



Full paper/Mémoire

H₃PW₁₂O₄₀-[bmim][FeCl₄]: A novel and green catalyst-medium system for microwave-promoted selective interconversion of alkoxyethyl ethers into their corresponding nitriles, bromides and iodides

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ABSTRACT

In the present work, the catalytic activity of 12-tungstophosphoric acid immobilized on [bmim][FeCl₄] ionic liquid as a highly efficient and eco-friendly catalytic system for rapid and chemoselective direct conversion of MOM- or EOM-ethers into their corresponding nitriles, bromides and iodides under microwave irradiation is reported. In these reactions, the products are obtained in high yields. The catalyst exhibited remarkable reactivity and was reused several times.

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1. Introduction

Catalysts play a great role in organic laboratories and industries. In comparison with homogeneous catalysts, heterogeneous catalysts have several advantages, such as facile recovery from the reaction mixture and possibility of reusing them. Furthermore, chemical stability and reactivity of heterogeneous catalysts efficiently increases [1]. One way for improving the properties of homogeneous catalysts [2,3] is their immobilization on solid supports [4–9] and in ionic liquids [10–13].

Heteropoly acids (HPAs) as transition metal oxygen anion clusters belong to a class of solid acid catalysts having both redox and acid properties [14–16]. These solid acids have enormous potential for catalyzing a wide variety of reactions and also have been developed for the synthesis of fine chemicals such as flavorings, and in the,

pharmaceutical and food industries [17]. Heteropoly acids have many advantages over liquid acid catalysts such as higher acid strength and thermal stability. They are non-corrosive, environmentally benign, commercially available and reusable. Among the heteropoly acids, 12-tungstophosphoric acid, H₃PW₁₂O₄₀, is the most widely used catalyst due to its high acid strength, good thermal stability and low reducibility [16].

Application of ionic liquids (ILs) has increased significantly in the chemical research area [18–31].

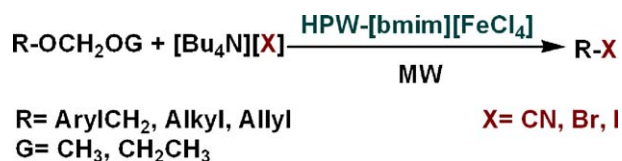
Dissolving of organometallic complexes in supported films of ionic liquids (SILP) has recently been introduced as a strategy for immobilization of molecular catalysts in a widely tailorable environment [32]. Due to the ionic nature of ILs, these compounds are good microwave energy absorbers and therefore, the reaction under MW irradiation can be performed at a temperature higher than normal heating. On the other hand, ILs are ideal for use in microwave-promoted synthesis due to their negligible vapor pressure and high thermal stability [33].

The direct conversion of protected alcohols to other functional groups is suitable for further chemical elaboration and is a useful tool for synthetic chemists [34]. Nitriles

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Scheme 1.

are useful intermediates for conversion to various functional groups and construction of *N*-heterocycles [35]. Furthermore, bromides and iodides are important and versatile intermediates for alkylation reactions and also for preparation of alkylmetal salts such as Grignard reagents [36]. There are numerous methods for the preparation of nitrile, bromide and iodide containing compounds in the literature; however, to the best of our knowledge, this is the first report of the synthesis of nitriles, bromides and iodides by direct conversion of alkoxyethyl ethers.

Recently, we reported the use of bulk and supported H₃PW₁₂O₄₀ as active catalysts for the protection/deprotection of alcohols [37,38]. Here, we report the direct conversion of methoxymethyl (MOM) and ethoxymethyl (EOM) ethers to their corresponding nitrile, bromides and iodides using H₃PW₁₂O₄₀ (HPW) immobilized on 1-butyl-3-methylimidazolium tetrachloroferrate, [bmim][FeCl₄], under microwave irradiation (Scheme 1).

2. Experimental

2.1. Materials and methods

All materials were purchased from Merck and Sigma–Aldrich chemical companies and were used without further purification. The products were identified by comparison of their spectral and physical data with those of authentic samples. All the reactions were monitored by TLC and all yields refer to the isolated products. ¹H NMR spectra were recorded on a Bruker–AC500P at 500 MHz. IR spectra were obtained by IR–435 Shimadzu spectrophotometer using KBr or sodium chloride pellets.

The microwave system used for these experiments includes the following items: Micro–SYNTH labstation, complete with glass door, dual magnetron system with pyramid-shaped diffuser, 1000 W delivered power, exhaust system, magnetic stirrer, “quality pressure” sensor for flammable organic solvents, ATCFO fiber optic system for automatic temperature. During experiments, power, temperature, time and pressure monitored and controlled with the “easyCONTROL” software.

2.2. Preparation of [bmim][FeCl₄]

In a round bottom flask equipped with a magnetic stirrer, anhydrous FeCl₃ (16.22 g, 0.1 mol) were slowly added to 1-butyl-3-methylimidazolium chloride (17.47 g, 0.1 mol). To ensure complete reaction, the reaction mixture was left stirring overnight. A red-brown liquid was obtained which was dried under high vacuum and stored under N₂.

2.3. Preparation of H₃PW₁₂O₄₀ immobilized on [bmim][FeCl₄], H₃PW₁₂O₄₀@[bmim][FeCl₄]

In a round bottom flask, H₃PW₁₂O₄₀ (5 mol%) was added slowly to highly pure [bmim][FeCl₄] (0.5 mL) and stirred roughly. To ensure complete homogenisation, the mixture was left stirring overnight. The catalyst was dried under reduced pressure and stored under N₂.

2.4. General procedure for interconversion of MOM- and EOM- ethers into their nitriles, bromides and iodides under MW irradiations

A mixture of EOM- or MOM-ether (1 mmol), [Bu₄N][X] (X = CN, Br and I) (2 mmol) in H₃PW₁₂O₄₀@[bmim][FeCl₄] (0.5 mL) was exposed to microwave irradiation (170 W, 130–142 °C) for the appropriate time. After completion of the reaction, indicated by TLC, water (10 mL) was added and the organic materials were extracted with diethyl ether (3 × 10 mL). The organic layer was dried over anhydrous Na₂SO₄. Evaporation of the solvent and purification on a short pad of silica gel (eluent: *n*-hexane/ethyl acetate, 5/1) gave the highly pure products.

2.4.1. Selected spectroscopic data

2.4.1.1. Phenylacetone nitrile (Table 2, entry 1). Oil, IR (KBr) ν (cm⁻¹) 3120, 3035, 2921, 2252, 1603, 1588, 1496, 1455, 1416, 1338, 735, 690, 615; ¹H-NMR (500 MHz, DMSO): δ (ppm) 3.87 (s, 2H), 7.47–7.67 (m, 5H); ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 23.8, 118.2, 128.5, 129.1, 130.1.

2.4.1.2. 2-(4-Methoxyphenyl)acetone nitrile (Table 2, entry 7). Oil, IR (KBr) ν (cm⁻¹) 2942, 2903, 2247, 1600, 1566, 1457, 1291, 1089, 1071, 1030, 840, 808, 690, 615; ¹H-NMR (500 MHz, DMSO): δ (ppm) 3.75 (s, 3H), 3.90 (s, 2H), 6.95 (d, *J* = 10.32 Hz, 2H), 7.30 (d, *J* = 9.18 Hz, 2H); ¹³C-NMR (125 MHz, DMSO): δ (ppm) 22.0, 55.8, 114.9, 119.6, 122.9, 129.4, 159.1.

2.4.1.3. Cinamonitrile (Table 2, entry 16). Oil, IR (KBr) ν (cm⁻¹) 3028, 2916, 2200, 1618, 1576, 1495, 1448, 1207, 966, 748, 688; ¹H-NMR (500 MHz, DMSO): δ (ppm) 4.01 (d, *J* = 16.65 Hz, 1H), 7.40–7.47 (m, 6H); ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 23.4, 96.4, 118.2, 127.5, 129.1, 131.3, 133.8, 150.5.

2.4.1.4. 1-Bromooctane (Table 2, entry 19). Oil, IR (KBr): ν (cm⁻¹) 2933, 2874, 2839, 1512, 1436, 1379, 1286, 1217, 1039, 908, 740, 642, 561; ¹H NMR (500 MHz, CDCl₃): δ (ppm) 0.89 (t, *J* = 8.37 Hz, 3H), 1.28–1.44 (m, 10H),

1.80–1.89 (m, 2H), 3.38 (t, $J = 8.37$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 14.2, 22.6, 27.8, 28.5, 28.9, 31.7, 32.6, 35.2.

2.4.1.5. *1-Iodoctane* (Table 2, entry 19). Oil, IR (KBr): ν (cm^{-1}) 2926, 2871, 2732, 1466, 1378, 1349, 1288, 1246, 1204, 1170, 1065, 906, 897, 781, 721, 699, 508; ^1H NMR (300 MHz, CDCl_3): δ (ppm) 0.82 (t, $J = 6.30$ Hz, 3H), 1.21–1.34 (m, 10H), 1.71–1.80 (m, 2H), 3.11 (t, $J = 5.94$ Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ (ppm) 6.6, 14.1, 22.5, 28.5, 29.1, 30.5, 31.8, 33.6.

3. Results and discussion

3.1. Optimization of reaction conditions

To obtain the optimized reaction conditions, the reaction of benzylmethoxymethyl ether with tetrabutylammonium cyanide, $[\text{Bu}_4\text{N}][\text{CN}]$, in the presence of a catalytic amount of $\text{H}_3\text{PW}_{12}\text{O}_{40}@[\text{bmim}][\text{FeCl}_4]$, was chosen as a model reaction. The best results obtained with the 1:2:0.005 molar ratio of benzylmethoxymethyl ether, $[\text{Bu}_4\text{N}][\text{X}]$ ($\text{X} = \text{CN}$, Br and I) and $\text{H}_3\text{PW}_{12}\text{O}_{40}@[\text{bmim}][\text{FeCl}_4]$, respectively, under microwave irradiation (170 W, 135–140 °C). In this reaction 0.5 mL of ionic liquid was used as support and medium. The same reaction was also carried out under thermal conditions (135 °C) but after 48 h, only 34% of the corresponding nitrile was obtained. Therefore, these interconversions were carried out under MW irradiation.

In order to show the effect of the ionic liquid on the catalytic activity, the reaction of benzylmethoxymethyl ether (1 mmol) with $[\text{Bu}_4\text{N}][\text{CN}]$ (2 mmol) in the presence of different amounts of bulk HPW and $\text{HPW}@[\text{bmim}][\text{FeCl}_4]$ was carried out under the same reaction conditions (Table 1). The obtained results showed that the catalytic activity of HPW increased significantly by immobilization in the ionic liquid. On the other hand, in the absence of HPW, the $[\text{bmim}][\text{FeCl}_4]$ was less efficient to catalyze this interconversion reaction. The results are summarized in Table 1.

It was observed that the other imidazolium-based ionic liquids such as $[\text{bmim}][\text{Cl}]$, $[\text{bmim}][\text{PF}_6]$, $[\text{bmim}][\text{BF}_4]$ and

$[\text{bmim}][\text{NTf}_2]$ gave a low yield of the product in the model reaction (Table 2, entries 1–4). Another disadvantage of $[\text{bmim}][\text{PF}_6]$ is instability of the $[\text{PF}_6]^-$ anion toward hydrolysis in contact with moisture, forming HF and POF_3 , which can dissolve glassware and damage steel autoclaves and reactors [39].

It is noteworthy that ionic liquids with inherent Lewis acidity resulted in the formation of the desired product in high yields (Table 2, entries 5 and 6). Using a room temperature Lewis acid ionic liquid, $[\text{bmim}][\text{FeCl}_4]$, (Table 2, entry 6) better result was obtained in comparison with $[\text{bmim}][\text{AlCl}_4]$ (Table 2, entry 5). The advantage of iron (III) chloride compared to aluminium (III) chloride is its hydrolytic stability and higher Lewis acidity strength. By combining the iron (III) chloride with an organic halide salt, room temperature ionic liquids with good solvating ability and negligible vapor pressure can be prepared which are inherently Lewis acidic and water stable in contrast to the analogous chloroaluminate system [40,41].

It was observed that changing the anion in the structure of the ionic liquid led to different results (Table 2). These observations may be due to the ability of the anion for stabilization of charged intermediate. By increasing the coordination ability of anion, the feasibility of ion pair formation between anion and charged intermediate (protonated ether) decreased which in turn decreases the product yield [30].

3.2. Direct conversion of MOM- and EOM-ethers into corresponding nitriles, bromides and iodides under microwave irradiation

Under the optimized conditions, direct conversion of structurally different primary aromatic, aliphatic and allylic MOM- and EOM-ethers to their corresponding nitriles, bromides and iodides was carried out and these useful products were obtained in good to excellent yields and short reaction times (Table 3). In the case of alkoxyethyl ethers bearing substituted aromatic rings, the nature of substituent has no significant effect on the reactivity of the alkoxyethyl ethers toward interconversion reactions.

Table 1

Direct conversion of benzylmethoxymethyl ether into its corresponding nitrile by different amounts of catalyst after 10 minutes.^a

Entry	Catalyst amount (mol%)	Catalyst	
		Yield (%) ^b	
		HPW	$\text{HPW}@[\text{bmim}][\text{FeCl}_4]$
1	0.2	0	15
2	0.3	11	40
3	0.4	20	83
4	0.5	24	95
5	0.6	31	95

^a Reaction conditions: benzylmethoxymethyl ether (1 mmol), $[\text{Bu}_4\text{N}][\text{CN}]$ (2 mmol) and $[\text{bmim}][\text{FeCl}_4]$ (0.5 mL).

^b Isolated yields.

Table 2
Direct conversion of benzylmethoxymethyl ether into its corresponding nitrile by various imidazolium-based ionic liquids.^a

Entry	Ionic liquids	Yield (%) ^b
1	[bmim][Cl]	69
2	[bmim][PF ₆]	73
3	[bmim][BF ₄]	78
4	[bmim][NTf ₂]	65
5	[bmim][AlCl ₃]	81
6	[bmim][FeCl ₄]	95

^a Reaction conditions: benzylmethoxymethyl ether (1 mmol), [Bu₄N][CN] (2 mmol), HPW (0.5 mol%) and ionic liquids (0.5 mL).

^b Isolated yields.

Table 3
Direct conversion of MOM- and EOM-ethers into their nitriles, bromide and iodides by HPW@[bmim][FeCl₄] and MW irradiation.^a

Entry	R	EOM-ethers			MOM-ethers		
		Yield, % (time, min) ^b			Yield, % (time, min) ^b		
		X = CN	X = Br	X = I	X = CN	X = Br	X = I
1	C ₆ H ₅ CH ₂	95 (2)	90 (2)	93 (2)	95 (2)	91 (2)	94 (2)
2	4-(CH ₃) ₃ C ₆ H ₄ CH ₂	91 (2.5)	88 (2.5)	91 (2.5)	92 (2.5)	87 (2.5)	91 (2.5)
3 ^c	4-(CH ₂) ₂ C ₆ H ₄ CH ₂	93 (2)	91 (2)	92 (2)	92 (2)	90 (2)	92 (2)
4	2-HOC ₆ H ₄ CH ₂	87 (3)	84 (3)	86 (3)	88 (3)	85 (3)	88 (3)
5	3-CH ₃ O-4-(OH)C ₆ H ₃ CH ₂	89 (2.5)	86 (2.5)	87 (2.5)	91 (2.5)	87 (2.5)	90 (2.5)
6	3-CH ₃ OC ₆ H ₄ CH ₂	92 (1.5)	89 (1.5)	92 (1.5)	93 (1.5)	88 (1.5)	93 (1.5)
7	4-CH ₃ OC ₆ H ₄ CH ₂	86 (3)	84 (3)	86 (3)	88 (3)	85 (3)	87 (3)
8	4-PhCH ₂ OC ₆ H ₄ CH ₂	92 (1.5)	90 (1.5)	92 (1.5)	94 (1.5)	89 (1.5)	93 (1.5)
9	2-ClC ₆ H ₄ CH ₂	88 (2.5)	85 (2.5)	89 (2.5)	89 (2.5)	85 (2.5)	88 (2.5)
10	4-ClC ₆ H ₄ CH ₂	90 (2.5)	87 (2.5)	89 (2.5)	90 (2.5)	88 (2.5)	91 (2.5)
11	2,4-Cl ₂ C ₆ H ₃ CH ₂	88 (3)	87 (3)	87 (3)	89 (3)	88 (3)	88 (3)
12	2-BrC ₆ H ₄ CH ₂	86 (3)	84 (3)	83 (3)	88 (3)	85 (3)	83 (3)
13	4-BrC ₆ H ₄ CH ₂	91 (2.5)	87 (2.5)	91 (2.5)	92 (2.5)	88 (2.5)	93 (2.5)
14	3-NO ₂ C ₆ H ₄ CH ₂	96 (1)	94 (1)	96 (1)	97 (1)	95 (1)	95 (1)
15	4-NO ₂ C ₆ H ₄ CH ₂	97 (0.5)	94 (0.5)	97 (0.5)	97 (0.5)	96 (0.5)	97 (0.5)
16	C ₆ H ₅ CH = CHCH ₂	97 (0.5)	95 (0.5)	97 (0.5)	97 (0.5)	95 (0.5)	97 (0.5)
17	C ₆ H ₅ CH ₂ CH ₂	92 (2)	89 (2)	91 (2)	93 (2)	90 (2)	93 (2)
18	CH ₃ (CH ₂) ₅ CH ₂	94 (2)	88 (2)	92 (2)	94 (2)	90 (2)	93 (2)
19	CH ₃ (CH ₂) ₆ CH ₂	94 (2)	89 (2)	93 (2)	94 (2)	91 (2)	93 (2)

^a Reaction conditions: alkoxyethyl ether (1 mmol), [Bu₄N][X] (2 mmol), HPW (0.5 mol%) and [bmim][FeCl₄] (0.5 mL).

^b Isolated yields.

^c 1 mol% of catalyst and 4 mmol of [Bu₄N][X] were used.

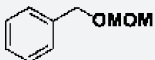
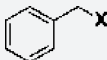
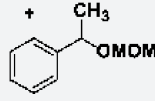
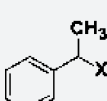
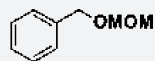
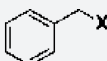
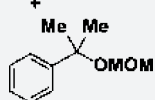
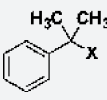
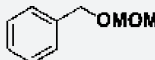
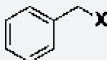
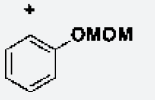
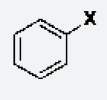
In order to explore the general applicability of this method, several competitive interconversion reactions were designed. As shown in Table 4, these reactions, using this catalytic system, were found to be highly chemoselective for primary MOM- and EOM-ethers in the presence of secondary, tertiary and phenolic ethers. In other words, in an equimolar binary mixture of primary and secondary MOM-ethers, the primary ether was converted quantitatively to its corresponding nitrile, bromide and iodide; while in the case of secondary ether the amounts of corresponding products were less than 48% (Table 4, entry 1). Also, excellent chemoselectivity was also observed for the transformation of primary ethers in the presence of tertiary and phenolic ethers which tertiary and phenolic ethers remained intact in the reaction mixture (Table 4, entries 2 and 3). In addition, this method can be selectively applied for the conversion of these MOM- and EOM- ethers

to nitriles, bromides and iodides in the presence of other hydroxyl protecting groups such as benzyl or methyl ethers (Table 3, entries 5–8).

3.3. Recyclability and reusability of catalyst

The reusability of the catalyst was examined in the conversion reaction of benzylmethoxymethyl ether to its corresponding nitrile. After completion of reaction, the heteropoly acid and IL were recovered by addition of Et₂O. The diethyl ether was further washed with water and the aqueous layer was evaporated under reduced pressure to obtain the catalyst. The combined organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure to isolate the product. The results showed that after third run, the yield of the product was 83% (Table 5).

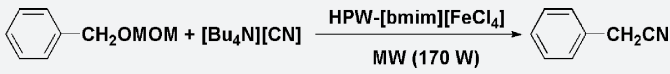
Table 4
Competitive interconversion reactions of various MOM-ethers to nitriles, bromides and iodides catalyzed by HPW@[bmim][FeCl₄] under MW irradiation.^a

Entry	MOM-ethers	Products	X = CN		X = Br		X = I	
			Yield (%) ^b	Time (min)	Yield (%) ^b	Time (min)	Yield (%) ^b	Time (min)
1			95		91		94	
	+ 			2		4.5		2
2			95		91		94	
	+ 		48		41		43	
3			95		91		94	
	+ 			2		4.5		2

^a Reaction conditions: MOM-ethers (1 mmol), [*n*-Bu₄N][X] (2 mmol), HPW (0.5 mol%) and [bmim][FeCl₄] (0.5 mL).

^b Isolated yields.

Table 5
Investigation of reusability of catalyst in conversion reaction of benzylmethoxymethyl ether into its corresponding nitrile.

		
Cycle	Time (min)	Yield (%) ^a
1	2	95
2	2	89
3	2	83

^a Isolated yields.

4. Conclusion

In conclusion, we demonstrated a convenient, efficient and chemoselective catalytic method for the direct transformation of MOM- and EOM-ethers into the other important functional groups such as nitriles, bromides and iodides under MW irradiation. The use of HPW@[bmim][FeCl₄] as a novel, green and reusable catalyst makes this procedure environmentally friendly and economically acceptable. Furthermore, easy workup, short reaction times and high yields of products are other noteworthy advantages of this catalytic system.

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