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CAN/[nbp]$FeCl_4$ as a Reusable Catalytic System for Direct Conversion of Trimethylsilyl Ethers to Their Acetates Under Microwave Irradiation

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A rapid and easy procedure for direct conversion of TMS-ethers to their acetates catalyzed by cerium(IV) ammonium nitrate (CAN) immobilized on n-butylpyridinium tetrachloroferrate ([nbp]$FeCl_4$) as a room temperature ionic liquid under microwave irradiation was developed. This methodology is enough mild so that the acid sensitive groups such as methoxy, furyl or thiophenyl were remained intact. No side products were observed by this method.

Keywords: Ionic liquid, Trimethylsilyl ethers, Acetates, Cerium(IV) salt, Microwave irradiation

INTRODUCTION

The selective transformation of one functional group to another in the presence of other(s) using non- to low-toxic chemicals in economically viable and environmentally benign conditions is a formidable task for synthetic organic chemistry. On the other hand, the demand for increasingly clean and efficient chemical synthesis is important from both economic and environmental points of view [1]. One commonly used method is carrying out important synthetic transformation in room temperature ionic liquids (RTILs) [2-4]. They exhibit a number of notable physical properties that may be exploited in synthetic processes. These compounds have negligible vapor pressure which makes them optimal replacements for the volatile or explosive organic solvents [5]. In addition, these ionic solvents can be recovered and reused [6]. The catalysts having polar or ionic character can be immobilized without any modification and thus the ionic solutions containing the catalyst can be easily and successfully separated from reagents or products [7,8].

In the past few years, the application of microwave irradiation for chemical synthesis has attracted considerable interest because it can enhance selectivity and reactivity, increasing chemical yields and shorten reaction times [9,10]. Dramatic rate increase in ionic liquids as reaction media under microwave irradiation has been recently reported [11].

Trimethylsilyl (TMS) ethers are the most versatile protecting groups for alcohols which are frequently used in organic syntheses due to their low cost, ease of installation and general stability to the most nonacidic media [12-14]. However, they are not stable under strongly acidic conditions. On the other hand, acetates serve as effective hydroxyl blocking agent which are stable to acidic conditions [15]. Thus one-pot conversion of TMS ethers to the corresponding acetates could be considered as a useful transformation in organic synthesis. Nevertheless, the methods available for this transformation are limited [16,17]. Recently, we have reported that Bi(III) salts can catalyzed this transformation [18,19]. However, the reported methods suffer one or more limitations such as the use of costly chemicals or environmentally

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harmful media, less selectivity, long reaction times or afford side product(s). Thus the development of facile synthetic methods towards these transformations constitutes an active area of investigation in organic synthesis.

EXPERIMENTAL

Apparatus and Conditions

The reaction was carried out at atmospheric pressure. The microwave system used for this experiment includes the following items: Micro-SYNTH Labstation, complete with glass door, dual magnetron system with pyramid-shaped diffuser, 1000 Watt delivered power, exhaust system, magnetic stirrer, “quality pressure” sensor for flammable organic solvents, ATCFO fiber optic system for automatic temperature control. Parameters in discover mode are: power, 180 W; temperature, 70 °C. All of the TMS-ethers were prepared according to the literature methods [19]. The synthesis and the characteristics of [nbp]$FeCl_4$ has previously been reported [29]. In all cases, prior to reaction, the ionic liquids were dried under vacuum at 80 °C.

General Procedure

A mixture of CAN (0.1 mmol) immobilized on [nbp]$FeCl_4$ (1 mmol, 0.2 ml), trimethylsilyl ether (1 mmol) and Ac_2O (1.2 mmol) were taken into a reaction tube and thoroughly mixed. The resulting mixture was placed in the microwave cavity and irradiated at 70 °C (power 180 W) for the appropriate time as shown in Table 1. After completion of the reaction, as indicated by TLC, the mixture was allowed to cool and extracted with diethyl ether (3 × 5 ml). The solvent was evaporated under reduced pressure. Column chromatography of the crude residue on silica gel using n-hexane as an eluent gave the corresponding acetates in 80-94% yields.

RESULTS AND DISCUSSION

In continuation with our outgoing work in the designing of “green” synthetic procedure [20-23] specially in ionic liquids [24] and microwave-assisted reactions [25,33], and also to expand our work to develop new synthetic methodologies catalyzed by Lewis acids immobilized in ionic liquids [31,32], herein we are gratified to report a facile, eco-friendly and efficient one-pot transformation of TMS ethers to their acetates with acetic anhydride in the presence of CAN immobilized on n-butylpyridinium tetrachloroferrate ([nbp]$FeCl_4$) under microwave irradiation (Scheme 1).

$$\text{R-OSi(CH}_3)_3 \xrightarrow[\text{Ac}_2\text{O, M.W.}]{\text{CAN/[nbp]FeCl}_4} \text{ROAc}$$

Scheme 1

It should be noted that, to the best of our knowledge, the use of CAN in the presence of an ionic liquid under microwave irradiation for the above transformation has never been reported in the literature. In this work, we first planned to study catalytic activity of CAN/[nbp]$FeCl_4$ in the esterification reaction under microwave irradiation, as a very simple model. Thus, benzyl trimethylsilyl ether (1 mmol) as a representative TMS ether was treated with acetic anhydride (1.2 mmol) with varying amounts of CAN/[nbp]$FeCl_4$ under different conditions. The best results were obtained on treating the TMS ether with acetic anhydride with CAN/[nbp]$FeCl_4$ ratio of 0.1 mmol/0.2 ml for 3 min at 70 °C. On the other hand, a similar reaction was studied under MW in the absence of CAN, which resulted in the formation of a trace amount of the desired product. This observation indicates that the ionic liquid [nbp]$FeCl_4$ mostly acts as a solvent in this reaction. The optimized reaction condition was then applied to the conversion of TMS ethers to their acetates in 80-94% yields (Table 1).

The presence of electron-donating and electron-withdrawing groups on the aromatic ring did not make any significant difference in the reaction rates (Table 1, entries 1-11). Sterically hindered benzyl TMS ethers (Table 1, entries 12, 13) were also converted to the acetates in good yields. This methodology is also enough mild so that the acid sensitive groups such as methoxy, furyl or thiophenyl were remained intact. On the other hand, no side products were observed by this method. Aliphatic trimethylsilyl ethers such as 1-heptyl-, cyclohexyl- or (-)-menthyl trimethylsilyl ethers also gave the corresponding acetates in high yields (Table 1, entries 16-19). *t*-Butyl trimethylsilyl ether undergoes deprotection to generate only the corresponding alcohol, without producing any acetate.

Table 1. Esterification of TMS-Ethers to Their Acetates in the Presence of CAN/[nbp]$FeCl_4$ Under Microwave Irradiation

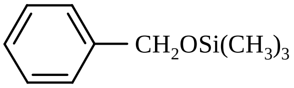
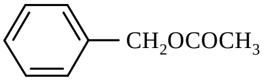
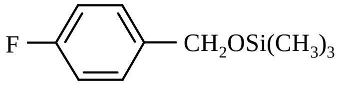
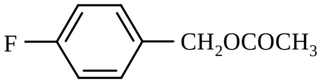
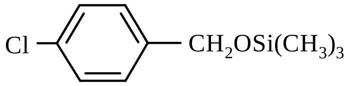
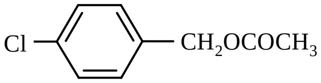
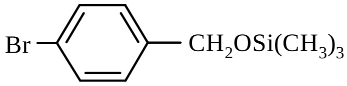
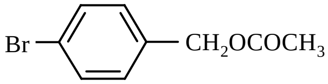
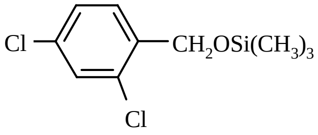
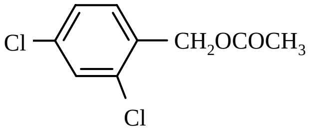
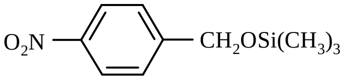
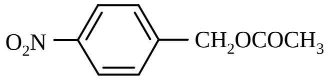
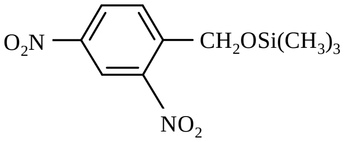
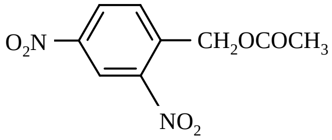
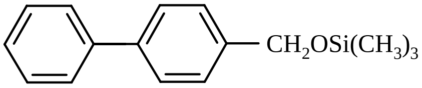
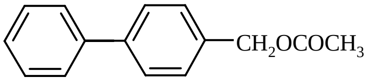
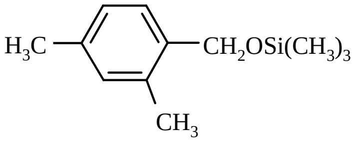
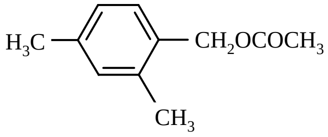
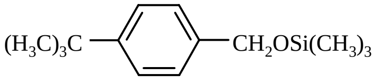
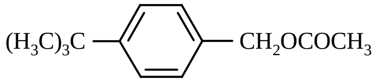
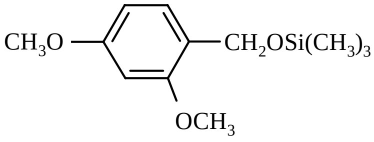
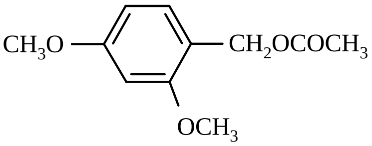
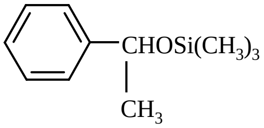
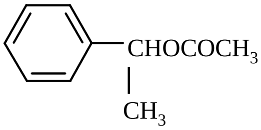
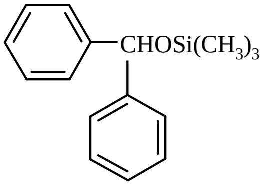
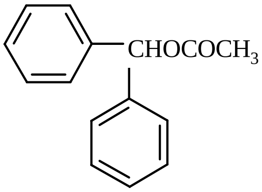
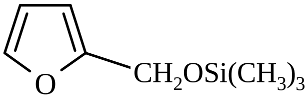
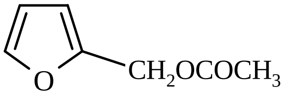
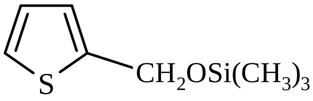
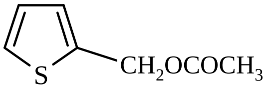
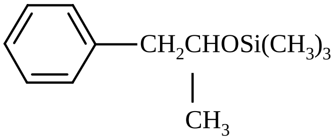
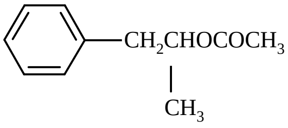
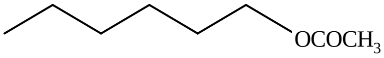
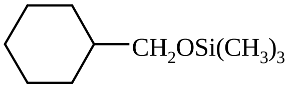
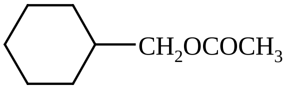
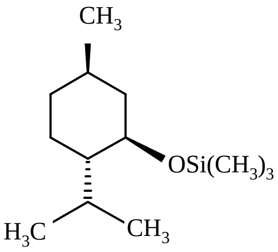
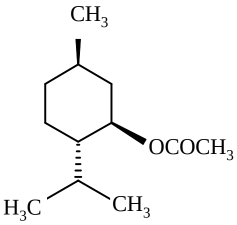
Entry	Substrate	Product[a]	Time (s)	Yield (%)[b]
1			180	93
2			180	90
3			180	92
4			180	94
5			180	90
6			228	85
7			240	84
8			210	88
9			192	90
10			198	87

Table 1. Continued

11			186	89
12			186	88
13			216	87
14			168	80
15			180	85
16			210	83
17			180	86
18			222	82
19			192	84[c]

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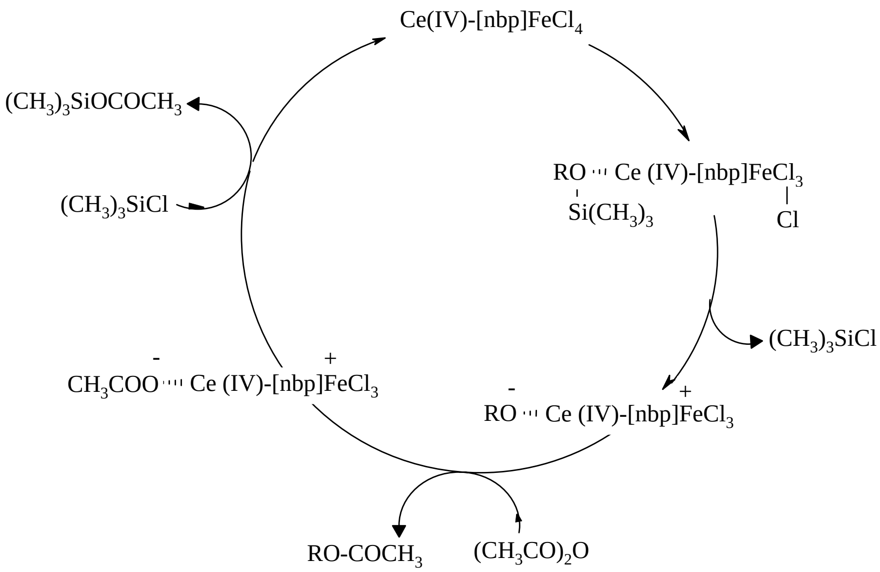
[a]All products were characterized by ^{1}H NMR, ^{13}C NMR, and IR. [b]Isolated and unoptimized yields. [c]With retention of configuration.



Scheme 2

On the other hand, the stability of phenyl trimethylsilyl ethers to the corresponding acetates, promoted us to investigate whether or not our method might also serve as a useful means for the selective esterification of alkyl-OTMS in the presence of aryl-OTMS. The competitive reaction showed that no esterification of aryl trimethylsilyl ether is occurred, thus confirming the selectivity of the method. We have proposed a mechanism for the direct conversion of TMS ethers to their acetates as indicated by Scheme 2.

We have also examined the reusability of the catalyst system. Since CAN/[nbpy]$FeCl_4$ was weakly soluble in diethyl ether, it can be separated from reaction medium by washing with Et_2O, dried at 80 °C under reduced pressure and reused for the further reactions. Although we did not carry out reactions with several batches of the recovered catalyst, the repetition with one batch indicated that its efficiency is similar to that of the fresh catalyst system. The performance of the recovered catalyst during these transformations was found to be satisfactory and no considerable variation in yields of the products was observed.

In conclusion, we established an efficient and low cost method for esterification of trimethylsilyl ethers with CAN immobilized on [nbp]$FeCl_4$ as an inexpensive and moisture tolerant room temperature ionic liquid. These transformations according to the methods described here are fast and performed in high to excellent yields which will be highly are useful, especially in the total synthesis of natural products.

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REFERENCES

[1] P. Anastas, T.C. Williamson, Green Chemistry-Frontiers in Benign Synthesis and Processes, Oxford University Press, 1988.
[2] D.-G. Gu, S.-J. Ji, Z.-Q. Jiang, M.-F. Zhou, T.-P. Loh, Synlett (2005) 959.
[3] P. Wasserscheid, W. Keim, Angew, Chem., Int. Ed. 39 (2000) 3772.
[4] A.K. Burrell, R.E. Del Sesto, S.N. Baker, T.M. McCleskey, G.A. Baker, Green Chem. 9 (2007) 449.
[5] I. López, G. Silvero, M.J. Arévalo, R. Babiano, J.C. Palacios, J.L. Bravo, Tetrahedron 63 (2007) 2901.

[6] D.-Q. Xu, B.-Y. Liu, S.-P. Luo, Z.-Y. Xu, Y.-C. Shen, Synthesis (2003) 2626.

[7] R. Sheldon, Chem. Commun. (2001) 2399.

[8] J.S. Yadav, B.V.S. Reddy, A.K. Basak, A. Venkat Narsaiah, Tetrahedron Lett. 44 (2003) 1047.

[9] C. Kuang, Q. Yang, H. Senboku, M. Tokuda, Synthesis (2005) 1319.

[10] A. Loupy, Microwaves in Organic Synthesis, Wiley-VCH, Weinheim, 2002.

[11] M. Xia, Y.-d. Lu, J. Mol. Catal. A Chem. 265 (2007) 2005.

[12] G. Sartori, R. Ballini, F. Bigi, G. Bosica, R. Maggi, P. Righi, Chem. Rev. 104 (2004) 1999.

[13] P.J. Kocienski, Protecting Groups, Georg Thieme Verlag, New York, 2000.

[14] T.W. Greene, P.G.M. Wuts, Protective Groups in Organic Synthesis, 3rd ed., John Wiley, New York, 1999.

[15] I. Mohammadpoor-Baltork, H. Aliyan, A.R. Khosropour, Tetrahedron 57 (2001) 5851.

[16] G.V.M. Sharma, A.K. Mahalingam, M. Nagarajan, A. Ilangoan, P. Radhakrishna, Synlett (1999) 1200.

[17] C.S. Reddy, G. Smitha, S. Chandrasekhar, Tetrahedron Lett. 44 (2003) 4693.

[18] I. Mohammadpoor-Baltork, A.R. Khosropour, H. Aliyan, Synth. Commun. 31 (2001) 3411.

[19] I. Mohammadpoor-Baltork, A.R. Khosropour, Monatsh. Chem. 133 (2002) 189.

[20] A.R. Khosropour, M.M. Khodaei, K. Ghozati, Chem. Lett. 33 (2004) 1378.

[21] M.M. Khodaei, A.R. Khosropour, M. Kookhazadeh, Tetrahedron Lett. 45 (2004) 1725.

[22] M.M. Khodaei, A.R. Khosropour, M. Beygzadeh, Synth. Commun. 34 (2004) 1551.

[23] A.R. Khosropour, M.M. Khodaei, K. Ghozati, Z. Naturforsch. B 60b (2005) 572.

[24] A.R. Khosropour, M.M. Khodaei, S. Ghaderi, Z. Naturforsch. B 61b (2006) 326.

[25] A.R. Khosropour, M.M. Khodaei, K. Ghozati, Tetrahedron Lett. 45 (2004) 3525.

[26] M.M. Khodaei, A.R. Khosropour, M. Kookhazadeh, Synlett (2004) 1980.

[27] M.M. Khodaei, A.R. Khosropour, M. Kookhazadeh, Can. J. Chem. 83 (2005) 209.

[28] A.R. Khosropour, M.M. Khodaei, M. Beygzadeh, M. Jokar, Heterocylces 65 (2005) 767.

[29] M.M. Khodaei, A.R. Khosropour, M. Jowkar, Synthesis (2005) 1301.

[30] A.R. Khosropour, I. Mohammadpoor-Baltork, H. Ghorbankhani, Catal. Commun. 7 (2006) 713.

[31] A.R. Khosropour, I. Mohammadpoor-Baltork, H. Ghorbankhani, Tetrahedron Lett. 47 (2006) 3493.

[32] A.R. Khosropour, M.M. Khodaei, K. Ghozati, Chem. Lett. 33 (2004) 304.

[33] A.R. Khosropour, I. Mohammadpoor-Baltork, M.M. Khodaei, M. Jowkar, Heterocylces 68 (2006) 1551.