α-Tosyloxylation of ketones with ion-supported[hydroxy(tosyloxy)iodo] benzene

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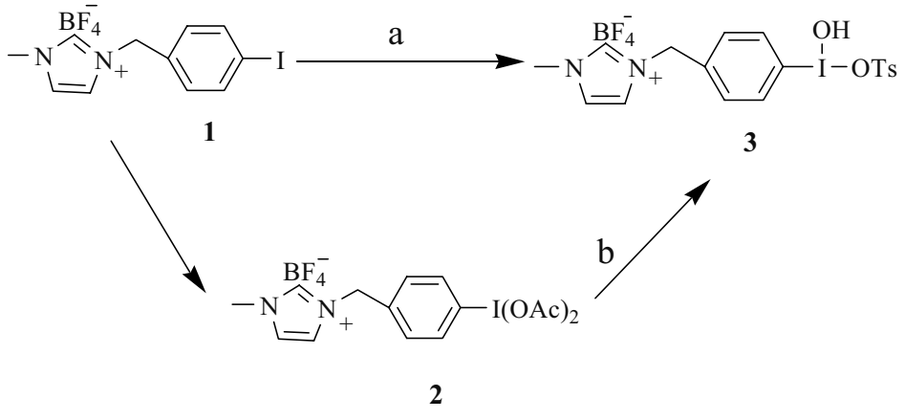
A new room-temperature ionic liquid (RTIL) supported [hydroxy(tosyloxy)iodo]benzene (ion-supported HTIB) reagent was synthesised by three kinds of effective methods in high yields, which combined the advantages of ionic liquids and the hypervalent iodine. Ion-supported HTIB was an effective reagent for one-step conversion of ketones to the corresponding α-tosyloxylated ketones in the ionic liquid [emim]BF_4 or acetonitrile under microwave. After the conversion reaction, the reagent was transformed into ion-supported iodobenzene, which could be recovered and regenerated easily without lost of activity.

Keywords: ionic liquids, [hydroxy(tosyloxy)iodo]benzene, α-tosyloxylation

α-Tosyloxyketones are environmentally benign alternatives to the toxic and lachrymatory α-haloketones. They are also useful organic intermediates for the synthesis of biologically important heterocyclic compounds such as azide derivatives,[1,2] thiazoles,[3,4] imidazo[2,1-a] isoquinolines,[5] 2-aroylbenzofurans,[6] imidazo[1,2-a] pyridine,[7] 2-aryl-7-cyano(ethoxycarbonyl)-6-methylthio-1*H*-imidazo[1,2-*b*] pyrazoles.[8,9] The classic methods for the synthesis of α-sulfonyloxy ketones involve the condensation of α-hydroxyalkyl ketones with a sulfonyl chloride, in which the synthetic processes often involve multiple steps.[10,11] For example, α-tosyloxy ketones were previously prepared through several ways, such as by the base-catalysed rearrangement of deoxybenzoin oxime tosylate,[12] by treatment of α-diazoacetophenone with *p*-toluenesulfonic acid (PTSA),[13] by the reaction of silver tosylate on α-bromodeoxybenzoin[14] and by the reaction of thallium (III) *p*-tolylsulfonate[15] with enolisable ketones. The multiple-step method quite limited its wide applied scope. Recently, Togo's group has develop a novel and efficient method for the synthesis of α-tosyloxyketones through the reaction of ketones, *m*-chloroperbenzoic acid (*m*-CPBA) and PTSA in the presence of a catalytic amount of iodobenzene.[16-18] in which iodobenzene was converted to the corresponding trivalent iodo compound, [(hydroxy)(tosyloxy)iodo]benzene (HTIB, Koser's reagent). The latter played a critical role in converting ketones into the expected product. This method was attractive in terms of simple experimental procedures and the low toxicity of the chemicals being used. Koser's reagent had been used not only for the direct α-tosyloxylation of ketones,[19-21] but also for the solvent-free and heavy-metal free facile synthesis of α-tosyloxy β-keto sulfones.[22] Koser's reagent was also used for the one-pot synthesis of α-formyloxy ketones from enolisable ketones and HTIB/polymer supported (HTIB).[23]

Microwave (MW) induced synthetic techniques have received considerable attentions as useful tools to accelerate a wide variety of organic transformations.[24] An efficient method for the α-tosyloxylation of acetophenone derivatives by HTIB under microwave irradiation was reported.[6] Although HTIB has demonstrated great potential in organic reactions, one remarkable drawback of using HTIB was that the corresponding byproduct iodobenzene generated by HTIB is hard to isolate by simple and convenient methods. This would become a significant issue where large scale synthesis is performed. Moreover, it is well known that if iodobenzene is not recycled, it will badly pollute the environment.

RTILs are gaining greater attention not only as potential environmentally benign media for many important organic reactions but also for their increasing applications in other areas.[25-27] One of the more recent developments is the use of RTILs as homogeneous supports. Much of this interest has been focused on the area of homogeneous supported synthesis.[28-32] We now report a homogeneous supported Koser's reagent based on a RTIL support. A new hypervalent iodine reagent 1-[4-hydroxy(tosyloxy)iodobenzyl]-3-methyl-imidazolium tetrafluoroborate **3** (ion-supported HTIB) was prepared in high yield via three different methods as outlined in Scheme 1.



Scheme 1 (a) m-CPBA/PTSA (b) PTSA.

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Method **1** *and method* **2**: Ion-supported (diacetoxyiodo)-benzene **2** was prepared as described in the literature.[33] Then compound **2** reacts with PTSA to give ion-supported HTIB **3** by a wet-process or by a grinding method through an indirect route. *Method* **3**: ion-supported iodobenzene **1** reacts with PTSA to give ion-supported HTIB **3** with m-CPBA as oxidant by a direct route. Ion-supported HTIB **3** combines the merits of both ionic liquids and the hypervalent iodine. After 30 days, compound **3** was deposited and characterised by elemental analysis again. As a result, the purity of **3** was satisfactory**.** Compound **3** features many advantages such as high stability, good loading capacity and good solubility (soluble in room temperature ionic liquids or water).

We have studied the one-step conversion of ketones to the corresponding α-tosyloxylated ketones by using ion-supported HTIB **3** in the ionic liquid [emim]BF_4 or acetonitrile under microwave conditions (Scheme 2).

The results in acetonitrile are listed (Table 1). This transformation was quite effective with good yields (75–90%). It was also found that various electron-donating and electron-withdrawing substituents on the aryl ring showed some effect on the reaction time and the yields of the α-tosyloxyketones.

Ion-supported HTIB **3** has a good solubility in ionic liquids, so [emim]BF_4 was chosen as the solvent to synthesise α-tosyloxyketones. When the reaction was carried out in [emim]BF_4, the reaction was much faster and the yield was higher (Table 2).

Reaction conditions: the molar ratio of ketone/**3** = 1/1.2; a*, [emim]BF_4; b*,CH_3CN; temperature 50–65 °C; microwave power 600W.

After the reactions, **3** was transformed to 1-(4-iodobenzyl)-3-methylimidazolium tetrafluoroborate (ion-supported iodobenzene) **1** which is a solid at room temperature. **1** could be separated easily from the reaction system, and recovered in high yields by simple filtration. The most important feature is that **1** can be regenerated and reused for the same reaction without decreasing its efficiency (Scheme 3 and Table 3).

Reaction conditions: the molar ratio of acetophenone/**3** = 1/1.2; solvent [emim] BF_4; time 15 min; temperature 65 °C; microwave power, 600W.

Table 1 α-Tosyloxylation of ketones with ion-supported HTIB in acetonitrile

Entry	Substrate		MW		Yield/%
	R_1	R_2	Time /min	Temp /°C	
1	CH_3	H	10	50	84
2	CH_3	CH_3	15	55	90
3	OEt	COOEt	10	65	89
4	CH_3	$COOC_2H_5$	15	60	85
5	Ph	H	20	65	86
6	*m*-NO_2-C_6H_5	H	25	60	75
7	*p*-CH_3-C_6H_5	H	10	60	83
8	*p*-Br-C_6H_5	H	8	60	84

Reaction conditions: the molar ratio of ketone/**3** = 1/1.2; microwave power, 600W.

Experimental

Melting points were determined using a WRS-1B digital thermometer and all melting points were uncorrected. The microwave-assisted reactions were carried out on a XH-100D microwave catalytic synthesis/extraction instrument. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker DRX-500AVANCE spectrometer with TMS as the internal standard. IR spectra were recorded on a Nicolet Protege 460 IR spectrometer. Mass spectra were obtained on a HP5890-GCQ and Agilent 5975I instrument. Elemental analyses were performed using an EA2400II instrument.

Synthesis of 1-[4-hydroxyl(tosyloxy)iodobenzyl]-3-methylimidazolium tetrafluoroborate **3**

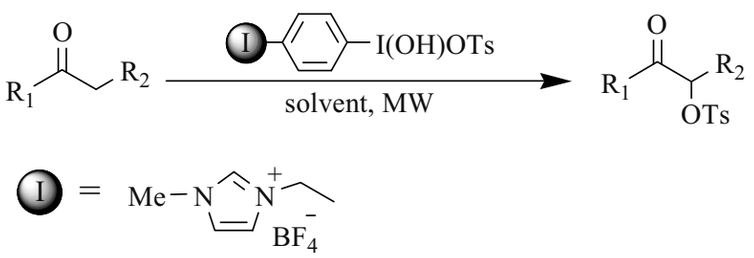
*Method 1***:** A mixture of PTSA monohydrate (0.76 g, 4.0 mmol) and **2** (2.02 g, 4.0 mmol) in acetonitrile (40 mL) was stirred at 30° C. After 30 min, the solution turned pale green. The solvent was removed under reduced pressure, and the residue was further dried under high vacuum (<5 mm Hg) at 50 °C for 12 h to afford **3** (2.26 g, 98.5%) as a viscous liquid.

Method 2: A mixture of **2** (1.51 g, 3.0 mmol) and PTSA monohydrate (0.57 g, 3.0 mmol) were gently blended in a glass mortar to give a homogeneous mixture. After 10 min, the mixture began to liquefy to give a viscous oily product, which was then dissolved in acetonitrile (20 mL). The solvent was removed under reduced pressure and the residue was further dried under high vacuum (<5 mm Hg) at 50 °C for 12 h to afford **3** (1.70 g, 98.9%) as a viscous liquid.

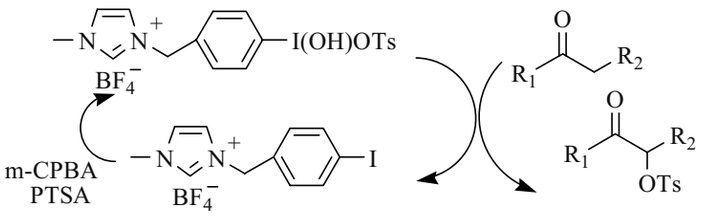
Table 2 Comparison of α-tosyloxylation of ketones with ion- supported HTIB in solvent [emim]BF_4 or CH_3CN

Entry	Substrate	Product	Reaction time/min		Yield/%	
			a*	b*	a*	b*
1	CH_3COCH_3	CH_3COCH_2OTs	5	10	86	84
2	$CH_3COCH_2CH_3$	CH_3COCH (OTs) CH_3: $CH_2OTsCOCH_2CH_3$ = 1:2	5	15	92	90
3	CH_2 $(COOEt)_2$	$TsOCH$ $(COOEt)_2$	6	10	92	89
4	$CH_3COCH_2CO_2Et$	CH_3COCH (OTs) CO_2Et	8	15	89	85
5	$PhCOCH_3$	$PhCOCH_2OTs$	15	20	92	86
6	*p*-$BrC_6H_4COCH_3$	*p*-$BrC_6H_4COCH_2OTs$	5	8	90	84
7	*m*-$O_2NC_6H_4COCH_3$	*m*-$O_2NC_6H_4COCH_2OTs$	15	25	86	75
8	*p*-$MeC_6H_4COCH_3$	*p*-$MeC_6H_4COCH_2OTs$	5	10	91	83

a*,[emin]BF_4; b*, CH_3CN.



Scheme 2



Scheme 3

Table 3 The yields of compound **3** for the recycling in α-tosyloxylation of acetophenone

Time	Yield/%
1	92.0
2	91.9
3	91.8
4	91.7
5	91.7

Method 3: **1** (0.78 g, 2.01 mmol) and PTSA monohydrate (0.35 g, 1.83 mmol) were dissolved in acetonitrile (20 mL), and then m-CPBA (0.32 g, 1.83 mmol) was added and the mixture was stirred for 30 min at 30 °C under a nitrogen atmosphere. The solvent was removed *in vacuo* to afford a semi-solid material, which was then dissolved in water (10 mL). Insoluble materials were removed by filtration, and the filtrate was concentrated *in vacuo*, the residue was further dried under high vacuum (<5 mmHg) at 50 °C for 12 h to afford **3** (1.04 g. 99.1%) as a viscous liquid.

General method for the synthesis of α-tosyloxylation of ketones

*Method 1***:** Ketones (1 mmol or 2 mmol) were added to a solution of ion-supported HTIB **3** (1.2 mmol or 2.4 mmol) in acetonitrile (6 mL), the mixture was stirred in a microwave reactor (600 W). The reaction times and temperatures are specified in Table 1. The product was purified as follows: the solvent was evaporated under reduced pressure to give a solid residue, which was washed with ether (10 mL × 2) to afford the expected ion-supported iodobenzene **1** as a white solid, and the washings were combined, and concentrated under reduced pressure to give the residue, which was further purified by preparative TLC on silica gel (benzene:ethyl acetate: 10 : 1) to give α-tosyloxyketones.

Method 2: Ketone (1 mmol or 2 mmol) was added to the solution of ion-supported HTIB **3** (1.2 mmol or 2.4 mmol) in [emim]BF_4 (10 mL) and the mixture was stirred in a microwave reactor (600 W). The reaction times are specified in Table 2. The product was extracted by ether, the expected ion-supported iodobenzene **1** was dissolved in the [emim]BF_4, the ether solution was concentrated under reduced pressure to give the residue, which was further purified by preparative TLC on silica gel (benzene:ethyl acetate = 10 : 1) to give α-tosyloxyketones.

General method of the regeneration and the reuse of ion-supported HTIB **3** *in [emim]BF_4*

As described in Method 2, after extraction with ether, the crude ionic liquid [emim]BF_4 containing ion-supported iodobenzene **1** (0.94–0.97 or 1.90–1.94 mmol) and a small amount of ether was dried under high vaccum (<5 mm Hg) for 12 h at 50 °C. The resulting material was then dissolved in acenitrile (10 mL), followed by addition of PTSA monohydrate (1.0 or 2.0 mmol) and *m*-CPBA (1.0 or 2.0 mmol) and the mixture was stirred for 1 h at 30 °C under nitrogen protection. The mixture was concentrated *in vacuo* to give a residue, which was washed with ether (10 mL × 2) to remove the excess amount of PTSA and *m*-CPBA. After drying under high vacuum, ion-supported HTIB **3** in [emim]BF_4 was obtained, and could be used for the synthesis of α-tosyloxylation of ketones.

Characterisation of 1-[4-hydroxyl(tosyloxy)-iodobenzyl]-3-methylimidazolium tetrafluoroborate (**3**): ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 2.29 (s, 3H, Ar-CH_3), 3.84 (s, 3H, imidazolium-CH_3), 5.38 (s, 2H, CH_2), 7.13 (d, *J* = 8.0 Hz, 2H, ArH), 7.23 (d, *J* = 8.0 Hz, 2H, ArH), 7.51 (d, *J* = 8.0 Hz, 2H, ArH), 7.71 (s, 1H, imidazolium-H), 7.74 (s, 1H, imidazolium-H), 7.78 (d, *J* = 8.0 Hz, 2H, ArH), 9.21 (s, 1H, imidazolium-H). ^{13}C NMR (DMSO-d_6): δ (ppm) 21.0, 36.2, 51.6, 95.5, 122.6, 124.3, 125.8, 128.3, 130.9, 134.8,137.1, 138.0, 138.2, 145.6. IR (Nujol): 3445 (–OH), 3155, 3113, 1717, 1635, 1599, 1577, 1563, 1408 (S = O), 1164 (S = O), 818 cm^{-1}. MS: *m/z* 298.9 (100), [M^+ -BF_4^- -OH -OTs], (HP5890-GCQ); 298 (M^+-BF_4^-- OH- TsOH), 218 (CH_3-C_6H_4-I^+), 217 (I-C_6H_4-CH_2^+), 91 (100) (C_6H_5-CH_2^+), 82 (1-methylimidazole)(Agilent 5975I). Anal. Calcd for $C_{18}H_{20}BF_4IN_2O_4S$: C 37.63, H 3.51, N 4.88. Found: C 37.50, H 3.57, N 4.83%.

α-*Tosyloxyacetone***:** M.p. 35 °C; lit[34] 37 °C. ^{1}H NMR (DMSO-d_6): δ (ppm) 2.07 (s, 3H, carbonyl-CH_3), 2.43 (s, 3H, Ar-CH_3), 4.84 (s, 2H, CH_2), 7.50 (d, *J* = 8.0 Hz, 2H, ArH), 7.83 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR (DMSO-d_6): δ (ppm) 21.1, 26.0, 72.5, 127.7, 130.2, 132.3, 145.2, 200.0.

Diethyl α-*(tosyloxy)malonate*: Oil.[35] ^{1}H NMR ($CDCl_3$): δ (ppm) 1.24 (t, *J* = 7.5 Hz, 6H, -2CH_3), 2.46 (s, 3H, Ar-CH_3), 4.21 (q, *J* = 7.5 Hz, 4H, CH_2), 5.29 (s, 1H, CH), 7.36 (d, *J* = 8.0 Hz, 2H, ArH), 7.84 (d, *J* = 8.0 Hz, 2H, ArH).^{13}C NMR ($CDCl_3$): δ (ppm) 13.8, 21.7, 62.9, 74.7, 128.3, 129.9, 132.5, 145.7, 163.2.

α-*Tosyloxyacetophenone*: M.p. 74.3–74.7 °C; lit[21] 74–76 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 2.45 (s, 3H, CH_3), 5.28 (s, 2H, CH_2), 7. 35 (d, *J* = 7.5 Hz, 2H, ArH), 7.48 (t, *J* = 7.5 Hz, 2H, ArH), 7.62 (t, *J* = 7.5 Hz, 1H, ArH), 7.85 (d, *J* = 7.5 Hz, 2H, ArH), 7.86 (d, *J* = 7.5 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$): δ (ppm) 21.7, 69.9, 128.0, 128.2, 128.9, 129.9, 132.7, 133.8, 134.2, 145.3, 190.3.

α-*Tosyloxy-p-bromoacetophenone*: M.p. 131.5–132.4 °C; lit[21] 131–133 °C.^{1}H NMR ($CDCl_3$): δ (ppm) 2.45 (s, 3H, CH_3), 5.22 (s, 2H, CH_2), 7.35 (d, *J* = 10.0 Hz, 2H, ArH), 7.44 (d, *J* = 8.5 Hz, 2H, ArH), 7.78 (d, *J* = 8.5 Hz, 2H, ArH),7.84 (d, *J* = 10.0 Hz, 2H, ArH).^{13}C NMR ($CDCl_3$): δ (ppm) 21.7, 69.8, 128.1, 129.3, 129.9, 131.4, 131.9, 132.3, 132.6, 145.3, 189.9.

α-*Tosyloxy-p-methylacetophenone*: M.p. 80.3–81.0 °C; lit[21] 82–83 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 2.38 (s, 3H, CH_3), 2.46 (s, 3H, CH_3), 5.20 (s, 2H, CH_2), 7.35 (d, *J* = 7.5 Hz, 2H, ArH), 7.42 (d, *J* = 8.0 Hz, 2H, ArH), 7.72 (d, *J* = 7.5 Hz, 2H, ArH), 7.85 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$): δ (ppm) 21.7, 21.7, 69.8, 126.4, 128.2, 129.2, 129.6, 130.0, 132.3, 132.6, 145.5, 189.8.

α-*Tosyloxy-m-nitroacetophenone*: M.p. 116.3–117.7 °C; lit[21] 116–117 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 2.46 (s, 3H, CH_3), 5.26 (s, 2H, CH_2), 7.37 (d, *J* = 10.0 Hz, 2H, ArH), 7.68–7.74 (m, 1H, ArH), 7.84 (d, *J* = 10.0 Hz, 2H, ArH), 8.21–8.22 (m,1H, ArH) 8.45–8.48 (m, 1H, ArH), 8.63–8.64 (m, 1H, ArH). ^{13}C NMR ($CDCl_3$): δ (ppm) 21.7, 69.9, 123.1, 128.2, 128.3, 130.1, 130.3, 132.3, 133.8, 135.1, 145.7, 148.5, 189.2.

Ethyl α-*tosyloxyacetoacetate*: Oil.[36] ^{1}H NMR ($CDCl_3$): δ (ppm) 1.21 (t, *J* = 7.5 Hz, 3H, CH_3), 2.30 (s, 3H, carbonyl-CH_3), 2.46 (s, 3H, Ar-CH_3), 4.16 (q, *J* = 7.5 Hz, 2H, CH_2), 5.20 (s, H, CH), 7.37 (d, *J* = 7.5 Hz, 2H, ArH), 7.83 (d, *J* = 7.5 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$): δ (ppm) 13.8, 21.7, 26.5, 61.4, 80.6, 128.3, 130.1, 132.3, 145.9, 163.5, 197.1.

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