
Chemoselective preparation of acylals using 1-methyl-3-(2-(sulfooxy)ethyl)-1H-imidazol-3-ium chloride as an efficient and reusable catalyst

S. Rezayati^{1, 2*}, S. Sajjadifar¹ and R. Hajinasiri²

¹Department of Chemistry, Payame Noor University, PO BOX 19395-4697 Tehran, Iran

²Chemistry Department, Qaemshahr Branch, Islamic Azad University, PO BOX 163, Qaemshahr, Iran

E-mail: sobhan.rezayati@yahoo.com

Abstract

An efficient and chemoselective procedure for the preparation of 1, 1-diacetates (acylals) from various aldehydes with acetic anhydride in the presence of Brønsted acidic ionic liquid [Msei]Cl as a reusable catalytic system under solvent-free condition at room temperature and short periods of times with excellent yields will be described. The catalyst was easily separated in simple work-up and was recycled several times without loss of reactivity under the described reaction conditions.

Keywords: [Msei]Cl; green chemistry; acylals; heterogeneous catalysis; solvent-free condition

1. Introduction

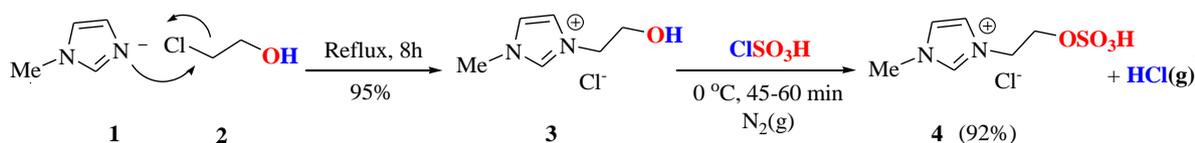
Recently, scientists and researchers have focused on the investigations whose aim has been to find those chemical processes or methodologies that are not dangerous for the environment. The term “green chemistry” includes the fabrication and catalysis of those chemical compounds which possess a reduced threat to human beings as well as the environment (Choudhary et al., 2006). During the past decade the chemical manufacturers started to use ionic liquids (ILs) as solvents for organic fabrication as catalysis and media for various extraction processes. This considerable interest towards ionic liquids is due to their unique characteristics such as being non-volatile, non-flammable, as well as their ability to be used many times, and also their potential for being a very proper media for the environment. Some of the ionic liquids are approved to be used as catalysts because they possess a kind of polarity, besides they have the ability to solve not only organic compounds but also the inorganic ones. Accordingly an accelerated rate reaction can be anticipated (Yadav et al., 2003). The benefits of these kinds of mixed catalysts include high activity and selectivity, easy catalyst separation, long catalytic life, thermal stability, and recyclability (Li et al., 2007; Karimi, & Ghoreishi-Nezhad, 2007; Melero

et al., 2006). In synthetic organic chemistry the selective protection of carbonyl groups has attracted a great deal of attention. Among different carbonyl protecting groups 1,1-diacetates (acylals) are very important since they possess the ability to preserve their stability under not only neutral and basic media but also the acidic ones (Kochhar et al., 1983). Acylals are the main synthetic precursors for the preparation of 1-acetoxydienes for Diels–Alder reaction (Snider & Amin, 1978) and are also useful intermediates in various transformations such as nucleophilic substitution reactions (Heerden et al., 1998; Sandberg & Sydnese, 1998; Sandberg & Sydnese, 2000; Sydnese & Sandberg, 1997; Yadav et al., 2001). Besides their protecting role, acylals are also important precursors for the synthesis of dienes, chiral allylic esters and they could also be applied as cross linking reagents for the cellulose in cotton (Frick & Harper, 1984; Shelke et al., 2009). Therefore, methods for their synthesis have received considerable attention. It is usual in organic chemistry to produce 1,1-diacetates by using aldehydes and acetic anhydride under acidic medium. In these kinds of reactions we are able to use several catalysts such as Cu(BF₄)₂.xH₂O (Chakarabarti et al., 2004), H₂SO₄–SiO₂ (Pourmousavi & Zinati, 2009), NBS (Karimi et al., 2000), CAN (Roy & Banerjee, 2002), SBA-15-Ph-PrSO₃H (Zareyee et al., 2013), H₆P₂W₁₈O₆₂.24H₂O (Romanelli et al., 2003), Bi(NO₃)₃.5H₂O (Aggen et al., 2004), PVA-FeCl₃ (Li, 2000), Fe⁺³ on montmorillonite (Li et al., 1998), zirconium sulfophenyl phosphonate (Curini et al., 2002), and

*Corresponding author

Received: 1 August 2013 / Accepted: 11 March 2015

Silica boron sulfonic acid (Sajjadifar & Rezayati, 2014). However use of the mentioned methods has some drawbacks including expensive reagents, low product yields, longer reaction time, toxicity of reagent and hard experimental procedure. [Msei]Cl as a new solid acid catalyst was reported. Wu and *et al.* (Scheme 1) (Wu et al., 2009) as used for the 2,4,5-triaryl-5*H*-chromeno[4,3-*b*]pyridines under microwave radiation conditions for the first time.



Scheme 1. Preparation of 1-methyl-3-(2-(sulfoxy)ethyl)-1H-imidazol-3-ium chloride

2. Experimental

2.1. Chemicals and reagents

All reagents were purchased from Aldrich or Merck Fine Chemicals and were used without further purification. Products were separated and purified by different chromatographic techniques and were identified by the comparison of their IR and NMR with those reported for the authentic samples. IR spectra of the compounds were obtained on a Perkin Elmer spectrometer version 10.03.06 using a KBr disk. The nuclear magnetic resonance (^1H NMR) spectra were recorded on a BRUKER DRX-400 AVANCE instrument at 400 MHz (in CDCl_3 solution) using TMS as internal standard. The purity of the substrate and reaction monitors was accompanied by TLC on Silica gel Polygram SILG/UV 254 plates. Melting points were determined using an Electrothermal apparatus and are uncorrected.

2.2. Typical procedures

2.2.1. Preparation of Brønsted Acidic Ionic Liquid

1-Methylimidazole 1 (4.1 g, 50 mmol) and 2-chloroethanol 2 (4.02 g, 50 mmol) were added in a flask containing 10 mL of CHCl_3 , and the mixture was refluxed for 8 h and CHCl_3 removed under vacuum. Unreacted 1-methylimidazole or 2-chloroethanol was extracted with ether (3×10 mL) to give 1-methyl-3-(2-hydroxyethyl) imidazolium chloride (yield 95%). IR spectra of compound 3: OH ($3200\text{--}3600\text{ cm}^{-1}$), C=C ($1450, 1575\text{ cm}^{-1}$), and C=N (1643 cm^{-1}) (Fig. 1).

A stoichiometric amount of 97% chlorosulfonic acid (3.4 mL, 50 mmol) in CCl_4 (10 mL) was added dropwise to compound 3 over a period of 45–60 min at 0°C , and HCl gas was evolved in an alkali trap immediately (Scheme 1). The mixture was

Brønsted acidic ionic liquid catalyst has attracted much more attention in recent years because of its ability to carry out this particular set of reactions, moreover, it is worth mentioning that it has been used for different organic alterations. Simplicity of operation, short reaction times, inexpensive reagents, green condition, and the high yields of products and reusable and green heterogeneous catalyst are the advantages of the present method.

washed with CCl_4 (3×10 mL) to remove the unreacted chlorosulfonic acid (yield 92%). IR spectra of compound 4: OH ($3200\text{--}3600\text{ cm}^{-1}$), C=C ($1440, 1579\text{ cm}^{-1}$), C=N (1648 cm^{-1}), S=O (1019 cm^{-1}), and S–O (623 cm^{-1}) (Fig. 1) (Wu et al., 2009).

2.3. General procedure for the preparation of 1,1-diacetates

A mixture of various aldehydes (1 mmol), acetic anhydride (2 mmol) and [Msei]Cl (0.03 mol%) were stirred at room temperature (Caution: this reaction is exothermic and hence due care must be exercised when scaling up this reaction). The yield and time required for each reaction is indicated in Table 3. The reaction was followed by TLC (*n*-hexane: EtOAc, 9:1). After completion of the reaction, CH_2Cl_2 (10 ml) was added to the mixture, filtered and the catalyst [Msei]Cl was washed again with CH_2Cl_2 (2×5 ml), then the final material was collected for reusing. The solvent was evaporated under reduced pressure to give crude products which were purified. Products were purified by column chromatography (silica gel, *n*-hexane:EtOAc, 9:1) to afford pure products in good to excellent yields. The products were identified by comparing their melting point, ^1H NMR and IR spectral data with those observed for the authentic samples.

2.4. Selected spectral data of the products

1,1-Diacetoxy-1-phenyl methane (Entry 1)

^1H -NMR (CDCl_3 , 400 MHz) δ : 2.14 (2s, 6H, 2 CH_3), 7.41-7.45 (m, 3H, Ar-H), 7.52-7.55 (m, 2H, Ar-H), 7.70 (s, 1H, CH). ^{13}C -NMR (CDCl_3 , 100 MHz) δ : 20.8, 89.7, 126.6, 128.6, 129.7, 135.4, 168.8. IR $\nu_{\text{max}}/\text{cm}^{-1}$: 3564, 3367, 3068, 2934, 1762, 1669, 1572, 1495, 1435, 1371, 1243, 1206, 1088, 1055, 1010, 842, 761, 701.

1,1-Diacetoxy-1-(furyl) methane (Entry 5)

$^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 2.16 (2s, 6H, 2CH₃), 6.41-6.41 (dd, 1H, $J = 1.6$, $J = 1.6$, Ar-H), 6.55 (d, 1H, $J = 3.2$, Ar-H), 7.47-7.48 (dd, 1H, $J = 0.8$, $J = 0.8$, Ar-H), 7.73 (s, 1H, CH); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 20.7, 83.4, 109.7, 110.4, 143.6, 147.8, 168.4. IR $\nu_{\text{max}}/\text{cm}^{-1}$: 3473, 3161, 3129, 3018, 2942, 1758, 1608, 1505, 1432, 1380, 1348, 1250, 1209, 1146, 1063, 1013, 971, 934, 832, 788, 751.

1,1-Diacetoxy-1-(4-nitrophenyl) methane (Entry 6)

$^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 2.17 (2s, 6H, 2CH₃), 7.70 (s, 1H, CH), 7.73-7.74 (d, 2H, $J = 4$ Hz, Ar-H), 8.28 (2H, d, Ar-H). $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 20.0, 88.3, 123.8, 127.8, 141.8, 148.5, 168.6. IR $\nu_{\text{max}}/\text{cm}^{-1}$: 3486, 3123, 3017, 2940, 2868, 1764.60, 1610, 1530, 1431, 1377, 1351, 1292, 1233, 1204, 1105, 1061, 1012, 977, 942.

1,1-Diacetoxy-1-(3-chlorophenyl) methane (Entry 9)

$^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 2.14 (2s, 6H, 2CH₃), 7.33-7.40 (m, 3H, Ar-H), 7.52 (m, 1H, Ar-H), 7.64 (s, 1H, CH). $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz): δ 20.8, 88.7, 125.0, 126.8, 129.9, 134.5, 137.2, 168.7.

3. Results and Discussion

In recent years, the use of solid acid catalysts and solvent-free conditions have been developed according to the fact that such catalysts not only simplify the purification processes and help to prevent the release of toxic reaction residues into the environment but also they are considered as reusable and environmentally benign catalysts (Rezayati et al., 2015; Hajinasiri & Rezayati, 2013; Rezayati & Sajjadifar, 2014; Rezayati et al., 2014). Preparation of the catalyst which was an easy task was done in two steps. The first step increased 2-chloroethanol to 1-methyl-1H-imidazole under reflux condition for at least 8 hours and the second step increased chlorosulfonic acid to this mixture reaction under N₂ atmosphere. This reaction was easy and clean, because HCl gas was evolved from the reaction vessel immediately. IR spectrum of [Msei]Cl showed the characteristic peak of S-O group at 579-600 cm⁻¹, S=O at 1067-1200 cm⁻¹, broad peak at 2900-3365 cm⁻¹ related to the OH of SO₃H groups, one absorptions at 1648 for C=N, two absorptions at 1440 cm⁻¹ and 1579 cm⁻¹ for C=C group (Fig. 1). These spectrums confirmed that this catalyst was exactly synthesized.

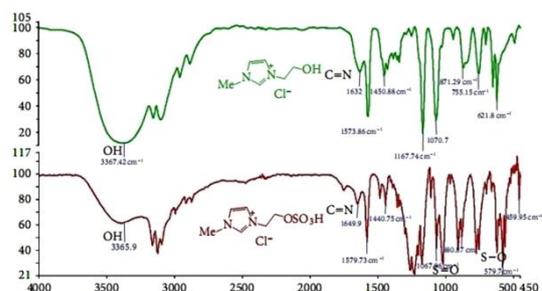
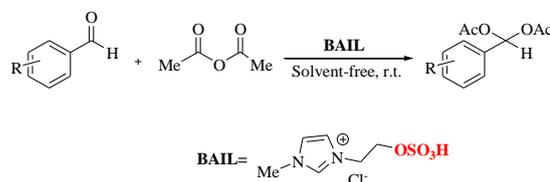


Fig. 1. Comparison of IR spectra of ionic liquid and Brønsted acidic ionic liquid

In the present research chemoselective and efficient method for the formation of 1,1-diacetates is described by using the reaction between aldehyde and acetic anhydride using [Msei]Cl as a new and Brønsted acidic ionic liquid catalysts under solvent-free conditions at room temperature (Scheme 2).



Scheme 2. Synthesis of acylals using Brønsted acidic ionic liquid (BAIL)

First, the effect of catalyst loading in the reaction of benzaldehyde and acetic anhydride under solvent-free conditions was studied (Table 1). As it is shown in the Table 1, the best result was obtained when 0.03 mol% of the catalyst was used (Table 1, Entry 3). Then, when 0.1 mol% of catalyst was used, the yield of the desired product decreased dramatically and we also witnessed long reaction (Table 1, Entry 6). In order to determine the role of [Msei]Cl better, the model reaction was carried out without the use of any catalyst; 5% yield within 24 hour (Table 1, Entry1).

Table 1. Optimization of amount of the catalyst loading

Entry	Catalyst (%)	Time (min)	Yield (%) ^a
1	0.00	24 h ^b	5
2	0.01	25	83
3	0.03	5	99
4	0.05	15	84
5	0.07	30	81
6	0.1	70	72

^aYield of isolated products

^bIn hour

In the second step, the effect of various solvent in this reaction was investigated (Table 2, Entries 1-7). The best yield was found using solvent-free conditions. Therefore, the above conditions were employed for the conversion of various aldehydes

to the corresponding acylals under solvent-free conditions (Table 2, Entry 8).

Table 2. The solvent effect for synthesis of 1,1-diacetate^a

Entry	Solvent (10 ml)	Time (min)	Yield (%) ^b
1	H ₂ O	95	74
2	H ₂ O:EtOH ^c	60	78
3	Ethanol	65	81
4	<i>n</i> -Hexane	55	83
5	Acetonitrile	80	65
6	Ethyl acetate	45	85
7	Dichloromethane	50	86
8	Solvent-Free	5	99

^aCondition reaction: benzaldehyde (1 mmol) and acetic anhydride (2 mmol) in presence [Msei]Cl (0.03 mol%) at room temperature

^bYield of isolated products

^c1:1 ratio

Table 3. Formation of 1,1-diacetate using [Msei]Cl under solvent-free conditions

Entry	Substrate	Time (min)	Yield (%) ^a	M.p. (°C)	Reference
1	Benzaldehyde	10	99	42-44	(Heravi et al., 2005)
2	Butyraldehyde	25	82	Oil	(Heravi et al., 2005)
3	4-Chlorobenzaldehyde	5	97	81-83	(Hajipour et al., 2008)
4	4-Hydroxybenzaldehyde	10	95	91-93	(Hajipour et al., 2008)
5	Furfural	15	96	50-52	(Hajipour et al., 2008)
6	4-Nitrobenzaldehyde	5	98	126-128	(Khan et al., 2006)
7	4-Bromobenzaldehyde	6	96	84-86	(Khan et al., 2006)
8	4-Methylbenzaldehyde	12	93	80-81	(Saini et al., 2007)
9	3-Chlorobenzaldehyde	7	94	64-65	(Hajipour et al., 2007)
10	3-Methoxybenzaldehyde	25	87	Oil	(Ghosh et al., 2004)
11	3-Nitrobenzaldehyde	10	91	66-68	(Ghosh et al., 2004)
12	2-Nitrobenzaldehyde	15	94	90-92	(Ghosh et al., 2004)
13	2-Hydroxybenzaldehyde	15	93	101-102	(Nagy et al., 2002)
14	4-Acetoxybenzaldehyde	20	87	88-90	(Nagy et al., 2002)
15	4-Cyanobenzaldehyde	7	99	100-102	(Kochhar et al., 1983)
16	2,6-Dichlorobenzaldehyde	18	87	88-90	(Firouzabadi et al., 2003)

^aYield of isolated products

The results listed in Table 3 show that aliphatic and aromatic aldehydes react smoothly with acetic anhydride compound to afford the corresponding 1,1-diacetates, moreover it is worth mentioning that all these products have good to excellent yields and reaction time. Here, versatility of the present methodology is well demonstrated by the fact that both aromatic (Table 3, Entries 1 and 3–16) and aliphatic (Table 3, Entry 2) aldehydes afforded their corresponding acylals in equally good yields. The powerful electron-releasing substituent OMe slightly decreased the yield and increased the reaction time (Table 3, Entry 10). Furfural (Table 3, Entry 5) and 4-Cyanobenzaldehyde (Table 3, Entry 15) also led to the formation of acylals in 96% and 99% yield without the formation of any side products, it was normally observed under strongly acidic conditions. In order to show the merit of the present work, most of the reported methods require reaction times in order to be completed, but in this

research all of the reactions were completed within 5-25 minutes (Table 3). These results showed that [Msei]Cl as catalyst for this condensation is appropriate and encouraged us to extend this catalyst for the synthesizing other compounds. The structures of compounds were confirmed by ¹H NMR, ¹³C NMR and IR spectra. In the ¹H NMR spectrum of compound 4 one signals due to the two methoxy groups which were visible at 2.17 ppm and one singlet at 7.27 ppm that due to C-H between two ester groups and two doublet about $\delta = 7.73-7.74$ (d, 2H, $J = 4$ Hz, Ar-Hz) and 8.28 ppm (d, 2H, Ar-H Hz) for the C-H protons. A comparative study on the catalytic activities of the catalyst with some of the reported catalysts was carried out using benzaldehyde as a model substrate (Table 4).

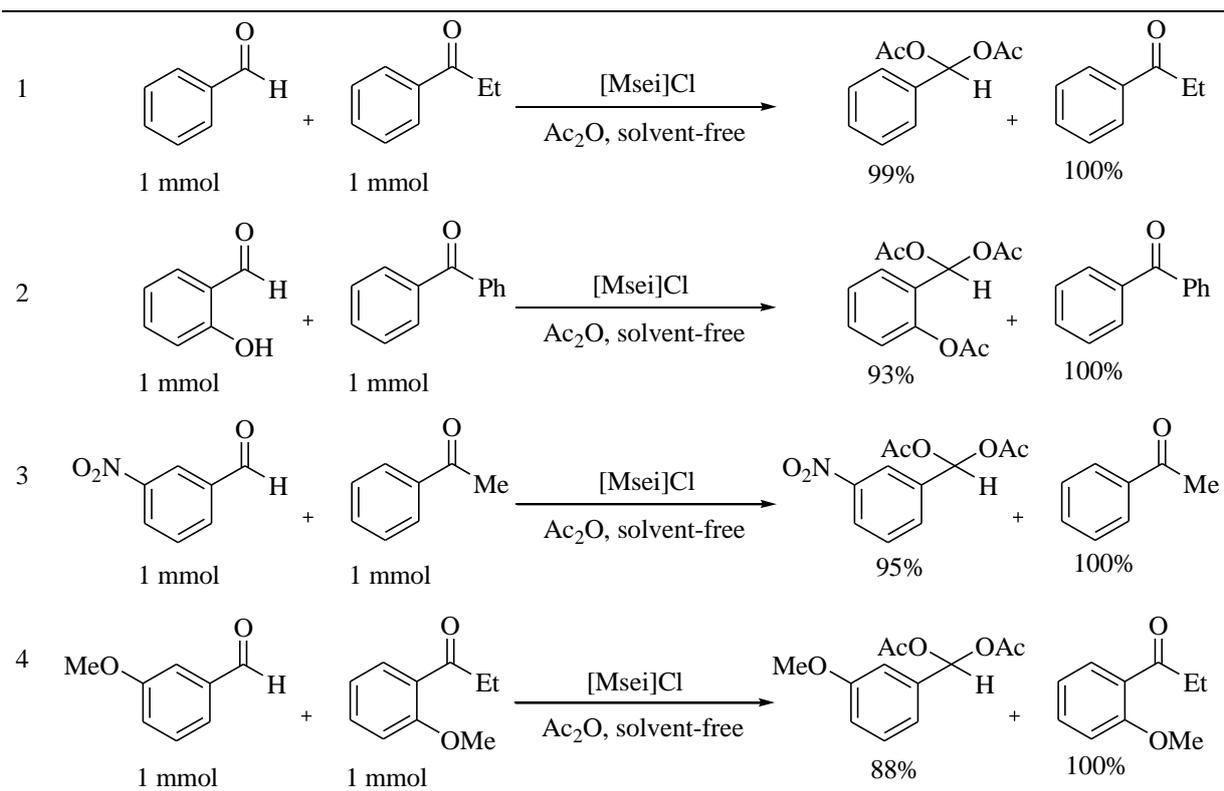
Table 4. Comparison of the present method with some other procedures for 1,1-diacetate synthesis

Catalyst/Solvent/Temperature	Time (min)	Catalyst loading	Yield (%) ^d	Reference
NBS	8 h ^c	10 mol%	98	(Karimi et al., 2000)
NbCl ₅	10	5 mmol%	97	(Gao et al., 2009)
SiO ₂ -NaHSO ₄	15	25 mol%	94	(Kannasani et al., 2012)
SPDTSA ^a	4	10 mg	94	(Nouri-Sefat et al., 2011)
Si-[SbSipim][PF ₆] ^b / 30 °C	3 h ^c	0.1 g	90	(Kang et al., 2013)
Amberlyst-15/ CH ₂ Cl ₂	60	500 mg	95	(Reddy et al., 2003)
Mg(CH ₃ SO ₃) ₂ -HOAc	12 h ^c	1.5 mol%	55	(Liu et al., 2012)
I ₂	2 h ^c	10 mol%	99	(Deka et al., 1997)
Bi(OTf) ₃ .XH ₂ O/ CH ₃ CN	45	31 mg	91	(Carrigan et al., 2001)
This Work	10	0.03 mol%	99	-

^aSilica-bonded propyl-diethylene-triamine-N-sulfamic acid^bSilica-supported functional ionic liquid^cIn hour^dYield of isolated products

In order to show the high selectivity of the procedure, we investigated competitive reactions for the synthesis of the acylals from various aldehydes and Ketones (electron-donating or electron-withdrawing) in presence of [Msei]Cl. In doing so, different reactions were designed. We found that ketones which proved resistant to the

reaction conditions did not produce any acylals under the optimized reaction condition even under reflux conditions. This result indicates that aldehydes are more reactive than ketones and this may be due to the higher electrophilicity of aldehydes in comparison to ketones (Table 5).

Table 5. Competition reaction via mixtures of some aldehydes and ketones with acetic anhydride in presence [Msei]Cl^a^aYield of isolated products

Recycling the catalyst is one of the most significant advantages of our method. The catalyst can be recycled after a simple work-up and then reused for at least seven runs without appreciable reduction in its catalytic activity (Table 6).

Table 6. The catalytic activity of [Msei]Cl in seven cycles

Run	1	2	3	4	5	6	7
Yield (%)	99	99	97	95	97	94	94

4. Conclusion

In summary, a clean and efficient catalyst for the preparation of 1,1-diacetates from various aldehydes with the use of acetic anhydride in the presence of [Msei]Cl as a new catalyst was studied and worked upon. Clean work-up, excellent chemoselectivity, simple experimental procedure, short period of conversion, excellent yields, and the elimination of corrosive liquid acids, are the advantages of the present method. This catalyst's is easily available, non-toxic and also eco-friendly in nature. The most important feature-of this procedure is that the catalyst can be recycled after a simple work-up and then be reused for at least seven runs without appreciable reduction in its catalytic activity.

Acknowledgment

The authors gratefully acknowledge partial support of this work by Payame Noor University (PNU) of Ilam, Iran.

References

- Aggen, D. H., Arnold, J. N., Hayes, P. D., Smoter, N. J., & Mohan, R. S. (2004). Bismuth compounds in organic synthesis. Bismuth nitrate catalyzed chemoselective synthesis of acylals from aromatic aldehydes. *Tetrahedron*, 60, 3675–3679.
- Carrigan, M. D., Eash, K. J., Oswald, M. C., & Mohan, R. S. (2001). An efficient method for the chemoselective synthesis of acylals from aromatic aldehydes using bismuth triflate. *Tetrahedron Letters*, 42, 8133–8135.
- Chakarabarti, A. K., Thilagavathi, R., & Kumar, R. (2004). Copper(II) Tetrafluoroborate-catalyzed formation of aldehyde-1,1-diacetates. *Synthesis*, 6, 831–833.
- Choudhary, D., Paul, S., Gupta, R., & Clark, J. H. (2006). Catalytic properties of several palladium complexes covalently anchored onto silica for the aerobic oxidation of alcohols. *Green Chemistry*, 8, 479–482.
- Curini, M., Epifano, F., Marcotullio, M. C., Rosati, O., & Nocchetti, M. (2002). Preparation and deprotection of 1,1-diacetates (acylals) using zirconium sulfophenyl phosphonate as catalyst. *Tetrahedron Letters*, 43, 2709–2711.
- Deka, N., Kalita, D. J., Borah, R., & Sarma, J. C. (1997). Iodine as acetylation catalyst in the preparation of 1,1-diacetates from aldehydes. *The Journal of Organic Chemistry*, 62, 1563–1564.
- Firouzabadi, H., Iranpoor, N., Nowrouzi, F., & Amani, K. (2003). Aluminum dodecatungstophosphate (AlPW₁₂O₄₀) as an efficient heterogeneous inorganic catalyst for the chemoselective synthesis of geminal diacetates (acylals) under solvent-free conditions. *Tetrahedron Letters*, 44, 3951–3954.
- Frick, J. G., & Harper, R. J. (1984). Acetals as crosslinking reagents for cotton. *Journal of Applied Polymer Science*, 29, 1433–1447.
- Gao, S. T., Zhao, Y., Li, C., Ma, J. J., & Wang, C. (2009). NbCl₅ as an efficient Catalyst for chemoselective synthesis of 1,1-diacetates under solvent-free conditions. *Synthetic Communications*, 39, 2221–2229.
- Ghosh, R., Maiti, S., Chakraborty, A., & Halder, R. (2004). Indium triflate: a reusable catalyst for expeditious chemoselective conversion of aldehydes to acylals. *Journal of Molecular Catalysis A: Chemical*, 215, 49–53.
- Hajinasiri, R., & Rezayati, S. (2013). Solvent-free synthesis of 1,2-disubstituted derivatives of 1,2-dihydroisoquinoline, 1,2-dihydroquinoline and 1,2-dihydropyridine. *Z. Naturforsch.*, 68b, 818–822.
- Hajipour, A. R., Khazdooz, L., & Ruoho, A. E. (2008). Brønsted acidic ionic liquid as an efficient catalyst for chemoselective synthesis of 1,1-diacetates under solvent-free conditions. *Catalysis Communications*, 9, 89–96.
- Hajipour, A. R., Zarei, A., & Ruoho, A. E. (2007). P₂O₅/Al₂O₃ as an efficient heterogeneous catalyst for chemoselective synthesis of 1,1-diacetates under solvent-free conditions. *Tetrahedron Letters*, 48, 2881–2884.
- Heerden, F. R. V., Huyser, J. J., Bradley, Williams, B. D., & Holzappel, C. W. (1998). Palladium-catalysed substitution reactions of geminal allylic diacetates. *Tetrahedron Letters*, 39, 5281–5284.
- Heravi, M. M., Bakhtiari, K., Taheri, S., & Oskooie, H. A. (2005). KHSO₄: a catalyst for the chemo-selective preparation of 1,1-diacetates from aldehydes under solvent-free conditions. *Green Chemistry*, 7, 867–869.
- Kang, L. Q., Cai, Y. Q., & Cheng, L. (2013). Solvent-free catalytic preparation of 1,1-diacetates using a silica-supported functional ionic liquid as catalyst. *Monatshfte für Chemie / Chemical Monthly*, 144, 247–249.
- Kannasani, R. K., Satyanarayana Peruri, V. V., & Battula, S. R. (2012). NaHSO₄-SiO₂ as an efficient and chemoselective catalyst, for the synthesis of acylal from aldehydes under solvent-free conditions. *Chemistry Central Journal*, 6, 136–139.
- Karimi, B., & Ghoreishi-Nezhad, M. (2007). Highly chemoselective acetalization of carbonyl compounds catalyzed by a novel recyclable ammonium triflate-functionalized silica. *Journal of Molecular Catalysis A: Chemical*, 277, 262–265.
- Karimi, B., Seradj, H., & Ebrahimian, G. R. (2000). Mild and efficient conversion of aldehydes to 1,1-diacetates catalyzed with *N*-Bromosuccinimide (NBS). *Synlett*, 5, 623–624.
- Khan, A. T., Choudhury, L. H., & Ghosh, S. (2006). Silica supported perchloric acid (HClO₄-SiO₂): A highly efficient and reusable catalyst for geminal diacylation of aldehydes under solvent-free conditions. *Journal of Molecular Catalysis A: Chemical*, 255, 230–235.
- Kochhar, K. S., Bal, B. S., Deshpande, R. P.,

- Rajadhyaksha, S. N., & Pinnick, H. W. (1983). Protecting groups in organic synthesis. Part 8. Conversion of aldehydes into geminal diacetates. *Journal of Organic Chemistry*, 48, 1765–1767.
- Li, Y. Q. (2000). A Rapid and Convenient Synthesis of 1,1-Diacetates from Aldehydes and Acetic Anhydride Catalyzed by PVC-FeCl₃ Catalyst. *Synthetic Communications*, 30, 3913–3917.
- Li, T. S., Zhang, Z. H., & Gao, Y. J. (1998). A rapid preparation of acylals of aldehydes catalysed by Fe³⁺ montmorillonit. *Synthetic Communications*, 28, 4665–4672.
- Liu, Q., Ai, H. M., & Feng, S. (2012). Ultrasound-Assisted synthesis of acylals from aldehydes using Mg(CH₃SO₃)₂-HOAc. *Synthetic Communications*, 42, 122–127.
- Li, Z., Ma, X., Liu, J., Feng, X., Tian, G., & Zhu, A. (2007). Silica-supported aluminum chloride: A recyclable and reusable catalyst for one-pot three-component Mannich-type reactions. *Journal of Molecular Catalysis A: Chemical*, 272, 132–135.
- Melero, J. A., Grieken, R. V., & Morales, G. (2006). Advances in the synthesis and catalytic applications of organosulfonic-functionalized mesostructured materials. *Chemical Reviews*, 106, 3790–3812.
- Nagy, N. M., Jakab, M. A., Konya, J., & Antus, S. (2002). Convenient preparation of 1,1-diacetates from aromatic aldehydes catalysed by zinc-montmorillonite. *Applied Clay Science*, 21, 213–216.
- Nouri-Sefat, M., Deris, A., & Niknam, K. (2011). Preparation of silica-bonded propyl-diethylene-triamine-*N*-sulfamic acid as a recyclable catalyst for chemoselective synthesis of 1,1-diacetates. *Chinese Journal of Chemistry*, 29, 2361–2367.
- Pourmousavi, S. A., & Zinati, Z. (2009). H₂SO₄-silica as an efficient and chemoselective catalyst for the synthesis of acylal from aldehydes under solvent-free conditions. *Turkish Journal of Chemistry*, 33, 385–392.
- Reddy, A. V., Ravinder, K., Reddy, V. L. N., Ravikanth, V., & Yenkaeswarlu, Y. (2003). Amberlyst-15-catalyzed efficient synthesis of 1,1-diacetates from aldehydes. *Synthetic Communications*, 33, 1531–1536.
- Rezayati, S., Erfani, Z., & Hajinasiri, R. (2015). Phospho sulfonic acid as efficient heterogeneous Brønsted acidic catalyst for one-pot synthesis of 14 - dibenzo[a,j]xanthenes and 1,8-dioxo-octahydro-xanthenes. *Chemical Papers*, 69, 536–543.
- Rezayati, S., Hajinasiri, R., Erfani, Z., Rezayati, S., & Afshari-sharifabad, S. (2014). Boric acid as a highly efficient and reusable catalyst for the one-pot synthesis of 1,8-dioxo-octahydroxanthenes under solvent-free conditions. *Iranian Journal of Catalysis*, 4, 157–162.
- Rezayati, S., & Sajjadifar, S. (2014). Recyclable boron sulfonic acid as an environmentally benign catalyst for the One-pot synthesis of coumarin derivatives under solvent-free condition. *Journal of Sciences, Islamic Republic of Iran*, 25, 329–337.
- Romanelli, G. P., Thomas, H. J., Baronetti, G. T., & Autino, J. C. (2003). Solvent-free catalytic preparation of 1,1-diacetates from aldehydes using a Wells-Dawson acid (H₆P₂W₁₈O₆₂·24H₂O). *Tetrahedron Letters*, 44, 1301–1303.
- Roy, S. C., & Banerjee, B. (2002). A mild and efficient method for the chemoselective synthesis of acylals from aldehydes and their deprotections catalysed by ceric ammonium nitrate. *Synlett*, 10, 1677–1688.
- Snider, B. B., & Amin, S. G. (1978). An international journal for rapid communication of synthetic organic chemistry. *Synthetic Communications*, 8, 117–125.
- Saini, A., Kumar, S., & Sandhu, J. S. (2007). RuCl₃·xH₂O: A new efficient catalyst for facile preparation of 1,1-diacetates from Aldehydes. *Synthetic Communications*, 38, 106–113.
- Sajjadifar, S., & Rezayati, S. (2014). Synthesis of 1,1-diacetates catalysed by silica-supported boron sulfonic acid under solvent-free conditions and ambient temperature. *Chemical Papers*, 68, 531–539.
- Sandberg, M., & Sydnes, L. K. (1998). The chemistry of acylals. Part II. Formation of nitriles by treatment of acylals with trimethylsilyl azide in the presence of a Lewis acid. *Tetrahedron Letters*, 39, 6361–6364.
- Sandberg, M., & Sydnes, L. K. (2000). The chemistry of acylals. 3. Cyanohydrin esters from acylals with cyanide reagents. *Organic Letters*, 2, 687–689.
- Shelke, K., Sapkal, S., Kategaonkar, A., Shingate, B., & Shingare, M. S. (2009). An efficient and green procedure for the preparation of acylals from aldehydes catalyzed by Alum [KAl(SO₄)₂·12H₂O]. *South African Journal of Chemistry*, 62, 109–112.
- Sydnes, L. K., & Sandberg, M. (1997). The chemistry of acylals. Part I. The reactivity of acylals towards grignard and organolithium reagents. *Tetrahedron*, 53, 12679–12690.
- Wu, H., Wan, Y., Chen, X., Chen, C., Lu, L., Xin, H., Xu, H., Pang, L., Ma, R., & Yue, C. J. (2009). Synthesis of 2,4,5-triaryl-5*H*-chromeno[4,3-*b*]pyridines under microwave radiation. *Journal of Heterocyclic Chemistry*, 46, 702–707.
- Yadav, J. S., Reddy, B. V. S., & Premalatha, K. (2003). 1-Butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF₄) Ionic Liquid: A Novel and recyclable reaction medium for the synthesis of Vic-Diamines. *Advanced Synthesis & Catalysis*, 345, 948–952.
- Yadav, J. S., Reddy, B. V. S., & Srihari, P. (2001). A facile synthesis of homoallyl ethers and acetates. *Synlett*, 5, 673–675.
- Zareyee, D., Moosavi, S. M., & Alaminezhad, A. (2013). Chemoselective synthesis of geminal diacetates (acylals) using eco-friendly reusable propylsulfonic acid based nanosilica (SBA15-Ph-PrSO₃H) under solvent-free conditions. *Journal of Molecular Catalysis A: Chemical*, 378, 227–231.