 66% (for $Ph_3POc^+OTs^-$) to 100% (for $Bu_3PEt^+OTs^-$) and the n : iso ratios range from 2.5 : 1 (for $Bu_3PEt^+OTs^-$) to 1 : 4 (for $Ph_3POc^+OTs^-$). This solvent effect is remarkable and is almost unparalleled in conventional homogeneous catalysis. In addition, our catalyst systems offer the advantage of extremely facile catalyst recovery post-reaction. Upon the addition of excess PPh_3, the catalytic results are very similar to each other (conversions range from 95 to 100% and n : iso ratios range from 1.5 : 1 to 2.2 : 1). We propose that in this case $(Ph_3P)_3Rh(CO)(H)$ forms initially (from $[Rh_2(OAc)_4]$, PPh_3, CO and H_2) and is then the catalytically active species in every reaction. Thus, one would expect very similar results, with only small influences being exerted by the phosphonium solvent.

At the end of the reaction, the reaction mixture was cooled and the liquid organic product was decanted and analysed by GC, GC-MS and NMR. This facile product recovery is the most significant advantage of these systems. The recovered solid was characterised in order to determine that the phosphonium salt had not changed during the course of the reaction, which was indeed the case. The organic products were analysed for rhodium content (by atomic absorption); in all cases, negligible amounts (if any) were observed, indicating that the rhodium catalyst remains within the (crystalline) structure of the solid solvent. These catalyst systems have been re-used several times and gave reproducible results.

Studies are now under way with a larger range of salts, substrates and reaction types to investigate the general applicability of these novel solvents which are analogous to conventional dipolar aprotic solvents but also offer the considerable advantage of facile catalyst recovery and cleaner, efficient catalytic reactions.

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Notes and references

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