Efficient Conversion of Ketones to α-Tosyloxyketones with *m*-Chloroperbenzoic Acid and *p*-Toluenesulfonic Acid in the Presence of Catalytic Amount of IL-Supported PhI in [emim]OTs

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Abstract: Various ketones were smoothly converted into the corresponding α-tosyloxyketones with MCPBA and *p*-toluenesulfonic acid in the presence of a catalytic amount of ionic-liquid (IL)-supported PhI in room temperature ionic liquid, [emim]OTs. Moreover, the present ionic-liquid reaction media containing a catalytic amount of IL-supported PhI could be reused for the same α-tosyloxylation of ketones and thiazoles directly, keeping good yields.

Key words: ionic liquid, IL-supported PhI, α-tosyloxyketone, ketone, MCPBA, *p*-toluenesulfonic acid, thiazole, catalyst

Synthetic use of hypervalent iodines for organic synthesis has been studied widely.[1] Among these hypervalent iodines, [(hydroxy)(tosyloxy)iodo]benzene (HTIB, Koser's reagent) is an efficient and sole reagent for the direct α-tosyloxylation of ketones.[2] α-Tosyloxyketones are very important strategic precursors for the construction of various heteroaromatics such as thiazoles, oxazoles, selenazoles, imidazoles, pyrazoles, benzofurans, and lactones.[2] We have also studied synthetic uses of [(hydroxy)(tosyloxy)iodo]arenes, 1-(arenesulfonyloxy)benziodoxolones, and poly[4-(hydroxy)(tosyloxy)iodo]styrene for the construction of thiazoles, imidazoles, imidazo[1.2-*a*]pyridines, and 2,1-benzothiazines.[3] Recently, PhI-catalyzed efficient α-acetoxylation of ketones with *m*-chloroperbenzoic acid (MCPBA) in AcOH in the presence of $BF_3{\cdot}OEt_2$ and water was reported to provide the corresponding α-acetoxyketones in moderate isolated yields,[4] and hypervalent iodine(III)-catalyzed oxidative cyclization of β-(4-hydroxyaryl)propanoic acids with MCPBA was also reported to give the corresponding spirolactones.[5] We also reported a direct one-pot preparation of various [(hydroxy)(sulfonyloxy)iodo]arenes from iodoarenes with MCPBA and sulfonic acids at room temperature,[6] and PhI-catalyzed α-tosyloxylation of ketones with MCPBA and *p*-toluenesulfonic acid.[7] On the other hand, today, ionic liquids have become very popular as organic reaction media due to the promotion of ionic reactions and recyclable reaction media.[8] Thus, these solvents possess interesting and useful advantages for organic reactions such as negligible vapor pressure, low flammability, high thermal stability, and easy reusability. Therefore, these solvents have been successfully used in Friedel–Crafts reaction,[9] hydrogenation,[10] Diels–Alder reactions,[11] Heck, Suzuki, Sonogashira, and olefin-metathesis reactions,[12] Michael additions,[13] oxidation,[14] condensation reaction,[15] formation of imines,[16] 1,2-rearrangement,[17] esterification of carboxylic acids and carboxylates,[18] Williamson ether synthesis,[19] and Grignard reaction.[20] Recently, we also reported highly efficient esterification of carboxylic acids and phosphonic acids with trialkyl orthoacetate in ionic liquid,[21] and demethylation of *N*,*N*-dimethylanilines with phenyl chloroformate in various ionic liquids.[22]

Here, we would like to report an oxidative conversion of ketones into α-tosyloxyketones with MCPBA and *p*-toluenesulfonic acid in the presence of a catalytic amount of ionic-liquid (IL)-supported PhI. As IL-supported PhI catalysts, ionic liquids **A** (oil), **B** (mp 126–128 °C), **C** (mp 170–172 °C), and **D** (mp 149–150 °C) were prepared to see their reactivity and reusability (Figure 1). Then, α-tosyloxylation of acetophenone in the presence of a catalytic amount of IL-supported PhI (10 mol%) **A** in typical room-temperature ionic liquids (2 mL), such as butylmethylimidazolium hexafluorophosphate ([bmim]PF_6), butylmethylimidazolium tetrafluoroborate ([bmim]BF_4), ethylmethylimidazolium tosylate([emim]OTs), and butylmethylpyrrolidinium bis(trifluoromethanesulfonyl)imide ([bmpy]NTf_2), with MCPBA and *p*-toluenesulfonic acid was carried out to give α-tosyloxyacetophenone in 41%,

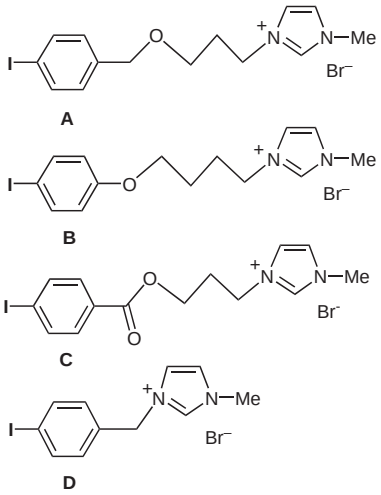

Figure 1 IL-supported PhI **A**–**D**

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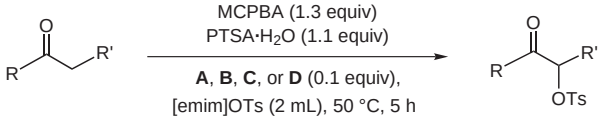
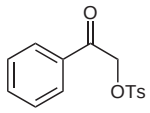
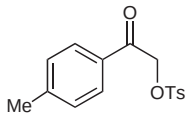
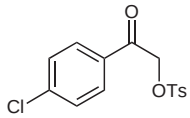
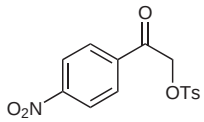
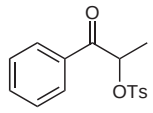
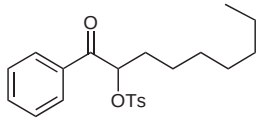
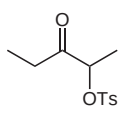
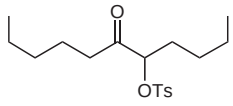
0%, 82%, and 51% yields, respectively. When **B** was used instead of **A**, in [bmim]PF_6, [bmim]BF_4, [emim]OTs, and [bmpy]NTf_2, α-tosyloxyacetophenone was obtained in 65%, 0%, 83%, and 56% yields, respectively. Thus, [emim]OTs showed the best reactivity among these four room-temperature ionic liquids. Then, α-tosyloxylation of various ketones with MCPBA and *p*-toluenesulfonic acid in the presence of a catalytic amount (10 mol%) of ionic liquid **A**, **B**, **C**, or **D** was carried out in [emim]OTs. As shown in Table 1, various α-tosyloxyketones were efficiently prepared in good to moderate yields from the reaction of ketones under the same conditions. Moreover, after the extraction of α-tosyloxyketones and byproduct (MCBA) with ethyl acetate from the reaction mixture, α-tosyloxyketones could be simply obtained by washing of the ethyl acetate extract with aqueous saturated $NaHCO_3$. The recovered ionic-liquid reaction media containing a catalytic amount of IL-supported PhI **A**, **B**, **C**, or **D** could be reused for the same α-tosyloxylation of ketone with MCPBA and *p*-toluenesulfonic acid, keeping good to moderate yields of α-tosyloxyketone as shown in Table 2 until the third time. Naturally, when iodobenzene instead of IL-supported PhI **A**–**D** in [emim]OTs was used, the recovered ionic-liquid reaction medium could not be reused due to the lack of iodobenzene.

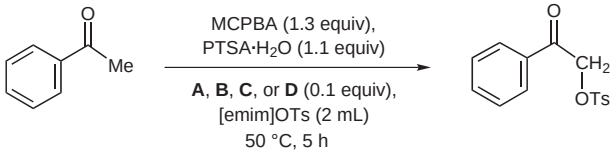
Table 1 α-Tosyloxylation of Ketones with IL-Supported PhI



Entry	Product	Yields (%)[a]			
		A	**B**	**C**	**D**
1		82	83	80	70
2		60	58	39	48
3		77	76	67	67
4		65	70	72	71
5		83[b]	75[b]	63[b]	70[b]
6		81[b]	75[b]	52[b]	56[b]
7		57	64	61	69
8		57	66	62	53

[a] Isolated yield.
[b] PTSA·H_2O (5.0 equiv) was used.

Table 2 α-Tosyloxylation of Ketone with MCPBA in Recovered Ionic-Liquid Reaction Media

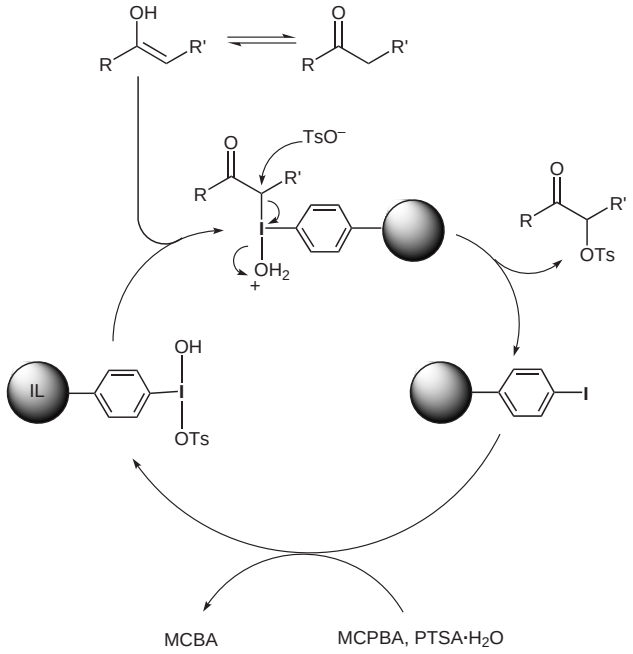


Iodoarene	Yield (%)		
	1st	2nd	3rd
A	82	82	73
B	76	71	36
C	78	80	74
D	78	78	69
Ph**I**	84	<1	0

A plausible reaction pathway for the present IL-supported PhI-catalyzed α-tosyloxylation of ketones is shown in Scheme 1. Finally, after the formation of α-tosyloxyacetophenone in the present reaction system, thioamides i.e., thioacetoamide and thiobenzamide, were added to the reaction mixture of [emim]OTs to provide the corresponding thiazoles in good to moderate yields as shown in Table 3. Especially, IL-supported PhI **A** showed the best reactivity. Moreover, after the extraction of thiazoles with ethyl acetate, the recovered ionic-liquid reaction media containing a catalytic amount of IL-supported PhI **A** could be reused for the same direct preparation of thiazoles, keeping good to moderate yields until the third time as shown in Table 4.

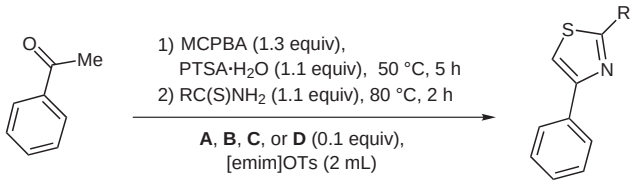
In conclusion, various ketones were smoothly converted into the corresponding α-tosyloxyketones with MCPBA and *p*-toluenesulfonic acid in the presence of a catalytic amount of IL-supported PhI in [emim]OTs. The present ionic liquid reaction media containing a catalytic amount of IL-supported PhI could be reused for the same α-tosyloxylation of ketones, keeping good to moderate yields. Moreover, thiazoles could be directly obtained from the ketone without isolation of α-tosyloxyketones, and the ionic-liquid reaction media containing a catalytic amount of IL-supported PhI could be reused for the same preparation of thiazoles.

Further synthetic study using IL-supported PhI in ionic liquids is under way in this laboratory.



Scheme 1 Reaction pathway for IL-supported PhI-catalyzed α-tosyloxylation of ketones

Table 3 Direct Preparation of Thiazoles Using Thioamides

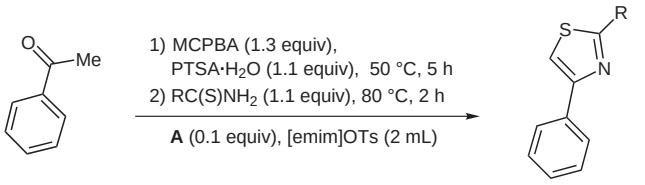


Iodoarene	Yield (%)	
	R = Me	R = Ph
A	72	66
B	37	63
C	58	62
D	62	66

Typical Experimental Procedure for Preparation of α-Tosyloxyketones[23]

To a mixture of acetophenone (1 mmol, 120 mg), **A** (0.1 mmol, 43.7 mg) and PTSA·H_2O (1.1 mmol, 209 mg) in [emim]OTs (2 mL) was added MCPBA (65% purity, 1.3 mmol, 345 mg). The obtained mixture was stirred for 5 h at 50 °C under an argon atmosphere. Then, the reaction mixture was extracted with EtOAc (20 × 2 mL). The extract was washed with aq sat. $NaHCO_3$ solution once and dried, and the solvent was removed to provide crude α-tosyloxyacetophenone (purity: >90%). Pure α-tosyloxyacetophenone was obtained in 82% yield by the treatment of flash column chromatography (eluent: hexane–EtOAc = 3:1). When the ionic-liquid reaction medium was reused, it was dried by vacuum pump for 2 h at r.t. to remove volatile materials. Then, acetophenone (1 mmol, 120 mg), PTSA·H_2O (1.1 mmol, 209 mg), and finally MCPBA (65% purity, 1.3 mmol, 345 mg) were added to the ionic liquid, and the obtained mixture was stirred for 5 h at 50 °C. After the reaction, α-tosyloxyacetophenone was isolated as the same procedure mentioned above.

Table 4 Direct Preparation of Thiazoles in Recovered Ionic-Liquid Reaction Media



	Yield (%)		
R	1st	2nd	3rd
Me	72	67	56
Ph	66	73	52

Typical Experimental Procedure for Preparation of Thiaozles[23]

To a mixture of acetophenone (1 mmol, 120 mg), **A** (0.1 mmol, 43.7 mg), and PTSA·H_2O (1.1 mmol, 209 mg) in [emim]OTs (2 mL) was added MCPBA (65% purity, 1.3 mmol, 345 mg). The obtained mixture was stirred for 5 h at 50 °C under an argon atmosphere. Then, thioacetoamide (1.1 mmol, 75.1 mg) was added to the reaction mixture, and the obtained mixture was warmed for 2 h at 80 °C. Then the reaction mixture was extracted with EtOAc (20 × 2 mL). The extract was washed with aq sat. $NaHCO_3$ solution once and dried, and the solvent was removed to provide crude 2-methyl-4-phenylthiazole (purity: >90%). Pure 2-methyl-4-phenylthiazole was obtained in 72% yield by the treatment of flash column chromatography (eluent: hexane–EtOAc = 9:1). When the ionic-liquid reaction medium was reused, it was dried by vacuum pump for 2 h at r.t. to remove volatile materials. Then acetophenone (1 mmol, 120 mg), PTSA·H_2O (1.1 mmol, 209 mg), and finally MCPBA (65% purity, 1.3 mmol, 345 mg) were added to the ionic liquid, and the obtained mixture was stirred for 5 h at 50 °C. Then thioacetoamide (1.1 mmol, 75.1 mg) was added to the reaction mixture, and the obtained mixture was warmed for 2 h at 80 °C. After the reaction, the mixture was extracted with EtOAc (20 × 2 mL). The extract was washed with aq sat. $NaHCO_3$ solution once and dried, and the solvent was removed to provide 2-methyl-4-phenylthiazole.

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(23) **α-Tosyloxyketones**

α-Tosyloxyacetophenone

Mp 90 °C (lit.[2h] 90–91 °C). IR (KBr): 1180, 1360, 1715 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.45 (s, 3 H), 5.27 (s, 2 H), 7.35 (d, *J* = 8.5 Hz, 2 H), 7.47 (t, *J* = 8.2 Hz, 2 H), 7.61 (t, *J* = 8.2 Hz, 1 H), 7.84 (d, *J* = 8.2 Hz, 2 H), 7.85 (d, *J* = 8.2 Hz, 2 H).

α-Tosyloxy-*p*-methylacetophenone

Mp 80 °C (lit.[24] 82–83 °C). IR (KBr): 1170, 1350, 1700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.41 (s, 3 H), 2.45 (s, 3 H), 5.24 (s, 2 H), 7.26 (d, *J* = 8.1 Hz, 2 H), 7.35 (d, *J* = 8.2 Hz, 2 H), 7.74 (d, *J* = 8.1 Hz, 2 H), 7.86 (d, *J* = 8.2 Hz, 2 H).

α-Tosyloxy-*p*-chloroacetophenone

Mp 123 °C (lit.[24] 125 °C). IR (KBr): 1190, 1360, 1710 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.46 (s, 3 H), 5.21 (s, 2 H), 7.35 (d, *J* = 8.4 Hz, 2 H), 7.45 (d, *J* = 8.6 Hz, 2 H), 7.80 (d, *J* = 8.6 Hz, 2 H), 7.84 (d, *J* = 8.4 Hz, 2 H).

α-Tosyloxy-*p*-nitroacetophenone

Mp 137 °C (lit.[24] 130–131 °C). IR (KBr): 1180, 1340, 1710 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.47 (s, 3 H), 5.25 (s, 2 H), 7.37 (d, *J* = 8.3 Hz, 2 H), 7.83 (d, *J* = 8.3 Hz, 2 H), 8.03 (d, *J* = 8.9 Hz, 2 H), 8.32 (d, *J* = 8.9 Hz, 2 H).

α-Tosyloxypropiophenone

Mp 68 °C (Lit.[24] 68–69 °C). IR (KBr): 1170, 1370, 1700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.60 (d, *J* = 7.0 Hz, 3 H), 2.41 (s, 3 H), 5.79 (q, *J* = 7.0 Hz, 1 H), 7.29 (d, *J* = 8.1 Hz, 2 H), 7.46 (t, *J* = 7.2 Hz, 2 H), 7.60 (t, *J* = 7.2 Hz, 1 H), 7.75 (d, *J* = 7.2 Hz, 2 H), 7.88 (d, *J* = 8.1 Hz, 2 H).

Thiazoles

2-Methyl-4-phenylthiazole

Mp 64 °C (lit.[25] 67 °C). IR (KBr): 1600 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.78 (s, 3 H), 7.31 (s, 1 H), 7.32 (t, *J* = 7.5 Hz, 1 H), 7.41 (t, *J* = 7.5 Hz, 2 H), 7.87 (d, *J* = 7.5 Hz, 2 H).

2,4-Diphenylthiazole

Mp 167 °C (lit.[26] 168 °C). IR (KBr): 1600 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.27 (t, *J* = 7.5 Hz, 1 H), 7.35–7.45 (m, 6 H), 7.75 (m, 2 H), 8.05 (d, *J* = 6.8 Hz, 2 H).

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