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The ionic liquid ethyltri-*n*-butylphosphonium tosylate as solvent for the acid-catalysed hetero-Michael reaction

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Abstract—A new and convenient method for the acid-catalysed Michael addition reactions of alcohols, thiols and amines to methyl vinyl ketone has been developed using the ionic liquid ethyltri-*n*-butylphosphonium tosylate. The reaction conditions are mild and obviate the need for toxic and expensive Lewis acid catalysts, offering advantages over more commonly used systems.

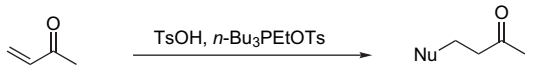
1. Introduction

The Michael addition[1] is a powerful reaction for the formation of carbon–carbon and carbon–hetero atom bonds.[2] Both Michael- and hetero-Michael additions are widely used in inter- and intra-molecular reactions to give products, which include important building blocks for many biologically active molecules. Hetero-Michael addition of amines to α,β-unsaturated carbonyl compounds gives β-amino ketones, which are attractive for their use as synthetic intermediates of anticancer agents, antibiotics and other drugs.[3] Michael addition of a thiol to an α,β-unsaturated ketone results in the formation of a sulfur–carbon bond; this is a key reaction in the synthesis of biologically active compounds such as the calcium antagonist diltiazem.[4] Similarly, β-oxy ketones are also important in organic synthesis.[5] Moreover the β-amino, β-thio and β-oxy ketone functionalities occur in many natural products.[6]

The uncatalysed addition reaction of alcohols to α,β-unsaturated ketones proceeds very slowly and gives only moderate yields of the β-oxy ketones. Other methods most commonly employed use red mercury oxide and boron trifluoride etherate as catalysts, which are both toxic.[7a,b] These methods also require working under an inert atmosphere. Other methods widely used are the acid- or base-catalysed reaction of the neat reagents but in this case the reaction mixture needs to be neutralised very carefully, otherwise the ethers decompose on distillation. A significant drawback to this method is that the reaction is difficult to control and can be very violent thus requiring cooling or the use of an inert solvent. The Mannich reaction is a classic method for the preparation of β-amino ketones[8a] but this reaction has serious disadvantages, including drastic reaction conditions and long reaction times.[8a–d] In contrast, the aza-Michael addition route usually requires acid- or base-catalysis to activate one of the substrates.[2,9] High costs coupled with environmental issues due to the large amount of acidic effluents being generated are drawbacks associated with Lewis acid-catalysed aza-Michael reactions.[10] Thiols are typically difficult to use in the presence of Lewis acidic metals since they are known to poison these catalysts. In the thia-Michael reaction, the thiols are generally activated by deprotonation.[11]

The past five years have seen concerted efforts to develop effective, economical and environmentally friendly methodologies for the hetero-Michael addition. Some of these exciting developments include the use of an azaphosphatrane nitrate salt,[12] $CeCl_3 \cdot 7H_2O$/NaI,[13] Nafion® SAC-13,[14] $Bi(NO_3)_3$,[15] $Bi(OTf)_3$,[16] $InBr_3$,[17] $Cu(BF_4)_2$,[18] and strong Brønsted acids.[19] There are also examples of the use of ammonium ionic liquids as catalysts and/or solvents for the hetero-Michael addition of thiols,[20] and aliphatic amines.[21]

With a view to establishing more practical reaction conditions, as well as facilitating the recovery of the products, we have investigated the application of the phosphonium ionic liquid, ethyltri-*n*-butylphosphonium tosylate (*n*-Bu_3PEtOTs) in the acid-catalysed hetero-Michael addition of a series of alcohols, thiols and amines to methyl vinyl ketone (MVK) as the prototypical Michael acceptor (Scheme 1). This method obviates the need for expensive metal catalysts and strong bases, and instead uses cheap and readily available reagents.



NuH = ROH, RNH_2, R_2NH, RSH
R = aliphatic, aromatic

Scheme 1. Acid-catalysed hetero-Michael addition in *n*-Bu_3PetOTs.

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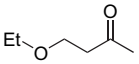
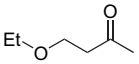
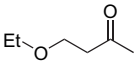
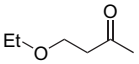
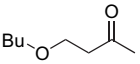
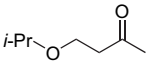
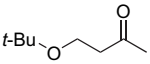
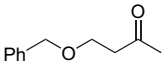
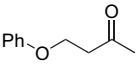
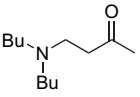
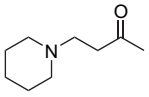
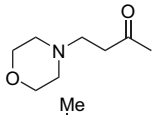
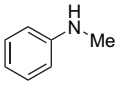
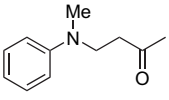
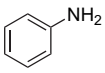
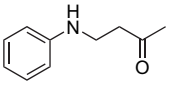
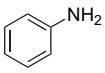
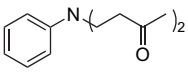
Phosphonium tosylates have proven to be effective solvents for organic synthesis, having the advantages of high thermal stability, tolerance towards air and moisture and low vapour pressures. Phosphonium tosylates are cheap, non-corrosive and some are solid at room temperature, making them easy to handle and to separate from the reaction products.[22,23]

2. Results and discussion

Ethyltri-*n*-butylphosphonium tosylate (*n*-$Bu_3PEtOTs$) was chosen because its melting point permits reactions at relatively low temperatures. It also crystallises readily, making it easy to separate from the product and recycle. In addition, it is economically and readily synthesised from commercially available starting materials (tri-*n*-butylphosphine and ethyl tosylate) at low cost. Initially the hetero-Michael reaction was attempted in the ionic liquid without any catalyst, however, no detectable yield of product was observed. *p*-Toluenesulfonic acid monohydrate ($TsOH\cdot H_2O$) was chosen as the catalyst because it is the conjugate acid of the solvent anion. The optimum quantity for the reaction was established as 2% by systematically varying the quantity of the catalyst and monitoring the yield of the product obtained.

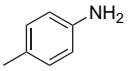
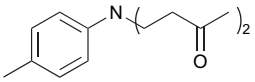
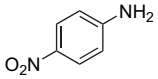
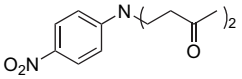
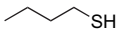
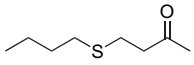
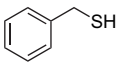
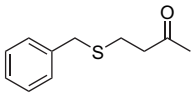
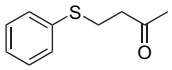
Selected results are summarised in Table 1. The reaction with the aliphatic alcohols, which are weak nucleophiles, (Entries 1–8) gave yields ranging from 12–75%, which compare well with other methods.[7,14] Varying the ratio of donor and acceptor did not affect the yields significantly (Entries 1–3). In our adaptation, the best isolated yield (59%) for the reaction with ethanol (Entry 3) compares well with the

Table 1. Hetero-Michael addition to methyl vinyl ketone (MVK)

Entry	Michael donor	MVK/Michael donor	Time [h]	Product	Yield (%)[a] (isolated)	Reference
1	EtOH	1:1	3		62[24]	27
2	EtOH	1.5:1	3		67	27
3	EtOH	1:1.5	3		66 (59)	27
4	EtOH	1:1	6		64	27
5	*n*-BuOH	1:1	3		76 (63)	28
6	*i*-PrOH	1:1	3		52 (45)	29
7	*t*-BuOH	1:1	3		22 (12)	30
8	$C_6H_5CH_2OH$	1:1	3		80 (75)	19
9	C_6H_5OH	1:1	3		100	26
10	Bu_2NH	1:1	1		82	31
11		1:1	1		83	32
12		1:1	1		80	31
13		1:1	3		90	12
14		1:1	3		95[b]	33
15		2.1:1	3		100 (98)	34

(*continued*)

Table 1. (*continued*)

Entry	Michael donor	MVK/Michael donor	Time [h]	Product	Yield (%)[a] (isolated)	Reference
16		2.1:1	3		100 (98)	34
17		2.1:1	3		100 (98)	33
18		1:1	3		95 (90)	20a
19		1:1	3		100 (96)	14
20		1:1	3		100	12

Reactions were conducted at 40 °C on a 5.0 mmol scale.
[a] Yield determined by ^{1}H NMR.
[b] A small amount (2%) of the bis-addition product was also obtained.

yields for the $BF_3 \cdot OEt_2$-catalysed reaction (52–77%)[7a] and is only slightly lower than the reaction catalysed with sodium ethanolate (71%).[24] The only method giving significantly higher yields (95%) is the acid-catalysed reaction of MVK in an excess of ethanol.[25] The reactions with *n*-butanol (Entry 5) and benzyl alcohol (Entry 8) were similar to those of the other primary alcohols and good yields of 63% and 75% were obtained. The reaction of benzyl alcohol compares well with the Brønsted acid-catalysed reaction where 72% yield was obtained after 48 h.[19] In comparison to the primary alcohols, the yield for isopropanol (Entry 6) was marginally lower (~45%) but still superior to the known base-catalysed (12–20%)[24] and the $BF_3 \cdot OEt_2$-catalysed reactions (34%).[7] Unsurprisingly, *tert*-butanol (Entry 7) gave lower yield (22%), as expected for a hindered nucleophile. A yield was not quoted for the equivalent $BF_3 \cdot OEt_2$/HgO-method.[7] In comparison to the pyridine-catalysed reaction of phenol (Entry 9) with MVK at 100 °C, the $Bu_3PEtOTs$/TsOH system was more efficient giving 100% conversion in only 3 h.[26] These oxo-Michael reactions in ethyltri-*n*-butylphosphonium tosylate cannot be compared with the corresponding reactions in imidazolium ionic liquids since there are no reports of oxo-Michael reactions in this class of ionic liquids.

A broad range of aliphatic and aromatic amines were also effective nucleophiles, generating 4-aminobutanone derivatives (Entries 10–17). The reactions were fast and excellent yields were obtained (82–98%) with both primary and secondary amines. These results compare very well with the recently reported improved method for the reaction of di-*n*-butylamine with MVK, involving Lewis acid catalysis by a $CeCl_3 \cdot 7H_2O$/NaI system supported in SiO_2, which gave the addition products in 84% yield after 5 h.[13] Whilst the yield is comparable with that obtained in the $Bu_3PEtOTs$/TsOH system (82%) the reaction time was greatly extended. Furthermore, the workup involved extraction, washing and flash chromatography, which are unnecessary with the reactions in the phosphonium ionic liquid. Similarly the reactions of piperidine and morpholine gave 4-piperidin-1-yl-butan-2-one and 4-morpholinobutan-2-one in 83% and 80% yields, respectively, which compares favourably with the reaction catalysed by the azaphosphatrane nitrate where yields of 88% and 90% were obtained after 20 h reaction time.[12] The $Cu(acac)_2$-catalysed reaction in the ionic liquid [bmim]BF_4, appears to be the most efficient for the reactions of aliphatic amines giving high yields in 10–60 min.[21b] Excellent yields were also obtained with aromatic amines (Entries 12–14) and these are superior to the yields obtained with strong Brønsted acids.[19]

We found that both aliphatic and aromatic thiols reacted equally well with methyl vinyl ketone in the $Bu_3PEtOTs$/TsOH system and the Michael adducts were obtained in excellent yields (95–100%) (Entries 18, 20). This is a favourable contrast with the Brønsted acid catalyst, Tf_2NH, which was used in acetonitrile as the solvent.[19] Thiophenol could not be used as a reactant in that system and a yield of only 66% was obtained after 1 h for benzyl mercaptan.[19] The yields were similar to those obtained with bismuth triflate.[16] While the reaction of thiophenol in the ammonium ionic liquid, 1-pentyl-3-methylimidazolium bromide was rapid and the Michael adduct was isolated in 75% yield after only 45 min,[20b] the reaction catalysed by an azaphosphatrane nitrate salt resulted in 95% yield after 40 h.[12] There appears to be an advantage in using ionic liquids as solvents/catalysts for this reaction.

3. Conclusion

We have developed a new method for the hetero-Michael addition of alcohols, thiols and amines to methyl vinyl ketone, which uses very small amounts of a non-aqueous, non-volatile and inexpensive acid as catalyst. The yields are good, even when equimolar amounts of the reagents are used. In addition, we are avoiding some of the problems associated with the other methods recently developed. The reaction conditions are mild and there is no need to work under an inert atmosphere.

The role of the ionic liquid in the hetero-Michael reaction is not yet understood and further investigations are necessary. These results show that the phosphonium ionic liquid acts differently to the ammonium-based ionic liquids in that both aliphatic and aromatic amines reacted equally well in the phosphonium ionic liquid while only aliphatic amines have been successful Michael donors in ammonium ionic liquids.[21] The oxo-Michael reaction has not been reported in ammonium ionic liquids and therefore comparisons cannot be made, however, the thia-Michael reaction has been well studied and excellent yields were reported, which are comparable to the results obtained in this study.[20]

4. Experimental

4.1. General

Chemicals were obtained from Aldrich or Lancaster. Methyl vinyl ketone and aniline were distilled prior to use, all other materials were used as received. ^{1}H and ^{13}C NMR spectra were recorded at 270 and 68 MHz, respectively, on a Jeol GX270 spectrometer. All spectra were measured in $CDCl_3$ as the solvent and the chemical shifts were referenced to tetramethylsilane (TMS) as an internal standard (0 ppm). The ^{31}P NMR spectrum was recorded at 121 MHz on a Bruker AM-300 spectrometer at 121 MHz in $CDCl_3$ as the solvent and phosphoric acid as the external standard. The IR spectrum was recorded using a KBr disc on a Nicolet 140 FTIR spectrometer in the range 4000–400 cm^{-1}. The accurate mass measurement was carried out at the EPSRC National Mass Spectrometry Service Centre, Chemistry Department, University of Wales, Swansea. The melting point was recorded on a Reichert hot-stage melting point apparatus and is uncorrected.

4.2. Preparation of ethyltri-*n*-butylphosphonium tosylate

Ethyltri-*n*-butylphosphonium tosylate was prepared by heating a solution of tri-*n*-butylphosphine (11 g, 54 mmol) and ethyl tosylate (11 g, 54 mmol) in dry toluene (40 mL) at 100 °C under a nitrogen atmosphere for 16 h. The solvent was evaporated to give a white solid, which was suspended in dry ether, filtered and washed with dry ether to furnish the product (96%) as a white solid, mp 73–76 °C (lit.: 74.5–75.2 °C),[22a] IR ν_{max}/cm^{-1} (KBr) 3086w (CH), 3050w (CH), 3021w (CH), 2950s (CH), 2929s (CH), 2865s (CH), 1465m (P–C), 1129vs (S═O), 1043s, 1014s, 815s, 710s, 681s, 579s; δ_H ($CDCl_3$) 0.91 (9H, t, *J* 7, 3×CH_3(CH$_2$)$_3$P), 1.22 (3H, dt, *J* 18 and 8, CH_3CH$_2$P), 1.42–1.56 (12H, m, 3×CH$_3$(CH_2)$_2$CH$_2$P), 2.17–2.39 (6H, m, 3×CH$_3$(CH$_2$)$_2$CH_2P), 2.32 (3H, s, CH_3C$_6$H$_5$), 2.33 (2H, dt, *J* 13 and 8, CH$_3$CH_2P), 7.11 (2H, d, *J* 8, *H*-3 and 3′ of tolyl), 7.16 (2H, d, *J* 8, *H*-2 and 2′ of tolyl); δ_C ($CDCl_3$) 6.1 (d, *J* 5, *C*H$_3$CH$_2$P), 12.6 (d, *J* 50, CH$_3$*C*H$_2$P), 13.5 (3C, d, *J* 7, *C*H$_3$(CH$_2$)$_3$P), 18.3 (3C, d, *J* 47, CH$_3$CH$_2$CH$_2$*C*H$_2$P), 21.3 (*C*H$_3$C$_6$H$_5$), 23.7 (3C, d, *J* 4, *C*H$_2$CH$_2$P), 23.9 (3C, d, *J* 13, *C*H$_2$CH$_2$CH$_2$P), 126.1 (C-3 and 3′ of tolyl), 128.4 (C-2 and 2′ of tolyl), 138.9 (C-4 of tolyl), 144.5 (C-1 of tolyl); δ_P +35.2; *m*/*z* (EI) 231.2236 (M^+, $C_{14}H_{32}P$ requires 231.2236), 171.0109 (M^-, $C_7H_7SO_3$ requires 171.0121).

4.3. Representative procedure

In a typical reaction methyl vinyl ketone (350 mg, 5 mmol), ethanol (230 mg, 5 mmol), *p*-toluenesulfonic acid (20 mg, 0.1 mmol) and ionic solvent *n*-Bu$_3$PEtOTs (2 g) were placed in a 25 mL round-bottomed flask fitted with a condenser and a magnetic stirrer bar. The mixture results in a homogeneous solution on heating at 40 °C and the reaction mixture was stirred at this temperature for 3 h. The product was isolated by Kugelrohr distillation or extraction with diethyl ether (3×10 mL) followed by filtration through a silica plug to give 4-ethoxybutan-2-one; δ_H ($CDCl_3$) 1.18 (3H, t, *J* 7, CH_3CH$_2$–O), 2.19 (3H, s, CH_3CO), 2.69 (2H, t, *J* 6, O–CH$_2$CH_2CO), 3.49 (2H, q, *J* 7, CH$_3$CH_2–O), 3.68 (2H, t, *J* 6, O–CH_2CH$_2$CO);[27] δ_C ($CDCl_3$) 15.0 (*C*H$_3$CH$_2$–O), 30.3 (*C*H$_3$C═O), 43.7 (O–CH$_2$*C*H$_2$CO), 65.4 (O–*C*H$_2$CH$_2$CO), 66.3 (CH$_3$*C*H$_2$–O), 207.2 (*C*═O).[27]

Similarly, all the products of the hetero-Michael reactions were analysed by ^{1}H NMR spectroscopy and the data compared with the literature (Table 1).

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