Efficient and Convenient Procedure for Protection of Hydroxyl Groups to the THP, THF and TMS Ethers and Oxidation of these Ethers to their Aldehydes or Ketones in [BPy]$FeCl_4$ as a Low Cost Room Temperature Ionic Liquid

Ahmad R. Khosropour, Mohammad M. Khodaei, and Sattar Ghaderi

Department of Chemistry, Faculty of Science, Razi University, Kermanshah 67149, Iran

Reprint requests to Dr. A. R. Khosropour. Fax: +98-831-427-4559. E-mail: arkhosropour@razi.ac.ir

Z. Naturforsch. **61b,** 326 – 330 (2006); received October 4, 2005

Alcohols were converted to the corresponding THP, THF or TMS ethers in high to excellent yields in 1-*n*-butylpyridinium chloroferrate media as a stable and low cost room temperature ionic liquid. In addition, oxidation of these ethers to their aldehydes or ketones without any overoxidation reactions in this ionic liquid was also performed.

Key words: Tetrahydropyranylation, Tetrahydrofuranylation, Trimethylsilylation, *n*-Butypyridinium Tetrachloroferrate

Introduction

Protection of functional groups and one-pot conversion to the next functional groups play the critical role in successful synthesis of multifunctional complex molecules. Among them, tetrahydropyranyl (THP), tetrahydrofuranyl (THF) and trimethylsilyl (TMS) ethers are the most versatile protecting forms of the hydroxyl groups, due to the reasonable stability to the nonacidic media widely utilized in organic synthesis [1 – 3]. On the other hand, oxidation of these ethers to their aldehydes or ketones is an important transformation in organic chemistry [4, 5]. A variety of reagents have been developed for the preparation of these compounds which include mainly Lewis acids, as well as other miscellaneous catalysts. In this context, Lewis acids such as $LiPF_4$ [6], $CuSO_4 \cdot 5H_2O/CH_3CN$ [7], $SO_3H\text{-}SiO_2/CH_2Cl_2$ [8], $PdCl_2(CH_3CN)_2$ [9], $In(OTf)_3/CH_2Cl_2$ [10], $H_6P_2W_{18}O_{62}\cdot 24H_2O$ (Wells-Dawson acid) [11], TPP·HBr/[bmim]PF_6 [12], and $K_5CoW_{12}O_{40} \cdot 3H_2O$ [13] for tetrahydropyranylation, peroxy-λ^3-iodane/ CCl_4 [14] for tetrahydrofuranylation, I_2 [15], α-$Zr(O_3PCH_3)_{12}(O_3PC_6H_4SO_3H)_{0.8}$ [16] and $LiClO_4$ [17] for trimethylsilylation of hydroxyl groups have been used. In contrast, only a limited number of reagents such as $Fe(NO_3)_3$-montmorillonite K-10 [18] and $(CH_2{=}CHCH_2PPh_3)_2S_2O_8$ [19] have been reported for the oxidation of these ethers to their carbonyl compounds. Although these methods are suitable for many synthetic conditions, but the practical application of these methods may suffer from one or more disadvantages such as the use of expensive or less easily available regents, vigorous reaction conditions, unsatisfactory yields, prolonged standing, and tedious manipulations in isolation of the pure products or the use of toxic volatile solvents. Therefore, due to the importance of these compounds a need still exists for versatile, simple, inexpensive and environmentally friendly processes whereby the protecting groups may be obtained under milder conditions.

Results and Discussion

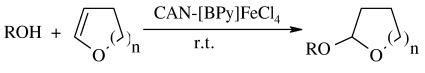
Room temperature ionic liquids (RTILs) could be suitable and environmentally safer replacements for the volatile, toxic and flammable organic solvents currently used in synthetic and catalytic reactions [20, 21]. These solvents possess a number of interesting properties, especially their lack of vapor pressure, a widely accessible temperature range with lack of flammability and ease of reuse. Most RTILs are composed of 1,3- dialkylimidazolium or 1-*n*-alkylpyridinium cations and anions such as $AlCl_4^-$, BF_4^-, $CF_3SO_3^-$, PF_6^-, and $(CF_3SO_2)_2N^-$ that cause some of the more important reactions including alkylation [22], Friedel-Crafts reactions [23], Diels-Alder reactions [24], Suzuki reactions [25], Michael addition [26], *etc.* But despite

0932–0776 / 06 / 0300–0326 $ 06.00

Table 1. Comparison of the effect of catalysts[a] in the dehydropyranylation of benzyl alcohol in the presence of $[BPy]FeCl_4$[b].

Entry	Catalyst	Time (h)	Yield (%)[c]
1	–	4	25
2	Montmorrilonite K-10[d]	2	40
3	$BiCl_3$	1	63
4	$Bi(NO_3)_3 \cdot 5H_2O$	1	80
5	$Ce(NO_3)_3 \cdot xH_2O$	0.5	82
6	$CeCl_3 \cdot 7H_2O$	1	67
7	CAN	0.3	96
8	$(NH_4)_6Mo_7O_{24}$	1	16
9	H_2SO_4/SiO_2[d]	1	60

[a] 10 mol-%; [b] 50 mol-%; [c] isolated yields; [d] 100% wt.



Scheme 1.

their wide range of synthetic application of TMS, THP and THF ethers, only little investigation has been performed for synthesis of these ethers in RTIL [12]. However, no progress has been made in using RTILs for one-pot interconversion of these ethers to their aldehydes or ketones. Thus the development of "green" and inexpensive synthetic methods towards these protecting forms constitutes an active area of investigation in organic chemistry. As part of our program aimed at developing new selective and environmentally friendly methodologies for the preparation of fine chemicals, especially research on ionic liquids [27–29], we found that 1-*n*-butyl pyridinium chloroferrate [30] ($[BPy]FeCl_4$) as a low cost RTIL, unlike to many other ionic liquids (*e. g.* $[BPy]AlCl_4$), is relatively stable, easy to handle and insensitive to air and moisture.

Herein, we wish to disclose a simple, efficient and convenient protocol for the protection of hydroxyl groups and subsequent interconversion of them to aldehydes or ketones in $[BPy]FeCl_4$ media. Initially, we have studied tetrahydropyranylation and tetrahydrofuranylation of alcohols and phenols in the presence of a catalytic amount of cerium(IV) ammonium nitrate (CAN) immobilized in $[BPy]FeCl_4$ as a RTIL (Scheme 1).

In order to investigate the influence of the catalysts in this reaction, dehydropyranylation of benzyl alcohol with DHP was carried out in the presence of different Lewis acids (Table 1). Among all the catalysts tested, CAN shows more effective catalytic reactivity in terms of yields and reaction times. As shown in Table 2, a wide series of aliphatic and aromatic alcohols reacted with DHP or DHF to afford the corresponding THP or THF ethers in the presence of 10 mol-% of CAN and 0.5 ml of the ionic liquid at ambient temperature in high to excellent yields. The presence of electron-donating and electron-withdrawing groups on the aromatic ring did not make any obvious difference in the reaction (Table 2, entries 1–9, 12–18, 26–34 and 37–40). Aliphatic as well as unsaturated (Table 2, entry 19) or secondary alcohols (Table 2, 20–25, 34 and 35) gave the corresponding THP or THF ethers in high yields under similar reaction conditions. Tertiary alcohols such as *t*-butyl alcohol, however, due to their

Table 2. Protection of alcohols and phenols to the THP and THF ethers in the presence of CAN-$[BPy]FeCl_4$.

Entry	Product (ROY)[a]	Y	Time (min)	Yield(%)[b]
1	$C_6H_5CH_2OY$	THP	18	96
2	2-$ClC_6H_4CH_2OY$	THP	25	93
3	4-$ClC_6H_4CH_2OY$	THP	19	94
4	2,4-$Cl_2C_6H_3CH_2OY$	THP	27	92
5	2-$BrC_6H_4CH_2OY$	THP	29	90
6	4-$BrC_6H_4CH_2OY$	THP	27	93
7	4-$FC_6H_4CH_2OY$	THP	28	94
8	2-$NO_2C_6H_4CH_2OY$	THP	40	86
9	4-$NO_2C_6H_4CH_2OY$	THP	32	87
10	furfuryl-OY	THP	30	90
11	thiophene-2-CH_2OY	THP	30	88
12	4-$PhC_6H_4CH_2OY$	THP	36	90
13	4-$CH_3C_6H_4CH_2OY$	THP	21	91
14	2,4-$(CH_3)_2C_6H_3CH_2OY$	THP	30	92
15	4-$(CH_3)_2CHC_6H_4CH_2OY$	THP	33	89
16	4-$(CH_3)_3CC_6H_4CH_2OY$	THP	35	93
17	4-$CH_3OC_6H_4CH_2OY$	THP	23	90
18	2,4-$(CH_3O)_2C_6H_3$ CH_2OY	THP	30	90
19	$C_6H_5CH{=}CHCH_2OY$	THP	33	85
20	$C_6H_5CH(CH_3)OY$	THP	38	90
21	4-$PhC_6H_4CH(CH_3)OY$	THP	36	89
22	$(C_6H_5)_2CHOY$	THP	40	92
23	$C_6H_5CH_2CH(CH_3)OY$	THP	30	91
24	α-tetralyl-OY	THP	40	88
25	(-)-menthyl-OY	THP	42	89
26	C_6H_5OY	THP	40	80
27	2-$CH_3C_6H_4OY$	THP	40	72
28	4-$C_2H_5C_6H_4OY$	THP	36	74
29	β-naphthyl-OY	THP	45	75
30	$C_6H_5CH_2OY$	THF	30	95
31	2-$BrC_6H_4CH_2OY$	THF	35	93
32	4-$(CH_3)_3CC_6H_4CH_2OY$	THF	33	91
33	4-$PhC_6H_4CH_2OY$	THF	40	92
34	$(C_6H_5)_2CHOY$	THF	45	90
35	$C_6H_5CH_2CH(CH_3)OY$	THF	30	91
36	thiophene-2-CH_2OY	THF	23	95
37	C_6H_5OY	THF	28	80
38	2-$CH_3C_6H_4OY$	THF	30	75
39	4-$C_2H_5C_6H_4OY$	THF	32	77
40	β-naphthyl-OY	THF	40	80

[a] The products were identified by comparison of their physical and spectral data with those of authentic samples or reported in literature; [b] isolated yields.

Table 3. Protection of alcohols and phenols to the TMS ethers in $[BPy]FeCl_4$.

Entry	Product	Time (min)	Yield (%)
1	$C_6H_5CH_2OTMS$	8	94
2	2-$ClC_6H_4CH_2OTMS$	8	95
3	2,4-$Cl_2C_6H_3CH_2OTMS$	9	89
4	4-$BrC_6H_4CH_2OTMS$	8	90
5	4-$FC_6H_4CH_2OTMS$	8	92
6	4-$PhC_6H_4CH_2OTMS$	12	88
7	4-$CH_3C_6H_4CH_2OTMS$	9	90
8	2,4-$(CH_3)_2C_6H_3CH_2OTMS$	10	90
9	4-$CH_3OC_6H_4CH_2OTMS$	6	94
10	2,4-$(CH_3O)_2C_6H_3$ CH_2OTMS	12	93
11	citronellyl-OTMS	14	89
12	α-tetralyl-OTMS	17	87
13	(-)-menthyl-OTMS	13	90
14	2-norbornyl-OTMS	18	83
15	2,6,6-trimethylbicyclo[3.1.1]heptan-2-OTMS	14	89
16	C_6H_5OTMS	8	92
17	2-$CH_3C_6H_4OTMS$	7	93
18	4-BrC_6H_4OTMS	9	90

[a] Products were identified by comparison of their physical and spectral data with those of authentic samples or reported in literature; [b] isolated yields.

$$ROH + HMDS \xrightarrow[r.t.]{[BPy]FeCl_4} RO\text{-}TMS$$

Scheme 2.

high sterically hindrance, remained unaffected even when the reaction mixtures were stirred at room temperature for one day, and the starting materials were quantitatively recovered. The reaction conditions are mild enough not to induce any isomerization for conjugated alcohols or damage to moieties such as methoxy, which often undergoes cleavage in strongly acidic reaction media. Side product formation was not observed in the reactions we studied. Another advantage of this promoter system is its recyclability. We found that after washing the reaction mixture with Et_2O and dried it at 80 °C, CAN immobilized in $[BPy]FeCl_4$ can be reused in five runs without any loss of activity.

In continuation, we also decided to study the trimethylsilylation of hydroxyl groups in $[BPy]FeCl_4$ as a RTIL. We undertook an optimization of the reaction conditions found that hydroxyl groups were converted to TMS ethers quantitatively in the absence of any catalyst when a mixture of alcohols and hexamethyldisilazane (HMDS) was stirred at r. t. in $[BPy]FeCl_4$ media (Scheme 2). The results are summarized in Table 3. They show the general applicability of the method for the conversion of a wide range of substituted and structurally diverse hydroxyl groups such as primary (Table 3, entries 1 – 11), secondary (Table 3, entries 12 – 14) and tertiary alcohols (Table 3, entry 15)

Table 4. Oxidation of THP, THF and TMS ethers to the corresponding aldehydes or ketones in the presence of PCC-$[BPy]FeCl_4$.

Entry	Substrate	Product[a]	Yield(%)[b] / Time (min)
1	$C_6H_5CH_2OTMS$	C_6H_5CHO	93 / 10
2	4-$ClC_6H_4CH_2OTMS$	4-ClC_6H_4CHO	92 / 15
3	2,4-$Cl_2C_6H_3CH_2OTMS$	2,4-$Cl_2C_6H_3CHO$	94 / 8
4	2-$NO_2C_6H_4CH_2OTMS$	2-$NO_2C_6H_4CHO$	87 / 13[c]
5	4-$NO_2C_6H_4CH_2OTMS$	4-$NO_2C_6H_4CHO$	90 / 15[c]
6	4-$CH_3C_6H_4CH_2OTMS$	4-$CH_3C_6H_4CHO$	93 / 10
7	2,4-$(CH_3)_2C_6H_3CH_2OTMS$	2,4-$(CH_3)_2C_6H_3CHO$	89 / 10
8	$C_6H_5CH{=}CHCH_2OTMS$	$C_6H_5CH{=}CHCHO$	85 / 10
9	furyl-CH_2OTMS	furfural	88 / 9
10	$(C_6H_5)_2CHOTMS$	$(C_6H_5)_2CO$	89 / 20[c]
11	2-norbornyl-OTMS	2-norbornanone	84 / 25[c]
12	(-)-menthyl-OTMS	(-)-menthone	87 / 20[c]
13	$C_6H_5CH_2OTHP$	C_6H_5CHO	94 / 9
14	4-$ClC_6H_4CH_2OTHP$	4-ClC_6H_4CHO	91 / 11
15	4-$FC_6H_4CH_2OTHP$	4-FC_6H_4CHO	89 / 10
16	2,4-$Cl_2C_6H_3CH_2OTHP$	2,4-$Cl_2C_6H_3CHO$	92 / 10
17	2-$NO_2C_6H_4CH_2OTHP$	2-$NO_2C_6H_4CHO$	88 / 20[c]
18	4-$NO_2C_6H_4CH_2OTHP$	4-$NO_2C_6H_4CHO$	90 / 20[c]
19	4-$CH_3C_6H_4CH_2OTHP$	4-$CH_3C_6H_4CHO$	90 / 10
20	2,4-$(CH_3)_2C_6H_3CH_2OTHP$	2,4-$(CH_3)_2C_6H_3CHO$	89 / 12
21	4-$CH_3OC_6H_4CH_2OTHP$	4-$CH_3OC_6H_4CHO$	91 / 8
22	2,4-$(CH_3O)_2C_6H_3$-CH_2OTHP	2,4-$(CH_3O)_2$-C_6H_3CHO	92 / 14 92 / 14
23	4-$PhC_6H_4CH_2OTHP$	4-PhC_6H_4CHO	88 / 20
24	furyl-CH_2OTHP	furfural	89 / 13
25	$(C_6H_5)_2CHOTHP$	$(C_6H_5)_2CO$	90 / 21[c]
26	Norbornyl-2-OTHP	2-norbornanone	80 / 20[c]
27	(-)-menthyl-OTHP	(-)-menthone	82 / 25[c]
28	$C_6H_5CH_2CH(CH_3)OTHP$	$C_6H_5CH_2COCH_3$	87 / 28[c]
29	$C_6H_5CH(CH_3)OTHP$	$C_6H_5COCH_3$	90 / 20
30	α-tetralyl-OTHP	α-tetralone	91 / 22[c]
31	2,4-$Cl_2C_6H_3CH_2OTHF$	2,4-$Cl_2C_6H_3CHO$	92 / 20
32	4-$CH_3C_6H_4CH_2OTHF$	4-$CH_3C_6H_4CHO$	90 / 25
33	4-$CH_3OC_6H_4CH_2OTHF$	4-$CH_3OC_6H_4CHO$	94 / 18
34	4-$PhC_6H_4CH_2OTHF$	4-PhC_6H_4CHO	89 / 30
35	$(C_6H_5)_2CHOTHF$	$(C_6H_5)_2CO$	90 / 32[c]
36	$C_6H_5CH_2CH(CH_3)OTHF$	$C_6H_5CH_2COCH_3$	92 / 35[c]
37	α-tetralyl-OTHF	α-tetralone	90 / 25[c]

[a] Products were identified by comparison of their physical and spectral data with those of authentic samples; [b] isolated yields; [c] in the presence of of 2 mmol of PCC.

$$RR'CHOY \xrightarrow[50\,^{\circ}C]{PCC/\ [BPy]FeCl_4} RR'C{=}O$$

R= H, alkyl or aryl

Scheme 3.

or phenols (Table 3, entries 16 – 18) to synthesize the corresponding TMS ethers. Under these moderate conditions, the yields were significantly improved to 83 – 95% and the reaction time was reduced dramatically (6 – 18 min). On the other hand, reusability of the RTIL in this reaction was also observed.

In the subsequent investigation, the oxidation reaction of these protecting forms of hydroxyl groups was

also examined. We found that one-pot conversion of THP, THF or TMS ethers to their aldehydes or ketones could be performed efficiently using pyridinium chlorochromate (PCC) in $[BPy]FeCl_4$ media at moderate temperature (Scheme 3). To the best of our knowledge no report is available in the literature to carry out this transformation in RTIL. All the experimental results are summarized in Table 4.

The method reported herein is fast and does not involve any special reaction conditions. A wide range of acyclic, alicyclic, and substituted benzylic, phenolic or heterocyclic THP, THF or TMS ethers could be converted to their corresponding aldehydes or ketones in high to excellent yields, and no overoxidation products were observed under the reaction conditions (Table 4, entries 1 – 37). In addition, sterically hindered secondary alcohols (Table 4, entries 10 – 12, 25 – 27 and 35) or acid-sensitive primary substrates like cinnamyl (Table 4, entry 8) or furfuryl (Table 4, entries 9 and 24) ethers were transformed to the corresponding aldehydes or ketones using the same conditions.

In conclusion, we have established an efficient and low cost method for tetrahydropyranylation, tetrahydrofuranylation and trimethylsilylation of alcohols or phenols, as well as oxidation of these ethers to their aldehydes or ketones in $[BPy]FeCl_4$ as an inexpensive and moisture tolerant room temperature ionic liquid. The transformations according to the methods described here are fast and occurred in high to excellent yields at moderate temperature; therefore, they could be highly useful especially in the total synthesis of natural products.

Experimental Section

General experimental procedure for tetrahydrofuranylation and tetrahydropyranylation of alcohols: To a mixture of $[BPy]FeCl_4$ (0.5 ml)and CAN (5.48 mg, 0.01 mmol), alcohol (1 mmol) and DHP or DHF (1.2 mmol) were added. The reaction mixture stirred magnetically at room temperature for the appropriate time as shown in Table 2. The reaction was followed by TLC or GLC. When the reaction was completed, the mixture was washed with Et_2O (3×5 ml). The crude products were separated by flash column chromatography on silica gel (60 – 120 mesh) using *n*-heptane/ethyl acetate (3:1) as eluent. The pure products were prepared in 72 – 96% yields.

General procedure for trimethylsilylation of alcohols: A mixture of alcohol (1 mmol) and HMDS (96.6 mg, 0.6 mmol) in $[BPy]FeCl_4$ (0.5 ml) was stirred at room temperature for the required time (Table 3). After completion of the reaction, the reaction mixture was washed with Et_2O (3×5 ml). The organic layer was evaporated under reduced pressure to produce the crude product, which was purified by flash column chromatography over silica gel (60 – 120 mesh) using *n*-heptane/ethyl acetate (3:1) as solvent. The pure products were prepared in 83 – 95% yields.

A typical protocol for the oxidation of benzyl trimethylsilyl ether (Table 4, entry 1): A mixture of benzyl trimethylsilyl ether (180 mg, 1 mmol) and PCC (215.5 mg, 1 mmol) in $[BPy]FeCl_4$ (0.5 ml) was stirred at 50 °C for 10 min. The reaction was monitored by TLC. After the reaction was complete, H_2O (10 ml) was added and the reaction solution was extracted with Et_2O (3×10 ml). The combined organic phase dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The products were purified by flash column chromatography over silica gel (60 – 120 mesh) using *n*-heptane/ethyl acetate (5:1) to afford benzaldehyde in 93% yield.

Acknowledgements

We are thankful to Isfahan University and Razi University Research Councils for partial support of this work.

[1] G. Sartori, R. Ballini, F. Bigi, G. Bosica, R. Maggi, P. Righi, Chem. Rev. **104**, 1999 (2004).
[2] T. W. Greene, P. G. M. Wuts, Protective Groups in Organic Synthesis, John Wiley, New York (1999).
[3] P. J. Kocienski, Protecting Groups, Georg Thieme Verlag, New York (2000).
[4] T. Oriyama, M. Kimura, G. Koga, Bull. Chem. Soc. Jpn. **64**, 885 (1994).
[5] G. Yang, X. Ding, F. Kong, Tetrahedron Lett. **38**, 6725 (1997).
[6] N. Hamada, T. Sato, Synlett 1802 (2004).
[7] A. T. Khan, L. H. Choudhury, S. Ghosh, Tetrahedron Lett. 45, 7891 (2004).
[8] K. Shimizu, E. Hayashi, T. Hatamachi, T. Kodama, Y. Kitayama, Tetrahedron Lett. **45**, 5135 (2004).
[9] Y. Wang, X. Wu, Z. Jiang, Tetrahedron Lett. **45**, 2973 (2004).
[10] T. Mineno, Tetrahedron Lett. **43**, 7975 (2002).
[11] G. P. Romanelli, G. Baronetti, H. J. Thomas, J. C. Autino, Tetrahedron Lett. **43**, 7589 (2002).
[12] L. C. Branco, C. A. M. Afonso, Tetrahedron **57**, 4405 (2001).
[13] M. H. Habibi, S. Tangestaninejad, I. Mohammadpoor-Baltork, V. Mirkhani, B. Yadollahi, Tetrahedron Lett. **42**, 2851 (2001).
[14] M. Ochiai, T. Sueda, Tetrahedron Lett. **45**, 3557 (2004).
[15] I. Saxena, N. Deka, J. C. Sarma, S. Tsuboi, Synth. Commun. **33**, 4005 (2003).

[16] M. Curini, F. Epifano, M. C. Marcotullio, O. Rosati, U. Costantino, Synth. Commun. **29**, 541 (1999).
[17] B. P. Bandgar, S. P. Kasture, Monatsh. Chem. **132**, 1101 (2001).
[18] M. M. Heravi, D. Ajami, M. M. Mojtahedi, M. Ghassemzadeh, Tetrahedron Lett. **40**, 561 (1999).
[19] M. Tajbakhsh, M. M. Lakouraj, A. Fadavi, Synth. Commun. **34**, 1173 (2004).
[20] T. Welton, Chem. Rev. **99**, 207 (1999).
[21] Z. Li, C. Xia, Tetrahedron Lett. **44**, 2069 (2003).
[22] M. J. Earle, P. B. McCormac, K. R. Seddon, Chem. Commun. 2245 (1998).
[23] A. Stak, B. L. MacLean, R. D. Singer, J. Chem. Soc., Dalton Trans. 63 (1999).
[24] C. E. Song, W. H. Shim, E. J. Roh, S. Lee, J. H. Choi, Chem. Commun. 1122 (2001).
[25] C. J. Mathews, P. J. Smith, T. Welton, Chem. Commun. 1249 (2000).
[26] V. Calo, A. Nacci, L. Lopez, L. Lorarro, Tetrahedron Lett. **41**, 8977 (2000).
[27] A. R. Khosropour, M. M. Khodaei, K. Ghozati, Chem. Lett. **33**, 1378 (2004)
[28] M. M. Khodaei, A. R. Khosropour, K. Ghozati, Tetrahedron Lett. **45**, 3525 (2004).
[29] M. M. Khodaei, A. R. Khosropour, M. Kookhazadeh, Synlett 1980 (2004).
[30] The ionic liquid was prepared by stirring of *n*-butylpyridinium chloride (172.5 mg, 1 mmol) with $FeCl_3$ (162 mg, 1 mmol) at room temperature for 10 min.