Journal of Applied Chemistry JAC http://chemistry.journals.semnan.ac.ir

A rapid and green synthesis of 1,1-diacetates from aldehydes catalyzed by triethylamine-bonded sulfonic acid $[Et_3N–SO_3H]Cl$

Mehrnoosh Golmohammadi Afkham, Ali Elhampour, Firouzeh Nemati*

Department of Chemistry, Semnan University

Article history:
Received:12/Jul/2015
Received in revised form:13/Aug/2015
Accepted:19/Aug/2015

Abstract

Bronsted acidic ionic liquid, $[Et_3N–SO_3H]Cl$, catalyzed the reaction of acetic anhydride with aryl aldehydes under solvent-free condition. Various 1,1-diacetates are obtained using 15 mol% of triethylamine-bonded sulfonic acid in satisfactory to excellent yields in very short reaction times at ambient temperature. Different groups including electron donating or electron withdrawing groups linked to benzene ring such as methyl, chloro, nitro and methoxy were tolerated under the optimized reaction conditions. This ionic liquid was air stable and easily prepared from accessible amine and chlorosulfonic acid. The present report is a green protocol as it eliminates the need of an organic solvent. Very short reaction times, high yields, simple operational procedure and green conditions are merits of this methodology.

Keywords: Acylal; Bronsted acidic ionic liquid; Solvent-free; Acetic anhydride.

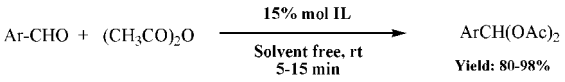
*. **Corresponding Author:** *E-mail address: fnemati_1350@yahoo.com; Tel.: +(98) 2333383171*

1. Introduction

Selective protection of carbonyl functionality from undesirable attacks during the multi-step synthesis is gaining importance in modern organic chemistry nowadays. A facile and efficient method for protection of carbonyl compound is formation of 1,1-diacetates as an useful protective group, has attracted substantial attention in the past decade for protection of aldehydes [1]. Diacetates (acylals) are important because they are synthetically useful precursors for some reactions [2, 3] or have been applied as a crosslinking reagents [4]. The relative moderate stability of acylals to neutral and basic condition [5-7] compared to corresponding acetals [8] and easy conversion into parent aldehyde [9-12] is another interesting feature in the field of protection and deprotection chemistry.

Acylals are usually synthesized from aldehydes and acetic anhydride using strong proton acids as catalysts, typically such as methane sulfonic acid [13] and phosphoric acid [14] or Lewis acids like zinc chloride [15] , WCl_6 [16], , I_2 [17] , $Sc(OTf)_3$ [18] , $Cu(OTf)_2$ [19], $LiBF_4$ [20]. Although some of these methods present an efficient procedure with good to excellent yields, but most of the currently available methods suffer from at least one disadvantages such as strong acidic condition, difficulty in the preparation of the catalyst, use of sensitive and expensive catalysts, tedious work up and effluent pollution or requirement for long reaction time, either low yield and so on. Therefore the discovery of an alternative catalyst that works for the efficient conversion of aldehydes into acylals is desirable.

Ionic liquids, a new class of eco-friendly catalysts and reagents in green modern synthesis [21-23] and biochemical transformations [24], have attracted expanding interest in the last decade for chemists because of their unique physio-chemical properties such as their purity, low volatility, non-flammability, high thermal and chemical stability, extremely low vapor pressure, reusability and ability to dissolve a wide range of organic and inorganic materials [25-29]. They also have various applications such as sensors, fuel cells, batteries, capacitors, thermal fluids, plasticizers, lubricants and extractants [30]. Therefore, the exploring the inexpensive and easily prepared ionic liquids in organic synthesis are prime of importance. Recently, Zolfigol et al. have been synthesized the acidic Bronsted ionic liquid triethylamine-bonded sulfonic acid, $[Et_3N–SO_3H]Cl$, *via* a simple and atom economic reaction from inexpensive amine and chlorosulfonic acid [31]. The use of acidic Bronsted ionic liquids (ABILs) are of special importance for the cases in which the proton acidity and the characteristic properties of an ionic liquid are coupled. This ionic liquid has been proved to be the excellent catalyst for some organic transformations [32]. However to the best of our knowledge, the synthesis of 1,1-diacetates using $[Et_3N–SO_3H]Cl$ has not been explored yet. Therefore, in continuation of our work on developing an environmentally friendly preparative method for organic transformations [33-36], we report herein the convenient synthesis of 1,1-diacetates using {$[Et_3N–SO_3H]Cl$} as green, efficient and recyclable catalyst under solvent-free conditions (scheme 1).



Scheme 1. Reaction condition.

2. Experimental procedure

2.1. Preparation of $[Et_3N–SO_3H]Cl$

A solution of triethylamine (0.50 g, 5 mmol) in CH_2Cl_2 (40 mL) was added dropwise to a stirring solution of chlorosulfonic acid (0.58 g, 5 mmol) in dry CH_2Cl_2 (40 mL) over a period of 10 min at 10 °C. Afterward, the reaction mixture was allowed to heat to room temperature (accompanied with stirring), and stirred for another 4 h. The solvent was evaporated under reduced pressure, and the liquid residue was triturated with diethyl ether (3×10 mL) and dried under powerful vacuum at 90 °C to give $[Et_3N–SO_3H]Cl$ as a viscous pale yellow oil in 96% yield [31].

2.2. General procedure for the synthesis of acylals derivatives

In a 25 mL flask, a mixture of aldehyde (1 mmol), freshly excess distilled acetic anhydride (5 mmol) and $[Et_3N–SO_3H]Cl$ (0.033g, 0.15 mmol) was stirred at room temperature under solvent-free conditions for an appropriate time (Table 2). After completion of the reaction as monitored by TLC; EtOAc (10 mL) was added to the reaction mixture and stirred for 10 min. The organic phase washed with aqueous $NaHCO_3$ and dried over anhydrous Na_2SO_4. The organic solvent was evaporated on a rotary evaporator under reduced pressure to give the pure acylals. Some of the products with lower purity were further purified using flash column chromatography (eluent: ethylacetate/hexane, 1:8).

Table 1. Optimization of amount of acetic anhydride and catalyst in model reaction.[a]

Entry	Condition	Acetic anhydride (mmol)	$[Et_3N-SO_3H]Cl$ (mol%)	Yield[b] (%)
1	Solvent-free	1	10	45
2	Solvent-free	1	15	49
3	Solvent-free	1	20	30
4	Solvent-free	3	10	56
5	Solvent-free	3	15	80
6	Solvent-free	3	20	59
7	Solvent-free	5	10	79
8	Solvent-free	5	15	93
9	Solvent-free	5	20	81
10	H_2O	5	15	trace
11	EtOH	5	15	trace
12	MeOH	5	15	trace
13	CH_3CN	5	15	trace
14	THF	5	15	trace
15	Toluene	5	15	trace
16	Solvent free	5	-	-

[a] Reaction condition: 3-nitobenzaldehyde (1 mmol), acetic anhydride, $[Et_3N–SO_3H]Cl$, solvent-free, room temperature, 9 minute.
[b] Isolated yield

2.3. The spectral data of selected compounds

Table 2, entry 2 [36]: M.p. 50-52°C; IR cm^{-1} (KBr): 3065, 3015, 1756; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.80 (s, 1H), 7.38-7.19 (m, 4H), 2.02 (s, 6H).

Table 2, entry 6 [38]: M.p. 124-126°C; IR cm^{-1} (KBr): 2955, 1763, 1622; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.27 (d, J = 7.9 Hz, 2H), 7.70 (d, J = 7.9 Hz, 2H), 7.48 (s, 1H), 2.15 (s, 6H).

Table 2, entry 11 [35]: M.p. 77-79°C; IR cm^{-1} (KBr): 2955, 1776, 1744; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.75 (s, 1H), 7.48 (d, J = 8.2 Hz, 2H), 7.19 (d, J = 8.2 Hz, 2H), 2.45 (s, 3H), 2.17 (s, 6H).

3. Results and discussion

Triethylamine-bonded sulfonic acid, $[Et_3N–SO_3H]Cl$, has been synthesized by one step according the reported procedure[31]. Initially, in order to get the optimum loading of the catalyst and amount of acetic anhydride, the reaction of 3-nitrobenzaldehyde (1 mmol) and acetic anhydride was performed in room temperature by varying the amount of catalyst and acetic anhydride in solvent free condition at room temperature (Table 1, entries1-9).

For exploring the role of solvent, the model reaction was performed using 5 mmol acetic anhydride and 15 mol% of catalyst in different solvents at room temperature. Among the various solvents tested, along 9 minutes, no products were obtained (Table 1, entries10-15). In addition, no target product could be detected in the absence of a catalyst (Table 1, entry 16). Therefore, we have been employed 15 mol% $[Et_3N–SO_3H]Cl$ and 5 mmol acetic anhydride for the synthesis of acylals from various aldehydes under solvent-free conditions at room temperature (Table 2).

In order to study the scope of the application of $[Et_3N–SO_3H]Cl$, a range of aryl aldehydes were examined under the optimized conditions. A variety of arylaldehydes with electron-withdrawing and electron-donating groups at *ortho*, *meta* and *para* positions were successfully transformed in to the desired acylal product with good to excellent yield under the optimized reaction conditions. The reactions proceed fast and clean. Furthermore, there is not much difference in yield or time of the reaction with different substituted benzaldehydes as evident from the Table 2. Only the aldehyde with powerful electron donating group (Table 2, entry 15) was not converted to the corresponding acylal [37].

Table 2. Synthesis of acylales derivatives.

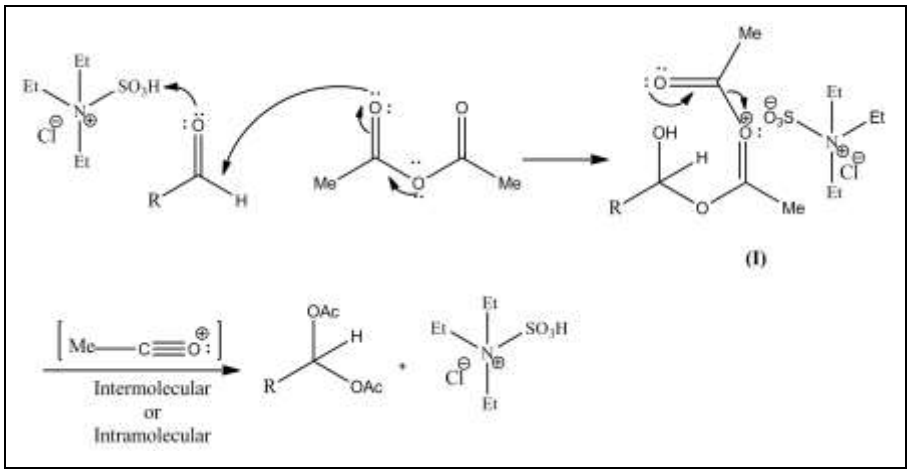
Entry	Substrate	Time (min)	Yield (%)[a]	Mp.°C(Lit.)
1	C_6H_5CHO	5	95	40.42 (42-43) [38]
2	2-Cl-C_6H_4CHO	5	90	50-52 (51-52) [39]
3	4-Cl-C_6H_4CHO	5	90	78.5-79.5 (78.9-80.1) [40]
4	2,4-$Cl_2C_6H_3CHO$	6	97	98-99.5 (99-100) [39]
5	3-NO_2-C_6H_4CHO	9	93	65-66 (65-66) [41]
6	4-NO_2-C_6H_4CHO	15	95	124-126 (124-126) [41]
7	4-Br-C_6H_4CHO	5	95	91-92.5 (92-95) [42]
8	4-F-C_6H_4CHO	5	92	49-51 (50-51) [43]
9	2-MeO-C_6H_4CHO	12	90	66-68 (68-70) [44]
10	4-MeO-C_6H_4CHO	10	95	61-63 (62-63 [45]
11	4-Me-C_6H_4CHO	12	89	77-79 (80-81) [38]
12	2-OH-C_6H_4CHO [b]	15	91	oil (103-104) [45]
13	3-MeO-4-OH-C_6H_3CHO [b,c]	15	98	77-79 (79-80) [46]
14	2-naphthylCHO	5	85	100-101 (100-101) [41]
15	4-$(Me)_2N$- C_6H_4CHO	120	no reaction	-
16	$C_6H_5COCH_3$	120	no reaction	-

[a] Isolated yield
[b] The hydroxyl group was also acylated.
[c] This reaction progressed in 110°C.

It was observed that due to chemoselectivity of the catalyst the competitive reaction for acylation of benzaldehyde in the presence of acetophenone, produced phenylmethylene diacetate as the sole product and no acylation was observed for acetophenone (Table 2, entry 16).

A plausible mechanism for the synthesis of acylal derivatives by {$[Et_3N–SO_3H]Cl$ is shown in Scheme 2. As $[Et_3N–SO_3H]Cl$ is a protic ionic liquid, therefore initially the arylaldehydes got protonated. It facilitated the nucleophilic attack of acetic anhydride for formation of intermediate I. Finally, intermediate **I** reacts with acylium ion, followed by proton transfer to afford the product, and ionic liquid regenerated.

To show the superiority of $[Et_3N–SO_3H]Cl$, the efficiency of this ionic liquid was compared with that of other ionic liquids reported earlier for synthesis of 1,1-diacetates. The data summarized in Table 3, show the advantages of this method in terms of reaction rate and yield as compared with those reported in the literature. Furthermore, our results also suggest that, the present catalyst is more advantageous from the economical and accessibility point of view.



Scheme 2. A plausible mechanism

Table 3. Comparison of ionic liquids used as catalysts for synthesis of phenylmethylene diacetate

Entry	Ionic liquids	Condition	Time(min)	Yield (%)	Ref.
1	$[Hmim]HSO_4$[a]	Rt, neat	25 min	90	47
2	$[bmim][FeCl_4]$[b]	Rt, neat	40 min	89	48
3	$[bmim][BF_4]$	Rt, H_2O	4.5 h	96	49
4	$([bmpy]HSO_4)$[c]	30ºC, ultrasonic	5 min	97	50
5	$[Et_3N–SO_3H]Cl$	Rt, neat	5 min	95	This work

[a] 1-H-3-methyl-imidazolium hydrogen sulfate
[b] 1-methyl-3-butyl imidazolium chloroferrate
[c] 1-butyl-3-methylpyridinium hydrogen sulphate
[d] 1-butyl-3-methylpyridinium hydrogen sulphate

4. Conclusions

In summary, we have described an efficient catalyst, which provides a general and rapid strategy for the synthesis of 1,1-diactate derivatives with good yields in a short reaction times. The simple preparation of catalyst makes the present method a highly attractive approach to acylal synthesis. Advantages of this methodology include the mild conditions, easy work-up and short reaction times.

5. Acknowledgements

We thank the Department of Chemistry and office of gifted student at Semnan University for their financial support.

References

[1] T.W. Greene and P.G. M. Wuts, Protective Groups in Organic Synthesis, 3rd edn. (John Wiley, New York, 1999), pp. 306-307.

[2] B.B. Sinder, S.G. Amin, Synth. Commun. **8**, 117 (1978).

[3] F. Ullmann, W. Gerhartz, Y.S. Yamamoto, F.T. Campbell, R. Pfefferkorn and J.F Rounsaville, Ullman's Enclycopedia of Industrial Chemistry, 5th edn. (John Wiley VCH, New York, 1985) Vol. A1, pp. 68.

[4] J.G. Frick and R.J. Harper, *J. Appl. Polymer Sci*. **29** (1984) 1433.

[5] M.A. Zolfigol, M.H. Zebarjadian, I. Mohammadpoor-Baltork and M. Shamsipur, *Synth. Commun*. **32** (2002) 2803.

[6] I. Mohammadpoor-Baltork and H. Aliyan, *Synth. Commun*. **29** (1999) 2741.

[7] I. Mohammadpoor-Baltork and H. Aliyan, *J. Chem. Res. (Synop)* (1999) 272.

[8] K. S. Kochhar, B. S. Bal, R. P. Deshpande, S. N. Rajadhyaksha and H. W. Pinnick, *J. Org. Chem*. **48** (1983) 1765.

[9] J. Kula, *Synth. Commun*. **16** (1986) 833.

[10] M. J. Gregory, *J. Chem. Soc*. *B.* (1970) 1201.

[11] E. R. Perez, A. L. Marrero, R. Perez and M. A. Autie, *Tetrahedron Lett.* **36** (1995) 1779.

[12] Y. Y. Ku, R. Patel and D. Sawick, *Tetrahedron Lett.* **34** (1993) 8037.

[13] M. Tomita, T. Kikuchi, K. Bessho, T. Hori and Y. Inubushi, *Chem. Pharm. Bull.* **11** (1963) 1484.

[14] F. Freeman and E. M. Karchefski, *J. Chem. Eng. Data* **22** (1977) 355.

[15] J.K. Michie, J.A. Miller, *Synthesis*, **10** (1981) 824.

[16] B. Karimi, G.R. Ebrahimian and H. Seradj, *Synth. Commun*. **32** (2002) 669.

[17] N. Deka, D.J. Kalita, R. Borah, J.C. Sarma, J. Org. Chem. **62** (1997)1563.

[18] V. K. Aggarwal, S. Fonquerna, G.P. Vennall, *Synlett*, **8** (1998) 849.

[19] K.L. Chandra, P. Saravanan, V.K. Singh, *Synlett*, **3** (2000) 359.

[20] J.S. Yadav, B.V.S. Reddy, C.Venugopal, T. Ramalingam, *Synlett*, **4** (2002) 604.

[21] T. Welton, *Chem. Rev*. **99** (1999) 1991.

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

[23] J.D. Holbrey, K.R. Seddon, *Clean. Prod. Process*. **1** (1999) 223.

[24] N. Jain, A. Kumar, S. Chauhan, S.M.S. Chauhan, *Tetrahedron* **61** (2005) 1015.

[25] J. Pavlinac, M. Zupan, K.K. Laali, S. Stavber, *Tetrahedron* **65** (2009) 5625.

[26] D. Saha, A. Saha, B.C. Ranu, *Tetrahedron Lett*. **50** (2009) 6088.

[27] A. Zare, A.R. Moosavi-Zare, A. Hasaninejad, A. Parhami, A. Khalafi-Nezhad, M.H.Beyzavi, *Synth. Commun*. **39** (2009) 3156.

[28] A. Zare, A. Parhami, A.R. Moosavi-Zare, A. Hasaninejad, A. Khalafi-Nezhad, M.H. Beyzavi, *Can. J. Chem*. **87** (2009) 416.

[29] A. Hasaninejad, A. Zare, M. Shekouhy, J. Ameri Rad, *J. Comb. Chem*. **12** (2010) 844.

[30] Z. N. Siddiqui, K. Khan, *Sustainable Chem. Eng.* **2** (2014) 1187.

[31] A. Zare, A.R. Moosavi-Zare, M. Merajoddin, M.A. Zolfigol, T. Hekmat-Zadeh, A. Hasaninejad, A. Khazaei, M. Mokhlesi, V. Khakyzadeh, F. Derakhshan-Panah, M.H. Beyzavi, E. Rostami, A. Arghoon, R. Roohandeh, *J. Mol. Liq*. **167** (2012) 69.

[32] A. Zare, F. Bahrami, M. Merajoddin, M. Bandari, A.R. Moosavi-Zare, M.A. Zolfigol, A.R Hasaninejad, M. Shekouhy, M.H. Beyzavi, V. Khakyzadeh, M. Mokhlesi, Z. Asgari, *Org. Prep. Proced. Int.* **45** (2013) 211.

[33] F. Nemati, S. Sabaqian, *J. Saudi. Chem. Soc*. (2014) DOI: 10.1016/j.jscs.2014.04.009

[34] F. Nemati, M.G. Afkham, A. Elhampour, *Green Chem. Lett. Rev*. **7** (2014) 79.

[35] F. Nemati, A. Elhampour, *J. App. Chem.* ***23*** *(2012) 29.*

[36] F. Nemati, A. Elhampour, *J. App. Chem.* ***26*** *(2013) 21*..

[37] F. Shirini, O. G. Jolodar, *J. Mol. Catal. A* **356** (2012) 61.

[38] A.R. Hajipour, A. Zarei, A.E Ruoho, *Tetrahedron Lett*. **48** (2007) 2881.

[39] L. Q. KangCai, Y. Q. Cheng, L. *Monatsh Chem*. **144** (2013) 247.

[40] T. S. Jin, G. Sun, Y. W. Li, T. S. Li, *Green Chem*. **4** (2002) 255.

[41] A. T. Khan, L. H. Choudhury, S. Ghosh, *J. Mol. Catal. A: Chem*. **255** (2006) 230.

[42] N.M. Nagy, M.A. Jakab, J. Konya, S. Antus, *Appl. Clay Sci*. **21** (2002) 213.

[43] Yin, L.; Zhang, Z. H.; Wang, Y. M.; Pang, M. L. *Synlett.* **10** (2004) 1727.

[44] A. Saini, S. Kumar, S. Sandhu, J. *Synth. Commun* **38** (2007) 106.

[45] B.R. Jermy, A. Pandurangan, *Catal. Commun*. **9** (2008) 577.

[46] F. Freeman, E. M. Karcherski, *J. Chem. Eng. Data* **22** (1977) 355.

[47] A. R. Hajipour, L. Khazdooz, A.E. Ruoho, *Catal. Commun.* **9** (2008) 89.

[48] D.S. Wanga, G.Y. Lib, Y.Q. Peng, *J. Chin. Chem. Soc.* **56** (2009) 834.

[49] J.S. Yadav, B.V.S. Reddy, P. Sreedhar, G. Kondaji, K. Nagaiah, *Catalysis Commun*. **9** (2008) 590.

[50] S. P. Borikar, T. Daniel, *Ultrason. Sonochem.* **18** (2011) 928.