

# [Bmim]BF<sub>4</sub>-immobilized rhenium-catalyzed highly efficient oxygenation of aldimines to oxaziridines using solid peroxides as oxidants

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## Abstract

Various rhenium-based catalysts immobilized in [bmim]BF<sub>4</sub> were found to be efficient for oxygenation of various aldimines to the corresponding oxaziridines in excellent yields under mild conditions using solid peroxides like UHP, SPC and SPB as oxidants. Among the various rhenium-based catalysts studied, MTO was found to be most efficient. The reusability and recyclability of MTO immobilized in [bmim]BF<sub>4</sub> was established by using it for three subsequent cycles for oxygenation of benzylidene-*tert*-butylamine using UHP as oxidant.

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**Keywords:** Ionic liquid; Rhenium; Oxygenation; Aldimine; Solid oxidants

## 1. Introduction

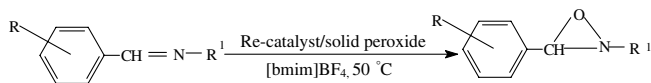
Evolution of environmentally acceptable organic synthesis is an ultimate goal of the present day chemistry. Most promising approaches to the “Green Synthesis” involve the replacement of conventional methods employing toxic/hazardous stoichiometric reagents by catalytic processes using transition metals [1] and the utilization of nonvolatile, recyclable reaction media [2]. In the recent years room temperature ionic liquids (RTIL's) owing to their unique properties such as non-volatile nature, negligible vapor pressures, tunable melting points, ability to dissolve wide range of inorganic and organic compounds, high thermal stability and recyclability/reusability have been acknowledged as green alternatives of the toxic and volatile organic solvents for chemical reactions [3].

Furthermore due to their ionic nature RTILs have emerged as ideal immobilization media for transition metal

catalysts, offering the advantage of ease of recovery of product and reuse of the catalysts [4]. A variety of reactions such as hydrogenation [5], hydroformylation [6], carbon–carbon bond forming [7], Diels–Alder [8], Heck [6a], Friedel–Crafts reactions [9] and oligomerization [10] have been reported in the literature using RTIL's as solvents. Because of their green credentials and potential to enhance reaction rates, catalytic efficiency and recyclability of the catalysts, RTIL's are finding ever-increasing applications in biphasic catalytic reactions for organic transformations. However there are scanty literature reports on the use of ionic liquids as reaction media/immobilization media for transition metal complexes for oxidation reactions [11].

In the recent past organometallic derivatives of transition metal oxides have gained increasing attention as catalysts for various synthetic transformations [12]. Among the recognized organometallic compounds, methyl trioxorhenium (MTO) is the best scrutinized and is known to be an effective catalyst for a variety of organic reactions [13]. Since the discovery of methyltrioxorhenium's (MTO) [14] ability to transfer oxygen for epoxidation of olefins with aqueous hydrogen peroxide by Herrmann et al. in

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Scheme 1.

1991, oxo-chemistry of rhenium has gained considerable importance [15]. The major drawback of efficient MTO/ $\text{H}_2\text{O}_2$  system is the limited stability of MTO due to its decomposition in water [16]. Solid peroxy compounds such as urea-hydrogen peroxide (UHP), sodium perborate (SPB) and sodium percarbonate (SPC) owing to their ease of synthesis, safe handling and storage stability have proven to be safe alternatives of dangerous anhydrous hydrogen peroxide [17]. Recently, MTO/UHP in ionic liquid [bmim] $\text{BF}_4$  has been used as a dry soluble catalytic system for the epoxidation of alkenes and Baeyer–Villiger reaction [18]. Oxygenation of aldimines is an important reaction as oxaziridines find wide applications as nitrogen and oxygen transfer reagents in synthetic organic chemistry [19]. Apart from conventional oxidant like mCPBA [20], other oxidizing agents such as *tert*-amyl hydroperoxide [21], molecular oxygen [22] and hydrogen peroxide in conjunction with acetic anhydride, nitriles, urea have been used to accomplish this transformation [23].

In this paper, we report for the first time a highly efficient and simple catalytic oxidation methodology for oxygenation of aldimines to oxaziridines using rhenium based catalysts immobilized in [bmim] $\text{BF}_4$  room temperature ionic liquid and solid peroxides as oxidants under mild reaction condition (see Scheme 1).

## 2. Results and discussion

We first studied the oxidation of benzylidene-*tert*-butylamine under various conditions in order to optimize the reaction conditions. The results of these optimization experiments are presented in Table 1. To explore the potential of various rhenium based catalysts we carried out the oxidation of benzylidene-*tert*-butylamine with UHP using various rhenium based catalysts in [bmim] $\text{BF}_4$  ionic liquid at 50 °C under nitrogen atmosphere. Among the various rhenium-based catalysts studied, methyltrioxorhenium was found to be most efficient for this transformation

Table 1  
Rhenium catalyzed oxidation of benzylidene-*tert*-butyl amine with UHP<sup>a</sup>

Entry	Catalyst	Oxidant	Solvent	Reaction time (h)	Yield (%) <sup>b</sup>
1	MTO	UHP	[bmim] $\text{BF}_4$	1.5	98
2	$\text{HReO}_4$	UHP	[bmim] $\text{BF}_4$	3.0	92
3	$\text{Re}_2\text{O}_7$	UHP	[bmim] $\text{BF}_4$	4.5	90
4	MTO	aq. $\text{H}_2\text{O}_2$	[bmim] $\text{BF}_4$	2.0	55
5	MTO	UHP	Methanol	2.5	80
6	MTO	UHP	EtahnoI	2.5	75
7	MTO	UHP	Acetonitrile	5.5	50
8	MTO	UHP	1,2-Dichloroethane	6.0	35

<sup>a</sup> Reaction conditions: catalyst (1 mol%), substrate (10 mmol), oxidant (20 mmol), at 50 °C under nitrogen atmosphere.

<sup>b</sup> Isolated yields.

(Table 1, entries 1–3). To compare the efficiency of this method we also studied the oxidation of benzylidene-*tert*-butylamine by using aq. hydrogen peroxide as oxidant in place of UHP under similar reaction conditions (Table 1, entry 4). The oxidation was found to be less efficient and afforded poor yield of the desired oxaziridine, confirming the deactivation of MTO due to its decomposition in water.

Table 2  
MTO catalyzed oxidation of aldimines with UHP in ionic liquid [bmim] $\text{BF}_4$

Entry	Aldimine	Product	Time (h)	Yield (%) <sup>b</sup>
1			1.5	98
2			1.0	98
3			1.0	96
4			1.0	98
5			0.75	96
6			1.75	97
7			3.0	96
8			2.5	94
9			1.5	97
10			3.5	80
11			1.0	98

<sup>a</sup> Reaction conditions: substrate (10 mmol), UHP (20 mmol), MTO (1 mol%, 0.1 mmol, 25 mg), [bmim] $\text{BF}_4$  (1.5 ml), at 50 °C under nitrogen atmosphere.

<sup>b</sup> Isolated yields.

To compare efficiency of MTO/UHP system in [bmim]BF<sub>4</sub> with organic solvents, we studied the oxidation of benzylidene-*tert*-butylamine in various organic solvents such as methanol, ethanol, acetonitrile, and dichloroethane under similar reaction conditions (Table 1, entries 5–8). Although among the various organic solvents studied, alcohols (EtOH, MeOH) were found to be better but [bmim]BF<sub>4</sub> remained most efficient from reaction time and yield points of view. The higher efficiency of MTO/UHP in ionic liquid may be attribute to the complete dissolution of both MTO and UHP in ionic liquid, which provides an efficient homogeneous oxidation system. Poor yields of oxaziridines with acetonitrile and dichloromethane solvents may be due to insolubility of UHP in these solvents. In a controlled blank experiment for 8 h, the oxygenation of benzylidene-*tert*-butylamine with UHP did not proceed in the absence of catalyst.

To generalize the protocol developed, oxygenation of various substituted aldimines was carried out by using substrate (10 mmol), UHP (20 mmol) in presence of catalytic amount of MTO (1 mol%) in [bmim]BF<sub>4</sub> ionic liquid at 50 °C under nitrogen atmosphere. These results are illustrated in Table 2 and clearly indicate that all the aldimines except benzylidene-aniline (entry 11) were selectively converted to the corresponding oxaziridines without any evidence for the formation of nitrones and any other side products. The oxidation of benzylidene-aniline (Table 2, entry 11) under these reaction conditions yielded corresponding benzaldehyde as the sole product. Among the various aldimines studied, those substituted with electron-donating groups on the phenyl ring were found to be more reactive and required lesser reaction times than aldimines derived from benzaldehyde and corresponding amine. However in case of CH<sub>3</sub>O group being present at *p*-position of phenyl ring (Table 2, entry 6) the reaction time was found to be more probably due to the stabilization of aldimine through extended conjugation. Aldimines having electron-withdrawing groups on the phenyl ring were in general found to be less reactive (Table 2, entries 7–8). The oxidation of furfurylidene-*tert*-butylamine (Table 2, entry 10) was found to be very slow and gave comparatively poor yield of the corresponding oxaziridine.

The reusability of this catalytic system was established by carrying out oxygenation of benzylidene-*tert*-butylamine

Table 3  
Rhenium catalyzed oxidation of benzylidene-*tert*-butylamine with SPC or SPB in ionic liquid [bmim]BF<sub>4</sub> under different reaction conditions

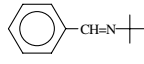
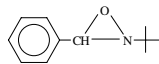
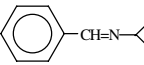
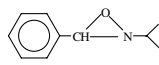
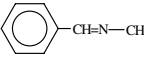
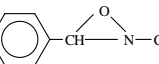
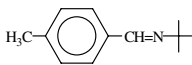
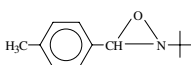
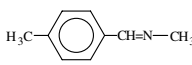
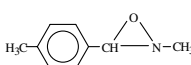
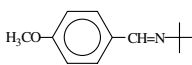
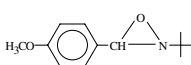
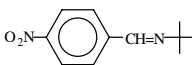
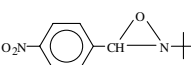
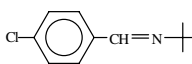
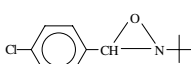
Entry	Additive	Catalyst	Reaction time (h)		Yield(%) <sup>a</sup>	
			SPC	SPB	SPC	SPB
1	AcOH	MTO	2.5	3.0	96	92
2	AcOH	HReO <sub>4</sub>	3.5	5.5	92	90
3	AcOH	Re <sub>2</sub> O <sub>7</sub>	4.5	6.0	80	82
4	–	MTO	5.0	5.0	35	20
5	TFA	MTO	2.0	3.0	97	94
6	H <sub>2</sub> SO <sub>4</sub>	MTO	6.0	6.0	–	–
7	HCl	MTO	6.0	6.0	–	–

<sup>a</sup> Isolated yields.

with recycled MTO immobilized in [bmim]BF<sub>4</sub> and UHP under similar reaction conditions. To recover MTO immobilized in [bmim]BF<sub>4</sub>, the product was separated from the reaction mixture by extraction with diethyl ether, residual ionic liquid layer was diluted with ethyl acetate and washed with water to remove urea. Organic layer was dried over anhydrous sodium sulphate followed by removal of ethyl acetate under reduced pressure. The recovered MTO immobilized in [bmim]BF<sub>4</sub> was reused as such for subsequent oxygenation of benzylidene-*tert*-butylamine (three times) with fresh UHP under similar reaction conditions. The observed fact that the yields of the oxaziridine and reaction times remained almost same in these experiments established the recyclability and reusability of both ionic liquid and MTO.

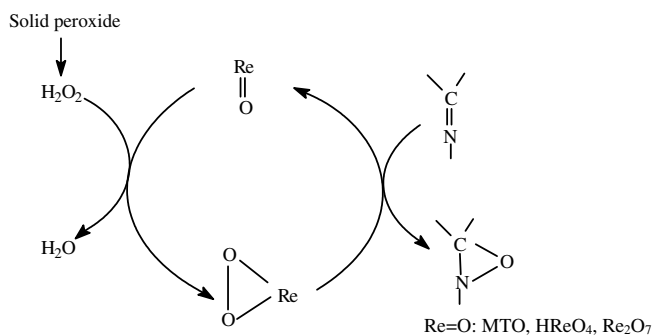
To explore the potential of other solid peroxy oxidants such as SPC and SPB, we carried out the oxygenation of

Table 4  
MTO catalyzed oxidation of aldimines with SPC/SPB in ionic liquid [bmim]BF<sub>4</sub>

Entry	Substrate	Product	Reaction time		Yield (%) <sup>b</sup>	
			SPC	SPB	SPC	SPB
1			2.5	3.0	96	92
2			2.5	3.5	97	94
3			1.75	2.5	96	94
4			1.5	2.5	96	92
5			1.5	1.75	97	95
6			2.0	2.75	92	89
7			4.5	6.5	84	80
8			5.0	6.0	82	75

<sup>a</sup> Reaction conditions: substrate (10 mmol), oxidant (20 mmol), MTO (1 mol%), 0.1 mmol, 25 mg) acetic acid (10 mmol), [bmim]BF<sub>4</sub> (1.5 ml) at 50 °C under nitrogen atmosphere.

<sup>b</sup> Isolated yields.



Scheme 2.

benzylidene-*tert*-butylamine using different rhenium based catalysts in [bmim]BF<sub>4</sub> in the presence of small amounts of acetic acid at 50 °C under nitrogen atmosphere. The results of these experiments are summarized in Table 3. The reactivity orders of various catalysts and oxidants were found to be as MTO > HReO<sub>4</sub> > Re<sub>2</sub>O<sub>7</sub> and SPC > SPB. The presence of acetic acid was found to be essential in these reactions and in its absence reactions were found to be very slow, probably due to the fact that presence of acid helps in the release of H<sub>2</sub>O<sub>2</sub> from both SPC and SPB. The use of trifluoroacetic acid in place of acetic acid gave comparable results but the reaction did not proceed with the use of inorganic acids such as HCl and H<sub>2</sub>SO<sub>4</sub>. It was also observed that the addition of acetic acid in one portion gave poor yield of oxaziridine while its drop-wise addition at 50 °C afforded maximum yield.

To establish the scope of this method, we carried out the oxygenation of various aldimines using SPC or SPB as oxidants and MTO as catalyst in presence of small amounts of acetic acid in [bmim]BF<sub>4</sub> at 50 °C under nitrogen atmosphere and these results are presented in Table 4. Again substituted aldimines bearing electron-donating groups on phenyl ring were found to be most reactive.

Absence of water in the system makes these reactions more selective towards the formation of oxaziridines rather than ring opening products. Also the use of ionic liquid as reaction/immobilization media for Re-catalysts makes it possible to reuse the catalyst with out deactivation. These facts establish the superiority of the present protocol than existing methods for oxygenation of aldimines.

Although the exact mechanism of this reaction is not clear at this stage, the probable mechanistic pathway may involve the formation of reactive peroxy rhenium species from the reaction of oxo-rhenium with hydrogen peroxide [24b] and subsequent oxygen transfer to aldimine to yield corresponding oxaziridine (Scheme 2).

### 3. Conclusion

In summary, we have developed a highly efficient and selective oxidation system for the oxygenation of aldimines to the corresponding oxaziridines. The key advantages of this developed protocol are (i) MTO/UHP both are completely soluble in [bmim]BF<sub>4</sub> ionic liquid, which provides

a more efficient complete homogeneous oxidation system. (ii) The use of solid peroxides offers nearly water free atmosphere, making the reactions more selective towards the oxaziridines rather than ring opening products. (iii) Recyclability and reusability of MTO immobilized in [bmim]BF<sub>4</sub> without loss of activity. Easy work up, high yields of the products, recyclability of the ionic liquid as well as catalyst and mild reaction conditions make this method an improved, green and environmentally acceptable synthetic tool for the oxygenation of aldimines to oxaziridines.

## 4. Experimental

### 4.1. Materials

All the aldimines were prepared following the literature procedures [24]. Room temperature ionic liquid [bmim]BF<sub>4</sub> was purchased from Aldrich. Solid peroxides such as UHP, SPC, SPB were purchased from Aldrich and used as such. All rhenium catalysts such as MTO, Re<sub>2</sub>O<sub>7</sub> and HReO<sub>4</sub> were purchased from Aldrich.

### 4.2. General experimental procedure for the rhenium catalyzed oxygenation of aldimines using UHP as oxidant system

To a stirred solution of aldimine (10 mmol), UHP (20 mmol) in [bmim]BF<sub>4</sub> ionic liquid (1.5 ml) was added Re-catalyst (0.1 mmol, 1 mol%) and mixture was heated at 50 °C under nitrogen atmosphere for the time given in Table 2. Progress of the reaction was monitored by TLC (SiO<sub>2</sub>). After completion, the reaction mixture was extracted with diethyl ether. The ether layer was washed with water (two times) and dried over anhydrous MgSO<sub>4</sub>. Evaporation of ether gave a crude mixture, which was purified by column chromatography to afford pure oxaziridine.

### 4.3. General experimental procedure for rhenium catalyzed oxygenation of aldimines using SPC/SPB as oxidants

In a stirred mixture of aldimine (10 mmol), SPC or SPB (20 mmol) in [bmim]BF<sub>4</sub> (1.5 ml) was added Re-catalyst (1 mol%) and acetic acid (0.6 ml, 10 mmol) drop wise at 50 °C. The mixture was stirred for the period given in Table 4. After completion of the reaction the mixture was extracted with diethyl ether and ether layer was washed with water (2 times). Finally, the organic layer was removed and dried over anhydrous MgSO<sub>4</sub>. The solvent was evaporated under reduced pressure to yield pure oxaziridine.

### 4.4. Product characterization data

The melting points were determined in open capillaries on a Buchi apparatus and are uncorrected. The <sup>1</sup>H NMR Spectra were recorded on Bruker 300 MHz spectrometer

and the chemical shifts are expressed in  $\delta$  parts per million relative to tetramethylsilane (TMS) as internal standard. The IR spectra were recorded on a Perkin Elmer FTIR X 1760 instrument. Mass spectra were recorded on Matrix assisted laser desorption ionization (MALDI) mass spectrometer.

**Benzylidene-*tert*-butylamine (Table 2, entry 1):** Colorless oil, IR (KBr) 3070, 2980, 1600, 1560, 1340, 1135  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\delta$  ppm) 1.08 (s, 9H,  $(\text{CH}_3)_3\text{C}-$ ), 4.60 (s, 1H), 7.00–7.60 (m, 5H, ArH) Mass  $m/z$  165 ( $\text{M}^+ + 1$ ).

**Benzylidene-*iso*-propylamine (Table 2, entry 2):** Colorless oil, IR (KBr): 3060, 2978, 1590, 1345, 1138  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\delta$  ppm) 1.15–1.20 (d, 6H,  $(\text{CH}_3)_2\text{CH}-$ ) 2.45 (sept, 1H,  $(\text{CH}_3)_3\text{CH}$ ) 5.02 (s, 1H), 7.20–7.78 (m, 5H, ArH); Mass  $m/z$  151 ( $\text{M}^+ + 1$ ).

**Benzylidene-methylamine (Table 2, entry 3):** Oil, IR (KBr): 3062, 2980, 1602, 1140  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\delta$  ppm) 2.80 (s, 3H,  $\text{CH}_3$ , 4.25s, 1H), 7.27–7.77 (m, 5H, ArH); Mass  $m/z$  123 ( $\text{M}^+ + 1$ ).

**Benzylidene-methylamine (Table 2, entry 3):** Oil, IR (KBr): 3060, 2979, 1600, 1230, 1140  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\delta$  ppm) 2.32 (s, 3H,  $\text{CH}_3$ ), 5.02 (s, 1H), 7.30–7.70 (m, 5H, ArH); Mass  $m/z$  123 ( $\text{M}^+ + 1$ ).

***p*-Toluidine-*tert*-butylamine (Table 2, entry 4):** Oil, IR (KBr): 3065, 2976, 1575, 1341, 1132  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\delta$  ppm) 1.10 (s, 9H,  $(\text{CH}_3)_3\text{C}-$ ), 2.30 (s, 3H, Ar $\text{CH}_3$ ), 4.62 (s, 1H), 7.16 (d, 2H, ArH), 7.35 (d, 2H, ArH); Mass  $m/z$  179 ( $\text{M}^+ + 1$ ).

***p*-Toluidine-methylamine (Table 2, entry 5):** Oil, IR (KBr): 3065, 2976, 1575, 1341, 1132.  $^1\text{H}$  NMR ( $\delta$  ppm) 2.28 (s, 3H, Ar $\text{CH}_3$ ), 2.74 (s, 3H,  $\text{CH}_3$ ), 4.0–4.75 (s, 1H), 7.18 (d, 2H, ArH), 7.36 (d, 2H, ArH); Mass  $m/z$  137 ( $\text{M}^+ + 1$ ).

***p*-Anisidine-*tert*-butylamine (Table 2, entry 6):** Oil, IR (KBr): 3062, 2981, 1600, 1342, 1134  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\delta$  ppm) 1.12 (s, 9H,  $(\text{CH}_3)_3\text{C}-$ ), 4.50 (s, 1H), 3.75 (s, 3H, O $\text{CH}_3$ ), 7.20 (d, 2H, ArH), 7.39 (d, 2H, ArH); Mass  $m/z$  195 ( $\text{M}^+ + 1$ ).

***p*-Nitro-benzylidene-*tert*-butylamine (Table 2, entry 7):** m.p. 64–65  $^\circ\text{C}$  (lit 66  $^\circ\text{C}$ ) [25]. IR (KBr) 3061, 2982, 1598, 1340, 1137  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\delta$  ppm) 1.14 (s, 9H,  $(\text{CH}_3)_3\text{C}-$ ), 4.65 (s, 1H), 7.30 (d, 2H), 7.82 (d, 2H), Mass  $m/z$  210 ( $\text{M}^+ + 1$ ).

***p*-Chloro-benzylidene-*tert*-butylamine (Table 2, entry 8):** m.p. 65–66  $^\circ\text{C}$  (lit 66–67  $^\circ\text{C}$ ) [26]. IR (KBr)  $\text{cm}^{-1}$  3060, 2980, 1600, 1341, 1136.  $^1\text{H}$  NMR ( $\delta$  ppm) 1.12 (s, 9H), 4.26 (s, 1H) 7.28 (d, 2H), 7.75 (d, 2H); Mass  $m/z$  200 ( $\text{M}^+ + 1$ ).

**Benzylidene-cyclohexylamine (Table 2, entry 9):** Colorless oil, IR (KBr)  $\text{cm}^{-1}$  3062, 2981, 1599, 1340, 1132.  $^1\text{H}$  NMR ( $\delta$  ppm) 0.85–1.10 (m, 10H), 2.15 (m, 1H), 4.50–4.82 (s, 1H), 7.82–7.32 (m, 5H, ArH); Mass  $m/z$  171 ( $\text{M}^+ + 1$ ).

**Furfurylidene-*tert*-butylamine (Table 2, entry 10):** Oil, IR (KBr)  $\text{cm}^{-1}$  3106, 1587, 1479, 800.  $^1\text{H}$  NMR ( $\delta$  ppm) 1.12 (s, 9H), 4.64 (s, 1H), 6.36 (dd, 1H), 6.62 (d, 1H), 7.40 (d, 1H); Mass  $m/z$  156 ( $\text{M}^+ + 1$ ).

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