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کارگاه آنلاین آشنایی با پایگاه های اطلاعات علمی بین المللی و ترکیه های جستجو

$\text{H}_3\text{PW}_{12}\text{O}_{40}@[\text{bmim}][\text{FeCl}_4]$: A Green Catalytic System for Alkoxy methylation of Alcohols and Their One-Pot Interconversion to Acetates and TMS-Ethers

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12-Tungstophosphoric acid immobilized on $[\text{bmim}][\text{FeCl}_4]$ was found to be an efficient catalyst for chemoselective methoxymethylation and ethoxymethylation of alcohols and also one-pot conversion of MOM- or EOM-ethers to their corresponding acetates and TMS-ethers under thermal conditions and microwave irradiation. These procedures were simple, rapid and the corresponding products were obtained in high yields. The catalyst exhibited remarkable reactivity and was reusable.

Keywords: Alkoxy methyl ether, Protection, Interconversion, 12-Tungstophosphoric acid, 1-Butyl-methylimidazolium tetrachloroferrate

INTRODUCTION

The alkoxy methylation of hydroxyl groups is highly important in organic synthesis, and such reactions are crucial in the preparation of many pharmaceutical agents and fine agrochemicals [1,2]. Methoxymethyl (MOM) or ethoxymethyl (EOM) ethers are important chemicals due to their accessibility and high stability under both basic and moderate acidic conditions [1,2]. On the other hand, one of the strategies to combine the economic and environmental factors is the one-pot interconversion of different functional groups which plays a critical role in the successful synthesis of multi-functional complex molecules. This process consists of two or more transformations, which occur without isolation of any intermediates and thus saves energy and raw materials as well as time [1,3,4]. So, due to the importance of these transformations, a lot of effort has been and is still being made to find and develop new types of such reactions. Besides the

alkoxy methyl ethers, esters or trialkylsilyl ethers are the most versatile protecting forms of the hydroxyl groups which are widely utilized in organic synthesis [1,2]. Therefore, interconversion of the less stable protecting forms to the more stable ones is important in organic synthesis.

In the last decades, the use of heteropoly acids (HPAs) as catalysts has attracted much attention in different industries for the synthesis of fine chemicals [5]. Among the heteropoly acids, 12-tungstophosphoric acid, $\text{H}_3\text{PW}_{12}\text{O}_{40}$, and its salts are the most widely used catalysts due to their high acid strength, thermal stability, low reducibility, easy work-up procedures and minimization of waste generation. Besides, they are non-corrosive, environmentally benign and can be reused and recycled [6]. However, a major disadvantage of bulk HPAs as catalysts is their low specific surface area, $10 \text{ m}^2 \text{ g}^{-1}$, which can be improved by immobilization on supports [7]. The use of heterogeneous catalysts in liquid phase offers several advantages over homogenous ones, including ease of recovery and recycling, atom utility and enhanced stability [8].

A recent trend in the development of environmentally benign processes is to use room temperature ionic liquids

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(RTILs) as reaction media. These organic salts have gained an increasing number of applications in catalysis [9-13] such as heavy metal separation [14,15], cellulose dissolution [16-18], energetic materials [19,20] and active pharmaceutical ingredients (APIs) [21]. One commonly used method is the immobilization of Brønsted or Lewis acids on ionic liquids. Several catalysts have been immobilized on ionic liquids and successfully recycled as a result of the non-volatile nature of these media. This ionic catalytic system affords much higher reaction rates and selectivities than those employed in classical organic solvents [11,12].

Moreover, the use of the microwave irradiation can further improve the efficiency of reactions. Since the dielectric property and ionic nature of ionic liquids lead to an efficient absorption of microwave energy they are highly suitable for the microwave-promoted organic reactions [22]. Microwave is a powerful and innovative tool for improving organic synthesis and it is an efficient and economical technology which facilitates better selectivity, higher reaction rates, formation of cleaner products with higher yields and minor wastes [23].

In recent years, we have used 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$) as an active, stable and reusable Brønsted acid catalyst for some organic transformations [24-27]. We have also examined some important transformations in the presence of Lewis acid immobilized on ionic liquids [28]. Given these experiences, we attempted to design a catalytic system on the basis of immobilization of $H_3PW_{12}O_{40}$ on ionic liquid. This provides a green catalytic system with high surface area and high accessibility of the catalyst. Herein, we report a green, simple and highly efficient procedure for the preparation of methoxymethyl (MOM) and ethoxymethyl (EOM) ethers by the reactions of appropriate alcohols with formaldehyde diethyl acetal (FDEA) and formaldehyde dimethyl acetal

(FDMA) as well as their direct interconversion to their corresponding acetates and trimethylsilyl (TMS) ethers in the presence of catalytic amount of $H_3PW_{12}O_{40}$ immobilized on 1-butyl-3-methylimidazolium tetrachloroferrate, [bmim][FeCl₄], as a room temperature ionic liquid (Scheme 1).

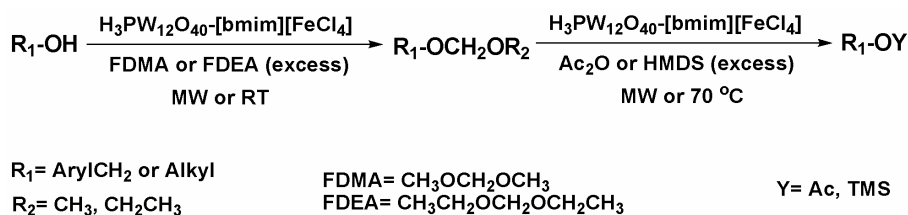
EXPERIMENTAL

All materials were purchased from Merck and Sigma-Aldrich chemical companies and were used without further purification. Spectroscopic data of MOM- and EOM-ethers [27], acetates [29,30] and TMS-ethers [31,32] have been reported in literature. 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-AC 500 MHz spectrometer. IR spectra were obtained by Shimadzu IR-435 spectrophotometer using KBr or sodium chloride pellets.

The microwave system used for these experiments included 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, and ATCFO fiber optic system for automatic temperature. During the experiments, power, temperature, time and pressure were monitored and controlled via the “easyCONTROL” software. Temperature was monitored with the aid of ATC-FO sensor TS3517 inserted directly into the corresponding reactions container.

Preparation of [bmim][FeCl₄]

In a round bottomed flask equipped with a magnetic stirrer, anhydrous FeCl₃ (16.22 g, 0.1 mol) was added slowly to 1-



Scheme 1

butyl-3-methylimidazolium chloride (17.47 g, 0.1 mol). To ensure complete reaction, the reaction mixture was left stirring over night. A red-brown liquid was obtained which was dried under high vacuum and stored under N₂.

Immobilization of H₃PW₁₂O₄₀ on [bmim][FeCl₄]

H₃PW₁₂O₄₀ (1 mol%) was added slowly to 1 ml of highly pure [bmim][FeCl₄] in a round bottomed flask and stirred roughly. To ensure complete homogenisation, the mixture was left stirring over night. The catalyst was dried under reduced pressure and stored under N₂.

General Procedure for the Preparation of MOM- and EOM-Ethers at Room Temperature and under Microwave Irradiation

To a solution of alcohol (1 mmol) in FDEA or FDMA (5 mmol) was added H₃PW₁₂O₄₀@[bmim][FeCl₄] (1 ml) and stirred at room temperature or exposed to microwave irradiation (80 W, 75-82 °C) for the appropriate time (Table 4). After completion of the reaction (monitored by TLC, eluent:*n*-hexane/ethyl acetate, 4:1), the excess FDMA or FDEA was removed under reduced pressure. The mixture was extracted with Et₂O (2 × 10 ml). The organic phase was dried over anhydrous Na₂SO₄ and rotary evaporation afforded a residue, which was then passed through a short pad of silica gel to obtain the highly pure MOM- and EOM-ethers.

General Procedure for the Interconversion of MOM- and EOM-Ethers to Acetates and TMS-Ethers under Thermal Conditions or MW Irradiation

A mixture of EOM- or MOM-ether (1 mmol), acetic anhydride or hexamethyldisilazane (5 mmol) in H₃PW₁₂O₄₀@[bmim][FeCl₄] (1 ml) was stirred under thermal conditions (70 °C) or microwave irradiation (150 W, 120-130 °C) for the appropriate time (Tables 9 and 10). After completion of the reaction, as indicated by TLC, the reaction mixture was quenched with water and extracted with Et₂O (3 × 10 ml). The organic layer was dried over anhydrous Na₂SO₄. Evaporation of the solution and purification with column chromatography over a short pad of neutral alumina (eluent:*n*-hexane/ethyl acetate, 5:1) gave the highly pure acetates or TMS-ethers.

Spectroscopic Data for Selected Products

Benzyl acetate (Table 9, entry 1). IR (KBr): ν (cm⁻¹) 3034, 2955, 1741, 1498, 1456, 1381, 1364, 1229, 1082, 1026, 966, 839, 750, 698; ¹H NMR (500 MHz, CDCl₃): δ (ppm) 2.11 (s, 3H, COCH₃), 5.13 (s, 2H, OCH₂), 7.34-7.38 (m, 5H, Ar).

2-Acethoxybenzyl acetate (Table 9, entry 4). IR (KBr): ν (cm⁻¹) 2941, 2291, 2252, 1757, 1445, 1375, 1244, 1041, 918, 750, 698; ¹H NMR (500 MHz, CDCl₃): δ (ppm) 2.05 (s, 3H, CH₂OCOCH₃), 2.31 (s, 3H, OCOCH₃), 5.08 (s, 2H, CH₂OCOCH₃), 7.08-7.44 (m, 4H, Ar).

4-Acethoxy-3-methoxybenzyl acetate (Table 9, entry 5). IR (KBr): ν (cm⁻¹) 2999, 2943, 2850, 2291, 2252, 1738, 1723, 1446, 1377, 1246, 1041, 918, 844, 750, 698; ¹H NMR (500 MHz, CDCl₃): δ (ppm) 2.12 (s, 3H, CH₂OCOCH₃), 2.35 (s, 3H, OCOCH₃), 3.78 (s, 3H, OCH₃), 5.12 (s, 2H, CH₂OCOCH₃), 6.99-7.07 (m, 3H, Ar).

4-Chlorobenzyl acetate (Table 9, entry 10). IR (KBr): ν (cm⁻¹) 3000, 2944, 1800, 1380, 1260, 1120, 1070, 930; ¹H NMR (500 MHz, CDCl₃): δ (ppm) 2.00 (s, 3H, COCH₃), 5.00 (s, 2H, CH₂O), 7.20-7.37 (m, 4H, Ar).

2,4-Dichlorobenzyl acetate (Table 9, entry 11). IR (KBr): ν (cm⁻¹) 3001, 2943, 2848, 2291, 2252, 1743, 1591, 1562, 1446, 1375, 1226, 1105, 1057, 1105, 1056, 918, 842, 816, 744; ¹H NMR (500 MHz, CDCl₃): δ (ppm) 2.16 (s, 3H, COCH₃), 5.19 (s, 2H, CH₂O), 7.27-7.47 (m, 3H, Ar).

4-Nitrobenzyl acetate (Table 9, entry 14). IR (KBr): ν (cm⁻¹) 2941, 2849, 2291, 2252, 1743, 1533, 1442, 1354, 1228, 1097, 1039, 918, 812, 734, 690, 605; ¹H NMR (500 MHz, CDCl₃): δ (ppm) 2.16 (s, 3H, COCH₃), 5.20 (s, 2H, CH₂O), 7.40-8.40 (m, 4H, Ar).

Benzylxytrimethylsilane (Table 10, entry 1). IR (KBr): ν (cm⁻¹) 3063, 3030, 2966, 1711, 1495, 1452, 1227, 1202, 1068, 1028, 916, 812, 758, 694, 605, 547; ¹H NMR (500 MHz, CDCl₃): δ (ppm) 0.16 (s, 9H, OSi(CH₃)₃), 4.70 (s, 2H, CH₂OSi(CH₃)₃), 7.24-7.33 (m, 5H, Ar).

(2-Methoxy-4-((trimethylsilyloxy)methyl)phenoxy)trimethylsilane (Table 10, entry 5). IR (KBr): ν (cm⁻¹) 3431, 2956, 2900, 1701, 1637, 1604, 1514, 1463, 1419, 1375, 1280, 1157, 1122, 1037, 904, 850, 754, 688, 634, 557; ¹H NMR (500 MHz, CDCl₃): δ (ppm) 0.16 (s, 9H, CH₂OSi(CH₃)₃), 0.24 (s, 9H, OSi(CH₃)₃), 3.83 (s, 3H, OCH₃), 4.63 (s, 2H, CH₂Si(CH₃)₃), 6.77-6.88 (m, 3H, Ar); ¹³C NMR (125 MHz,

CDCl_3): δ (ppm) 55.4, 64.7, 77.4, 110.0, 111.1, 119.4, 120.2, 135.0, 143.8, 150.9.

(4-Chlorobenzoyloxy)trimethylsilane (Table 10, entry 10). IR (KBr): ν (cm^{-1}) 2924, 2852, 1463, 1040; ^1H NMR (500 MHz, CDCl_3): δ (ppm) 0.16 (s, 9H, $\text{CH}_2\text{OSi}(\text{CH}_3)_3$), 4.69 (s, 2H, $\text{CH}_2\text{OSi}(\text{CH}_3)_3$), 7.30-7.37 (m, 4H, Ar).

(2,4-Dichlorobenzoyloxy)trimethylsilane (Table 10, entry 11). IR (KBr): ν (cm^{-1}) 2957, 2899, 1602, 1519, 1456, 1415, 1346, 1251, 1203, 1097, 1014, 842, 750, 688, 644; ^1H NMR (500 MHz, CDCl_3): δ (ppm) 0.11 (s, 9H, $\text{CH}_2\text{OSi}(\text{CH}_3)_3$), 5.02 (s, 2H, $\text{CH}_2\text{OSi}(\text{CH}_3)_3$), 7.08-7.11 (m, 3H, Ar).

(4-Nitrobenzoyloxy)trimethylsilane (Table 10, entry 14). IR (KBr): ν (cm^{-1}) 3001, 2941, 2850, 2291, 1492, 1442, 1087, 1039, 918, 842, 742.634, 607; ^1H NMR (500 MHz, CDCl_3): δ (ppm) 0.15 (s, 9H, $\text{OSi}(\text{CH}_3)_3$), 4.63 (s, 2H, $\text{CH}_2\text{OSi}(\text{CH}_3)_3$), 5.08 (s, 2H, PhCH_2O), 6.94-6.98 (m, 2H, Ar), 7.24-7.43 (m, 7H, Ar).

RESULTS AND DISCUSSION

Protection Reactions

First, the effectiveness of $\text{H}_3\text{PW}_{12}\text{O}_{40}@[\text{bmim}][\text{FeCl}_4]$ was investigated in the synthesis of MOM- and EOM-ethers. To this end, the reaction of benzyl alcohol with formaldehyde dimethyl acetal (FDMA) was monitored in the presence of different molar ratios of FDMA and the catalyst at room temperature. The best results for the methoxymethylation of benzyl alcohol were obtained with molar ratios of 1:5:0.005 for alcohol, FDMA and catalyst, respectively (Tables 1 and 2).

To show the effect of immobilization of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ on $[\text{bmim}][\text{FeCl}_4]$ on the catalytic activity of $\text{H}_3\text{PW}_{12}\text{O}_{40}$, the protection reaction of benzyl alcohol (1 mmol) with FDMA (5 mmol) took place in the presence of equal amounts of $\text{H}_3\text{PW}_{12}\text{O}_{40}@[\text{bmim}][\text{FeCl}_4]$, bulk $\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{H}_3\text{PW}_{12}\text{O}_{40}@[\text{SiO}_2]$ and $\text{H}_3\text{PW}_{12}\text{O}_{40}@[\text{ZrO}_2]$. The results showed that the catalytic activity of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was increased by immobilizing on $[\text{bmim}][\text{FeCl}_4]$ in comparison with bulk $\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{H}_3\text{PW}_{12}\text{O}_{40}@[\text{SiO}_2]$ and $\text{H}_3\text{PW}_{12}\text{O}_{40}@[\text{ZrO}_2]$. In the absence of $\text{H}_3\text{PW}_{12}\text{O}_{40}$, the ionic liquid was less efficient to catalyze the methoxymethylation reaction of benzyl alcohol with FDMA. The results are summarized in Table 2.

To investigate the effect of microwave irradiation in this transformation, the methoxymethylation of benzyl alcohol

under microwave irradiation was also performed. The results showed that the power of microwave irradiation played an important role in this protocol. The protection of benzyl alcohol with FDMA under microwave irradiation showed that the highest yield was obtained at the power of 80 W (Table 3).

The optimized reaction conditions were used for the successful protection of primary and secondary alcohols with FDMA and FDEA in the presence of $\text{H}_3\text{PW}_{12}\text{O}_{40}@[\text{bmim}][\text{FeCl}_4]$ at room temperature and under microwave irradiation and the corresponding MOM- and EOM-ethers were obtained in high yields (Table 4), whereas, under the same conditions, phenols and tertiary alcohols remained intact in the reaction mixture.

The obtained results showed that the reaction times decreased significantly under microwave irradiation compared to the reaction time at room temperature. This was due to the ionic nature of the ionic liquid which increased the microwave energy absorption which, in turn, increased the reaction rate. This is significant from the economical and environmental points of view.

In order to demonstrate the chemoselectivity of the method in question, a set of competitive reactions was started between primary, secondary, and tertiary alcohols and phenols (Table 5). The results indicated that the present protocol is potentially applicable to the chemoselective conversion of primary and secondary alcohols in the presence of tertiary alcohols and phenols. In addition, regarding the compounds containing both benzylic and phenolic hydroxyl groups, only benzylic hydroxyl groups were converted to the corresponding ethers with excellent chemoselectivity (Table 4, entries 4 and 5).

Interconversion of Alkoxyethyl Ethers to Their Corresponding Acetates and TMS-Ethers

The effectiveness of $\text{H}_3\text{PW}_{12}\text{O}_{40}@[\text{bmim}][\text{FeCl}_4]$, as a catalyst and medium, was investigated for the conversion of MOM- and EOM-ethers to other hydroxyl-protecting groups such as acetates and trimethylsilyl (TMS) ethers. These reactions took place by means of acetic anhydride (Ac_2O) and hexamethyldisilazane (HMDS) as protecting agents. Accordingly, different parameters such as temperature, molar ratio of reactants and amounts of the catalyst were optimized under thermal conditions and microwave irradiation.

In order to optimize the amounts of Ac_2O and HMDS, the

Table 1. Protection of Benzyl Alcohol with Different Amounts of FDMA and FDEA by H₃PW₁₂O₄₀@[bmim][FeCl₄] at Room Temperature

Entry	FDMA		FDEA	
	Amount (mmol)	Yield (%) ^a	Amount (mmol)	Yield (%) ^a
1	1	46	1	40
2	4	81	4	76
3	5	92	5	92
4	6	92	6	92

^aIsolated yield.

Table 2. Comparison of the Catalytic Activity for Methoxymethylation of Benzyl Alcohol Using Bulk and Supported H₃PW₁₂O₄₀ under MW Irradiation and at Room Temperature

Entry	Catalyst (mol%)	H ₃ PW ₁₂ O ₄₀ @[bmim][FeCl ₄]		H ₃ PW ₁₂ O ₄₀		H ₃ PW ₁₂ O ₄₀ @SiO ₂		H ₃ PW ₁₂ O ₄₀ @ZrO ₂		[bmim][FeCl ₄] ^a	
		Yield (%) ^b		Yield (%) ^b		Yield (%) ^b		Yield (%) ^b		Yield (%) ^b	
		MW	RT	MW	RT	MW	RT	MW	RT	MW	RT
1	0.1	67	63	47	40	42	38	46	36	18	4
2	0.2	78	76	55	51	54	50	55	43		
3	0.3	87	84	63	60	63	59	61	54		
4	0.4	94	91	91	91	94	91	88	84		
5	0.5	96	92	91	91	94	91	88	84		
6	0.6	96	92	91	91	94	91	88	84		

^aReaction was performed in the presence of 1 ml of [bmim][FeCl₄]. ^bIsolated yield.

Table 3. Optimization of Microwave Power for Protection of Benzyl Alcohol with FDMA in the Presence of H₃PW₁₂O₄₀@[bmim][FeCl₄]

Row	Microwave power (W)	Yield (%) ^b	Temperature (°C)	Time (s)
1	50	81	51	60
2	75	92	68	60
3	80	96	75	30
4	100	96	90	30

^aReaction conditions: benzyl alcohol (1 mmol), FDMA (5 mmol), H₃PW₁₂O₄₀ (0.005 mmol) and IL (1 ml). ^bIsolated yield.

Table 4. Protection of Alcohols by $H_3PW_{12}O_{40}@[bmim][FeCl_4]$ under Microwave Irradiation and at Room Temperature^a

Entry	R ¹	MOM-ether				EOM-ether			
		MW		RT		MW		RT	
		Time (s)	Yield (%) ^b	Time (s)	Yield (%) ^b	Time (s)	Yield (%) ^b	Time (s)	Yield (%) ^b
1	C ₆ H ₅ CH ₂	40	96	480	92	40	94	480	92
2	4-(CH ₃) ₃ C ₆ H ₄ CH ₂	40	97	480	93	40	95	480	91
3	4-CH ₂ OHC ₆ H ₄ CH ₂	35	96	450	96	35	95	450	95
4	2-HOC ₆ H ₄ CH ₂	30	96	450	93	30	95	450	93
5	3-CH ₃ O-4-(OH)C ₆ H ₃ CH ₂	30	95	420	91	30	93	420	91
6	3-CH ₃ OC ₆ H ₄ CH ₂	30	94	400	92	30	93	420	90
7	4-CH ₃ OC ₆ H ₄ CH ₂	30	96	400	92	30	96	420	91
8	4-PhCH ₂ OC ₆ H ₄ CH ₂	35	93	450	92	35	94	450	93
9	2-ClC ₆ H ₄ CH ₂	20	97	400	91	20	95	400	91
10	4-ClC ₆ H ₄ CH ₂	20	98	360	93	20	97	360	92
11	2,4-Cl ₂ C ₆ H ₃ CH ₂	15	98	360	93	20	98	360	93
12	2-BrC ₆ H ₄ CH ₂	20	96	400	92	20	93	400	91
13	4-BrC ₆ H ₄ CH ₂	20	97	360	92	20	97	360	93
14	3-NO ₂ C ₆ H ₄ CH ₂	50	88	510	87	50	87	510	88
15	4-NO ₂ C ₆ H ₄ CH ₂	50	86	510	84	55	86	510	83
16	C ₆ H ₅ CH=CHCH ₂	20	98	360	95	20	98	360	93
17	C ₆ H ₅ CH ₂ CH ₂	30	96	420	92	30	95	420	91
18	CH ₃ (CH ₂) ₅ CH ₂	25	97	400	94	25	96	400	92
19	CH ₃ (CH ₂) ₆ CH ₂	25	97	400	93	25	97	400	91
20	C ₆ H ₅ CHCH ₃	50	92	480	90	50	92	480	91
21	(C ₆ H ₅) ₂ CH	60	90	540	88	60	91	540	87
22	Cycloheptyl	60	88	540	85	60	87	540	86
23	(+)-Menthyl	60	89	540	86	60	87	540	86
24	2-Adamantyl	75	85	600	81	75	85	600	84

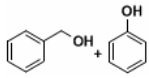
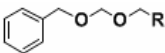
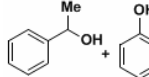
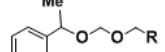
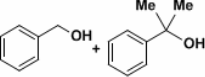
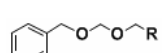
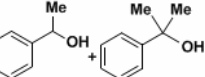
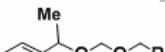
^aReaction conditions: alcohol (1 mmol), FDMA or FDEA (5 mmol), $H_3PW_{12}O_{40}$ (0.5 mol%) and IL (1 ml). ^bIsolated yield.

direct transformation of benzylmethoxymethyl ether (1 mmol) to its corresponding acetate and TMS-ether with acetic anhydride and hexamethyldisilazane in the presence of $H_3PW_{12}O_{40}@[bmim][FeCl_4]$ was chosen as the model reaction. The best results were obtained with 5 mmol Ac₂O or HMDS in 1.0 ml of $H_3PW_{12}O_{40}@[bmim][FeCl_4]$ under thermal conditions and microwave irradiation (Table 6). The reaction temperature and MW power were also optimized in the same reaction. The results, which are shown in Tables 7 and 8, indicate that the highest yields were obtained at 70 °C

for thermal conditions and at 150 W (120-122 °C) for MW irradiation.

Under the optimized conditions, a wide range of MOM- and EOM-ethers was subjected to trimethylsilylation and acetylation in the presence of $H_3PW_{12}O_{40}@[bmim][FeCl_4]$ under thermal conditions and MW irradiation. The results are shown in Tables 9 and 10. It was observed that a wide range of benzylic MOM- and EOM-ethers bearing electron withdrawing as well as electron donating groups such as chloro, bromo, nitro, methoxy, hydroxy, *t*-butyl and

Table 5. Competitive Protection Reactions of Alcohols and Phenol with FDMA and FDEA by H₃PW₁₂O₄₀@[bmim][FeCl₄] under MW Irradiation^a

Entry	Substrates	Product ^b	R	Yield (%) ^c	Time (s)
1			H	96	40
			Me	94	
2			H	92	50
			Me	92	
3			H	96	40
			Me	94	
4			H	92	50
			Me	92	

^aReaction conditions: alcohol or phenol (1 mmol), FDMA or FEDA (5 mmol), H₃PW₁₂O₄₀ (0.5 mol%), IL (1 ml) and 80 W power of MW. ^bPhenol and tertiary alcohol remained intact in reaction mixtures. ^cIsolated yield.

Table 6. Optimization of Ac₂O and HMDS Amounts in Interconversion of Benzylmethoxymethyl Ether to the Corresponding Acetate and TMS-ether under Thermal Conditions

Entry	Ac ₂ O		HMDS	
	Amount (mmol)	Yield (%) ^a	Amount (mmol)	Yield (%) ^a
1	1	41	1	42
2	4	77	4	78
3	5	90	5	91
4	6	90	6	91

^aIsolated yield.

Table 7. Optimization of Microwave Power for Interconversion of Benzylmethoxymethyl Ether to the Corresponding Acetate and TMS-ether^a

Row	Power (W)	Acetylation		Trimethylsilylation	
		Yield (%) ^b	Temperature (°C)	Yield (%) ^b	Temperature (°C)
1	130	56	76	55	66
2	145	87	108	86	103
3	150	93	122	93	120
4	160	93	172	93	169

Table 8. Optimization of Temperature in the Interconversion of Benzylmethoxymethyl Ether to the Corresponding Acetate and TMS-Ether^a

Row	Temperature (°C)	Acetylation		Trimethylsilylation	
		Yield (%) ^b	Time (min)	Yield (%) ^b	Time (min)
1	RT	22	60	23	60
2	50	54	60	51	60
3	70	91	20	90	30
4	80	91	20	90	30
5	100	91	20	90	30

^aReaction conditions: MOM-ether (1 mmol), Ac₂O or HMDS (5 mmol), H₃PW₁₂O₄₀ (1 mol%) and IL (1 ml). ^bIsolated yield.

Table 9. Interconversion of MOM- and EOM-ethers to the Corresponding Acetates Using H₃PW₁₂O₄₀@[bmim][FeCl₄] under Microwave Irradiation and Thermal Conditions^a

Entry	R ¹	MOM-ether				EOM-ether			
		MW		Heat		MW		Heat	
		Time (min)	Yield (%) ^b	Time (min)	Yield (%) ^b	Time (min)	Yield (%) ^b	Time (min)	Yield (%) ^b
1	C ₆ H ₅ CH ₂	1.5	93	20	90	1.5	92	25	90
2	4-(CH ₃) ₃ C ₆ H ₄ CH ₂	1	97	15	95	1	94	15	94
3	4-CH ₂ OHC ₆ H ₄ CH ₂	1.5	96	20	90	1.5	91	20	88
4	2-HOC ₆ H ₄ CH ₂	2	92	30	90	2	91	30	89
5	3-CH ₃ O-4-(OH)C ₆ H ₃ CH ₂	2	92	30	90	2	91	30	90
6	3-CH ₃ OC ₆ H ₄ CH ₂	1.5	93	20	92	1.5	93	20	91
7	4-CH ₃ OC ₆ H ₄ CH ₂	1.5	97	20	94	1.5	96	20	94
8	4-PhCH ₂ OC ₆ H ₄ CH ₂	2.5	92	35	88	2.5	91	35	90
9	2-ClC ₆ H ₄ CH ₂	1	94	15	91	1	93	15	92
10	4-ClC ₆ H ₄ CH ₂	1	97	15	96	1	97	15	96
11	2,4-Cl ₂ C ₆ H ₃ CH ₂	1	97	15	93	1	95	15	95
12	2-BrC ₆ H ₄ CH ₂	1	96	15	94	1	94	15	90
13	4-BrC ₆ H ₄ CH ₂	1	96	15	92	1	93	15	91
14	3-NO ₂ C ₆ H ₄ CH ₂	4	89	60	88	4	87	60	84
15	4-NO ₂ C ₆ H ₄ CH ₂	4	90	60	85	4	88	60	79
16	C ₆ H ₅ CH=CHCH ₂	1	94	15	92	1	92	15	90
17	C ₆ H ₅ CH ₂ CH ₂	1.5	94	20	94	1.5	96	20	94
18	CH ₃ (CH ₂) ₅ CH ₂	2	91	20	88	2	91	20	90
19	CH ₃ (CH ₂) ₆ CH ₂	2	94	20	2	94	97	20	92
20	C ₆ H ₅ CHCH ₃	4	89	45	85	4	88	45	87
21	(C ₆ H ₅) ₂ CH	4	83	70	81	4	83	70	80
22	Cycloheptyl	5	87	80	82	5	86	80	80
23	(+)-Menthyl	4.5	86	75	82	4.5	83	75	80
24	2-Adamantyl	4.5	89	75	84	5	85	75	83

^aReaction conditions: MOM- or EOM-ether (1 mmol), Ac₂O (5 mmol), H₃PW₁₂O₄₀ (1 mol%) and IL (1ml).

^bIsolated yield.

Table 10. Interconversion of MOM- and EOM-Ethers to the Corresponding TMS-ethers Using H₃PW₁₂O₄₀@[bmim][FeCl₄] under Microwave Irradiation and Thermal Conditions^a

Entry	R ¹	MOM-ether				EOM-ether			
		MW		Heat		MW		Heat	
		Time (min)	Yield (%) ^b	Time (min)	Yield (%) ^b	Time (min)	Yield (%) ^b	Time (min)	Yield (%) ^b
1	C ₆ H ₅ CH ₂	2.5	93	30	91	2.5	92	30	91
2	4-(CH ₃) ₃ C ₆ H ₄ CH ₂	1.5	93	15	93	1.5	91	15	90
3	4-CH ₂ OHC ₆ H ₄ CH ₂	2.5	93	30	91	2.5	93	30	90
4	2-HOC ₆ H ₄ CH ₂	2.5	90	30	88	2.5	90	30	85
5	3-CH ₃ O-4-(OH)C ₆ H ₃ CH ₂	2	93	30	91	2.5	93	30	90
6	3-CH ₃ OC ₆ H ₄ CH ₂	2	93	25	90	2	93	25	90
7	4-CH ₃ OC ₆ H ₄ CH ₂	2	95	20	94	2	93	20	92
8	4-PhCH ₂ OC ₆ H ₄ CH ₂	3	92	40	87	3.5	91	40	89
9	2-ClC ₆ H ₄ CH ₂	2	93	20	91	2	90	20	90
10	4-ClC ₆ H ₄ CH ₂	1.5	95	15	94	1.5	96	15	93
11	2,4-Cl ₂ C ₆ H ₃ CH ₂	1.5	95	15	92	1.5	94	15	92
12	2-BrC ₆ H ₄ CH ₂	1.5	93	20	90	1.5	91	20	90
13	4-BrC ₆ H ₄ CH ₂	1.5	93	15	92	1.5	96	15	90
14	3-NO ₂ C ₆ H ₄ CH ₂	4.5	85	70	82	4.5	83	70	81
15	4-NO ₂ C ₆ H ₄ CH ₂	4.5	87	75	85	4.5	85	75	81
16	C ₆ H ₅ CH=CHCH ₂	1.5	94	20	90	1.5	93	20	90
17	C ₆ H ₅ CH ₂ CH ₂	2	92	20	91	2	93	20	90
18	CH ₃ (CH ₂) ₅ CH ₂	2	93	20	89	2	91	20	89
19	CH ₃ (CH ₂) ₆ CH ₂	2	91	20	90	2	93	20	92
20	C ₆ H ₅ CHCH ₃	4	89	45	86	4	89	45	87
21	(C ₆ H ₅) ₂ CH	5.5	90	85	86	5.5	90	85	84
22	Cycloheptyl	5.5	86	85	84	5.5	85	85	80
23	(+)-Menthyl	4.5	88	70	86	4.5	86	70	84
24	2-Adamantyl	5	85	75	84	5	86	75	83

^aReaction conditions: MOM- or EOM-ether (1 mmol), HMDS (5 mmol), H₃PW₁₂O₄₀ (1 mol%) and IL (1 ml).^bIsolated yield.

benzyloxy and also primary and secondary alkoxyethyl ethers easily underwent one-pot interconversion with acetic anhydride and HMDS to give the corresponding acetates and TMS-ethers, respectively, with excellent isolated yields. However, the electron withdrawing groups or steric hindrance had an insignificant effect on the yields and reaction times.

It is noteworthy that in the conversion of alkoxyethyl ethers bearing aromatic rings to their corresponding acetates

no Friedel-Crafts reaction was observed (Table 9, entries 1-17).

The experimental procedure for these transformations is remarkably simple and requires no toxic organic solvents or inert atmospheres. However, the synthesis could not be conducted in the absence of the ionic liquid. The use of [bmim][FeCl₄] helps to bring about a green and economic process.

In microwave-assisted conditions, cleavage of the alkoxymethyl ethers and direct transformation to acetates and TMS ethers occurred similarly with excellent yields and short reaction times. In such cases, the reactions occurred in sealed vessels and 150 W applied power. Obviously, the reaction times were shorter than for those under thermal conditions.

In order to show the effect of [bmim][FeCl₄] on the catalytic activity of H₃PW₁₂O₄₀ in the interconversion of alkoxymethyl ethers to their corresponding acetates and TMS-ethers, the catalytic activity of H₃PW₁₂O₄₀@[bmim][FeCl₄] was compared with bulk H₃PW₁₂O₄₀, H₃PW₁₂O₄₀@SiO₂ and H₃PW₁₂O₄₀@ZrO₂. The results showed that supporting H₃PW₁₂O₄₀ on the [bmim][FeCl₄] increased the catalytic activity of H₃PW₁₂O₄₀ in comparison with the others, while [bmim][FeCl₄] was much less efficient to catalyze the reaction

(Table 11).

Catalyst Reuse and Recovery

Recyclability of the H₃PW₁₂O₄₀@[bmim][FeCl₄] was investigated in the methoxymethylation of benzyl alcohol with FDMA. At the end of the reaction, excess FDMA was evaporated, and Et₂O was added and the product, which was soluble in diethyl ether, was separated. Then, fresh alcohol and FDMA were added to H₃PW₁₂O₄₀@[bmim][FeCl₄]. The recycling study showed that the catalyst could be recycled several times at room temperature only with a slight decrease in its activity, while under MW irradiation, it was possible to reuse the H₃PW₁₂O₄₀@[bmim][FeCl₄] only three times (Table 12).

Table 11. Comparison of Catalyst Activity of Bulk and Supported H₃PW₁₂O₄₀ for the Interconversion of Benzylmethoxymethyl Ether to the Corresponding Acetate and TMS-Ether under MW Irradiation and Thermal Conditions

Entry	Catalyst (mol%)	H ₃ PW ₁₂ O ₄₀ @[bmim][FeCl ₄]		H ₃ PW ₁₂ O ₄₀		H ₃ PW ₁₂ O ₄₀ @SiO ₂		H ₃ PW ₁₂ O ₄₀ @ZrO ₂		[bmim][FeCl ₄] ^a	
		Yield (%) ^b		Yield (%) ^b		Yield (%) ^b		Yield (%) ^b		Yield (%) ^b	
		MW	Heat	MW	Heat	MW	Heat	MW	Heat	MW	Heat
1	0.6	15	13	45	41	60	54	61	54	21	12
2	0.8	40	42	55	54	82	79	78	70		
3	0.9	83	59	76	71	82	79	78	70		
4	1	95	92	80	77	82	79	78	70		
5	1.5	95	92	80	77	83	91	78	70		

^aReaction was performed in the presence of 1 ml of [bmim][FeCl₄]. ^bIsolated yield.

Table 12. Results Obtained Using Recycled H₃PW₁₂O₄₀@[bmim][FeCl₄] in the Protection of Benzyl Alcohol with FDMA

Run	MW		RT	
	Yield (%) ^a	Time (s)	Yield (%) ^a	Time (s)
1	96	40	92	480
2	87	40	89	480
3	82	40	87	480
4	-	-	84	480
5	-	-	80	480

^aIsolated yield.

CONCLUSIONS

In conclusion, a mild, eco-friendly, simple, and efficient method for the conversion of primary and secondary alcohols to their corresponding alkoxy-methyl ethers at room temperature is reported. This method was also found to be an efficient catalytic system for the direct and one-pot transformation of alkoxy-methyl ethers to their corresponding acetates and TMS-ethers under thermal conditions and microwave irradiation in the presence of H₃PW₁₂O₄₀@[bmim][FeCl₄] as a green catalyst and medium. The ionic nature of the catalyst causes a rapid acceleration in the reaction rate under microwave irradiation. Operational simplicity, short reaction times, application of an environmentally benign and non-toxic catalyst, excellent yields, good recyclability and high degree of chemoselectivity are among the main advantages of the present procedure for both protection and transformation reactions.

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REFERENCES

- [1] T.W. Greene, P.G.M. Wuts, *Green's Protective Groups in Organic Chemistry*, 4th ed., Wiley Interscience, New York, 2006.
- [2] P.J. Kocienski, *Protecting Groups*, George Thieme, Stuttgart, 1994.
- [3] N. Iranpoor, H. Firouzabadi, M. Gholinejad, *Can. J. Chem.* 84 (2006) 1006.
- [4] N. Iranpoor, H. Firouzabadi, R. Azadi, *Tetrahedron Lett.* 47 (2006) 5531.
- [5] T. Okuhara, N. Mizuno, M. Misono, *Adv. Catal.* 41 (1996) 113.
- [6] M.A. Schwegler, H. Van Bekkum, N. Munck, *Appl. Catal.* 74 (1991) 191.
- [7] I.V. Kozehevnikov, K.R. Kloetstra, A. Sinnema, H.W. Zandbergen, H. van Bekkum, *J. Mol. Catal. A: Chem.* 114 (1996) 287.
- [8] M. Dusi, T. Mallat, A. Baiker, *Catal. Rev. Sci. Eng.* 42 (2000) 213.
- [9] A.C. Cole, J.L. Jensen, I. Ntai, K.L.T. Tran, K.J. Weaver, D.C. Forbes, J.H. Davis Jr., *J. Am. Chem. Soc.* 124 (2002) 5962.
- [10] J.H. Davis Jr., *Chem. Lett.* 33 (2004) 1072.
- [11] V.I. Pârvulescu, C. Hardacre, *Chem. Rev.* 107 (2007) 2615.
- [12] Y. Gu, G. Li, *Adv. Synth. Catal.* 351 (2009) 817.
- [13] A. Mirjafari, I. Mohammadpoor-Baltork, M. Moghadam, S. Tangestaninejad, V. Mirkhani, A.R. Khosropour, *Tetrahedron Lett.* 51 (2010) 3274.
- [14] A.E. Visser, R.P. Swatloski, W.M. Reichert, P. Mayton, S. Sheff, A. Wierzbicki, J.H. Davis Jr., R.D. Rogers, *Chem. Commun.* (2001) 135.
- [15] M.L. Dietz, *Sep. Sci. Technol.* 41 (2006) 2047.
- [16] R.P. Swatloski, S.K. Spear, J.D. Holbrey, R.D. Rogers, *J. Am. Chem. Soc.* 124 (2002) 497.
- [17] N. Sun, R.P. Swatloski, M.L. Maxim, M. Rahman, A.G. Harland, A. Haque, S.K. Spear, D.T. Daly, R.D. Rogers, *J. Mater. Chem.* 18 (2008) 283.
- [18] M. Bagheri, H. Rodríguez, R.P. Swatloski, S.K. Spear, D.T. Daly, R.D. Rogers, *Biomacromolecules* 9 (2008) 381.
- [19] M. Semiglak, A. Melten, R.D. Rogers, *Acc. Chem. Res.* 40 (2007) 1182.
- [20] M.D. Soutullo, R.A. O'Brein, K.E. Gaines, J.H. Davis Jr., *Chem. Commun.* (2009) 2529.
- [21] W.L. Hough, M. Smiglak, M.H. Rodriguez, R.P. Swatloski, S.K. Spear, D.T. Daly, J. Pernak, J.E. Grisel, R.D. Carliss, M.D. Soutullo, J.H. Davis Jr., R.D. Rogers, *New J. Chem.* 31 (2007) 142.
- [22] N.E. Leadbeater, M.H. Torenus, H. Tye, *Comb. Chem. High Throughput Screening* 7 (2004) 511.
- [23] C.O. Kappe, *Chem. Soc. Rev.* 37 (2008) 1127.
- [24] R. Fazaeli, S. Tangestaninejad, H. Aliyan, *Appl. Catal. A: Gen.* 318 (2007) 218.
- [25] I. Mohammadpoor-Baltork, M. Moghadam, S. Tangestaninejad, V. Mirkhani, S.F. Hojati, *Polyhedron* 27 (2008) 750.
- [26] I. Mohammadpoor-Baltork, M. Moghadam, S. Tangestaninejad, V. Mirkhani, A. Mirjafari, *Polyhedron* 27 (2008) 2612.

- [27] I. Mohammadpoor-Baltork, M. Moghadam, S. Tangestaninejad, V. Mirkhani, A. Mirjafari, *Can. J. Chem.* 86 (2008) 831.
- [28] A.R. Khosropour, M.M. Khodaei, S. Ghaderi, Z. *Naturforsch. B* 61b (2006) 326.
- [29] F. Shirini, M.A. Zolfigol, A. Safari, *J. Chem. Res. (S)* (2006) 154.
- [30] C.S. Reddy, G. Smitha, S. Chandrasekhar, *Tetrahedron Lett.* 44 (2003) 4693.
- [31] B. Karimi, B. Golshani, *J. Org. Chem.* 65 (2000) 7228.
- [32] G. Maity, S.C. Roy, *Synth. Commun.* 23 (1993) 1667.

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