

4-Dodecylbenzenesulfonic acid (DBSA): an efficient, eco-friendly and chemoselective catalyst for the synthesis of 1, 1- diacetates under solvent-free conditions at room temperature

M. Esmailpour and A. Z. Sardarian*

Chemistry Department, College of Science, Shiraz University, Shiraz 71454, Iran
E-mail: sardarian@susc.ac.ir

Abstract

4-Dodecylbenzenesulfonic acid (DBSA) has been shown to be an efficient, mild, green, stable and chemoselective Brønsted acid catalyst for the synthesis of 1, 1-diacetates (acylals) of aldehydes under solvent-free conditions. The mild condition, eco-friendly, excellent yields, short reaction times and using an easily available, inexpensive and reusable catalyst are important features of this method.

Keywords: 4-Dodecylbenzenesulfonic acid; solvent-free; chemoselective; 1,1-Diacetates; aldehydes; acetic anhydride

1. Introduction

Selective protection of the carbonyl group plays an important role in the multistep organic synthesis of complex compounds [1]. There are many available reagents for protection of aldehydes in organic synthesis. 1, 1-Diacetates are one useful carbonyl-protecting group because of their stability under both neutral and basic media and under acidic conditions [2]. Furthermore, chemoselective preparations of the 1, 1-diacetates in the presence of ketones have been reported [3-4]. Acetals are also efficient chiral auxiliary groups for enantioselective synthesis [1, 5]. Due to stability of 1,1-diacetates toward a variety of reaction conditions, geminal diacetates have been used as important building blocks for aldehydes and have played important roles in organic synthesis[6-9]. The preparation of acylals has been achieved by the reaction of aldehydes with Ac_2O under different acid catalysts such as FeCl_3 [2], PCl_3 [10], SbCl_3 [11], ZnCl_2 [12], $\text{FeCl}_3/\text{SiO}_2$ [13], CoCl_2 [14], WCl_6 [15], InCl_3 [16], $\text{Cu}(\text{OTf})_2$ [17], $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ [18], $\text{Sc}(\text{OTf})_3$ [19], $\text{Bi}(\text{OTf})_3 \cdot x\text{H}_2\text{O}$ [20], LiBF_4 [21], strong protic acids such as $\text{H}_2\text{NSO}_3\text{H}$ [22], H_3PO_4 , H_2SO_4 , $\text{CH}_3\text{SO}_3\text{H}$ [23] and other types of catalysts such as HY- [24], β -Zeolite (50 wt %) [25], PEG-Supported sulfonic acid [26], Saccharin sulfonic acid [27], Silica-bonded S-sulfonic acid [28], Silica sulfuric acid [29], Silica Phosphoric Acid [30], $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{MCM-41}$ (20 wt %) [31] and Amberlyst-15 [32]. Although some

of these methods have convenient protocols with good to high yields, the majority of these methods are associated with drawbacks involving the use of halogenated solvents, low chemoselectivity, high temperature, strong acidic conditions, tedious procedure for the preparation of catalyst, long reaction times, moisture sensitivity of the catalyst, high toxicity, low yield and lack of substrate tolerance. While triflates such as $\text{Cu}(\text{OTf})_2$ and $\text{Sc}(\text{OTf})_3$ have recently emerged as the most effective catalysts for the reaction, the high cost and susceptibility to aqueous medium of the metal triflates do not make them good contenders for use in synthesis.

Therefore, the development of a more efficient alternative method that is suitable, mild, selective, faster, clean, noncorrosive and environmentally benign and has a better yield is of interest.

Dodecylbenzenesulfonic acid (DBSA), an anionic surfactant, can act as a combined Brønsted acid-surfactant-catalyst (BASC). It performs the dual role of both an acid catalyst to activate the substrate molecules and a surfactant to increase the concentration of organic reactants by forming micellar aggregates in water [33].

DBSA have been used in chemical synthesis such as synthesis of xanthenes [34, 35], bis(indol-3-yl)alkane derivatives [36], carbon-carbon bond-forming reactions [37], reaction of homoallyl alcohols and aldehydes in water [38], *N*-alkylation of aldoximes [39], synthesis of tetrahydrobenzopyrans [40], dehydration reactions in water [41], Thia-Michael addition reactions [42] and cyclotrimerization of acetophenones [35].

*Corresponding author

Received: 6 August 2012 / Accepted: 18 May 2013

Herein, we hope to introduce an efficient, catalytic, rapid, stable and high-yielding protocol for the acylal synthesis by DBSA, which is an amphiphathic Brønsted acid, commercially available, highly reactive, cheap, stable, and an emulsifier and activator of the molecule surface [33].

2. Experimental

2.1. General

All chemicals were purchased from Merck or Fluka Chemical Companies. The known products were identified by comparison of their melting points, spectral data. NMR spectra were recorded on a Bruker Avance DPX-250 (1H NMR 250 MHz and ¹³C NMR 63 MHz) spectrometer in DMSO-*d*₆, using TMS as an internal standard. IR spectra were obtained using a Shimadzu FT-IR 8300 spectrophotometer. Melting points were determined in open capillary tubes in a Büchi-545 circulating oil melting point apparatus.

2.2 General Procedure for Preparation of 1, 1-Diacetates

To a mixture of aldehyde (1 mmol) and acetic anhydride (3 mmol), DBSA (0.2 mmol) was added and the mixture was stirred at room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction, CH₂Cl₂ (10 mL), saturated NaHCO₃ (10mL) and water (10 mL) were added, and the organic layer was extract from aqueous layer and washed twice with water (2×10 mL). Further purification by column chromatography on silica gel afforded the pure 1, 1-diacetate. Aqueous layer was acidified by HCl (5%, 15mL) and then Et₂O (10 mL) was added. DBSA catalyst was recovered by extraction of this acidic solution and evaporation of diethyl ether under reduced pressure. It is noteworthy that DBSA could be reused without significant decrease in activity.

2.3 Selected spectral data

Diacetoxy-1-(phenyl) methane: White solid, melt point: 42–44 °C.

¹H-NMR (250MHz, CDCl₃): δ = 1.92 (s, 6H, CH₃), 7.30-7.46 (m, 5H, Ar-H), 7.67 (s, 1H, CH). ¹³C-NMR (63MHz, CDCl₃): δ = 20.7, 89.7, 126.5, 128.6, 129.7, 135.6, 168.6 ppm. IR (KBr): 1015, 1227, 1255, 1449, 1515, 1764, 2938, 3034, 3064 cm⁻¹.

Diacetoxy-1-(4-methylphenyl)methane: White solid, melt point: 80-82 °C.

¹H-NMR (250MHz, CDCl₃): δ = 2.11 (s, 6H, CH₃), 2.42 (s, 3H, CH₃), 7.26 (d, J = 17.5Hz, 2H, CH), 7.42 (d, J = 10Hz, 2H, CH), 7.71 (s, 1H, CH).

NMR (63MHz, CDCl₃): δ = 20.9, 21.3, 89.8, 126.6, 129.2, 132.8, 139.8, 168.8 ppm. IR (KBr): 817, 930, 963, 1008, 1075, 1209, 1233, 1755, 1765 cm⁻¹.

Diacetoxy-1-(3-nitrophenyl)methane: White solid, melt point: 63-65 °C.

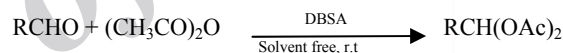
¹H-NMR (250MHz, CDCl₃): δ = 2.16 (s, 6H, CH₃), 7.61 (t, J = 5Hz, 1H, CH), 7.73 (s, 1H, CH), 7.82 (d, J = 7.5 Hz, 1H, CH), 8.25 (d, J = 7.5 Hz, 1H, CH), 8.40 (t, J = 2.5Hz, 1H). ¹³C-NMR (63MHz, CDCl₃): δ = 20.8, 88.4, 121.9, 124.6, 129.8, 133.0, 137.5, 148.2, 168.6 ppm. IR (cm⁻¹): 1008, 1362, 1443, 1547, 1773.

Diacetoxy-1-(cinnamyl)methane: White solid, melt point: 83-85 °C

¹H-NMR (250MHz, CDCl₃): δ = 2.15 (s, 6H, CH₃), 6.24 (dd, J = 18.6 Hz, 1H, CH), 6.83 (d, J = 18.6 Hz, 1H, CH), 7.29–7.34 (m, 5H, ArH), 7.39 (d, J = 8.6 Hz, 1H, CH). ¹³C-NMR (63MHz, CDCl₃): δ = 20.8, 89.8, 121.8, 127.0, 128.7, 128.8, 135.2, 135.6, 168.6 ppm. IR (KBr): 673, 761, 1013, 1217, 1478, 1609, 1760, 2887, 2976, 3023.

3. Results and Discussion

In this protocol, we disclose the reaction of aldehydes with acetic anhydride to afford corresponding 1,1-diacetates (Scheme 1).



Scheme 1.

In an initial endeavor, we tried to convert 4-chlorobenzaldehyde (1 mmol) to the corresponding acylal by acetic anhydride (3 mmol) in the presence of various solvents and also under solvent-free condition at room temperature. When the reaction was carried out in various solvents such as EtOH, H₂O, CH₂Cl₂, MeCN, EtOAc and PEG-400, the corresponding acylal was afforded in less yields than under solvent-free conditions, and as shown in the Table 1 the solvent-free reaction gave the best results.

Table 1. Effect of solvent on the protection of 4-chlorobenzaldehyde with acetic anhydride catalyzed by DBSA

Entry	Solvent	Time (min)	Yield (%)
1	EtOH	25	15
2	H ₂ O	30	45
3	CH ₂ Cl ₂	8	80
4	MeCN	10	82
5	CH ₃ CO ₂ Et	8	83
6	PEG-400	30	61
7	Solvent-free	5	94

The effect of the catalyst loading on the reaction indicated that less than 0.2 mmol of DBSA led to incomplete acylation (Table 2, entries 1-4).

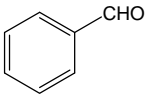
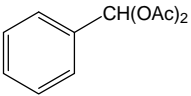
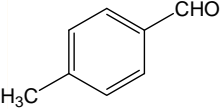
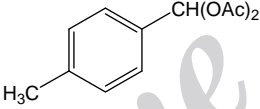
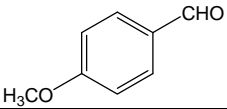
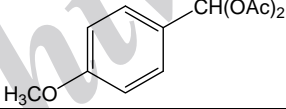
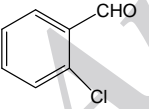
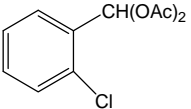
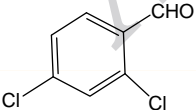
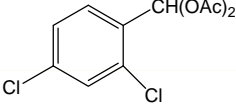
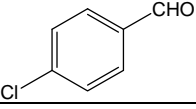
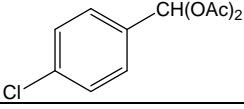
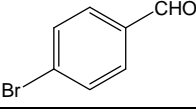
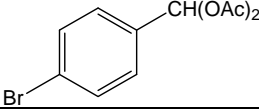
Excellent yield was obtained with 0.2 mmol of the catalyst with three equivalents of Ac_2O (Table 2, entry 5). No further increase in the yield was observed on increasing the amount of catalyst under the same condition (Table 2, entry 6).

Table 2. Conversion of 4-chlorobenzaldehyde to the corresponding 1, 1-diacetate with acetic anhydride in the presence of DBSA

Entry	Catalyst (mmol)	Time (min)	Yield (%)
1	No catalyst	360	0
2	0.05	30	36
3	0.1	20	62
4	0.15	10	81
5	0.2	5	94
6	0.3	8	83

To establish generality and versatility of the present method and to examine the tolerance of the other functional groups present in the substrates, diverse aldehydes including aromatic, α,β -unsaturated and aliphatic aldehydes compounds were subjected to acylal formation under optimized conditions in the presence of DBSA. The results were presented in Table 3.

Table 3. Conversion of various aldehydes to the corresponding 1,1-diacetates by DBSA^a

Entry	Substrate	Product	Time (min)	Yield (%) ^b	Mp. °C (Lit)	Ref.
1			5	94	42-44 (44-45)	[22]
2			4	96	80-82 (81-82)	[22]
3			5	96	63-64 (64-65)	[22]
4			8	88	57-59 (59)	[43]
5			10	90	87-89 (89)	[44]
6			5	92	81-83 (82-83)	[22]
7			6	93	91-93 (92-95)	[45]

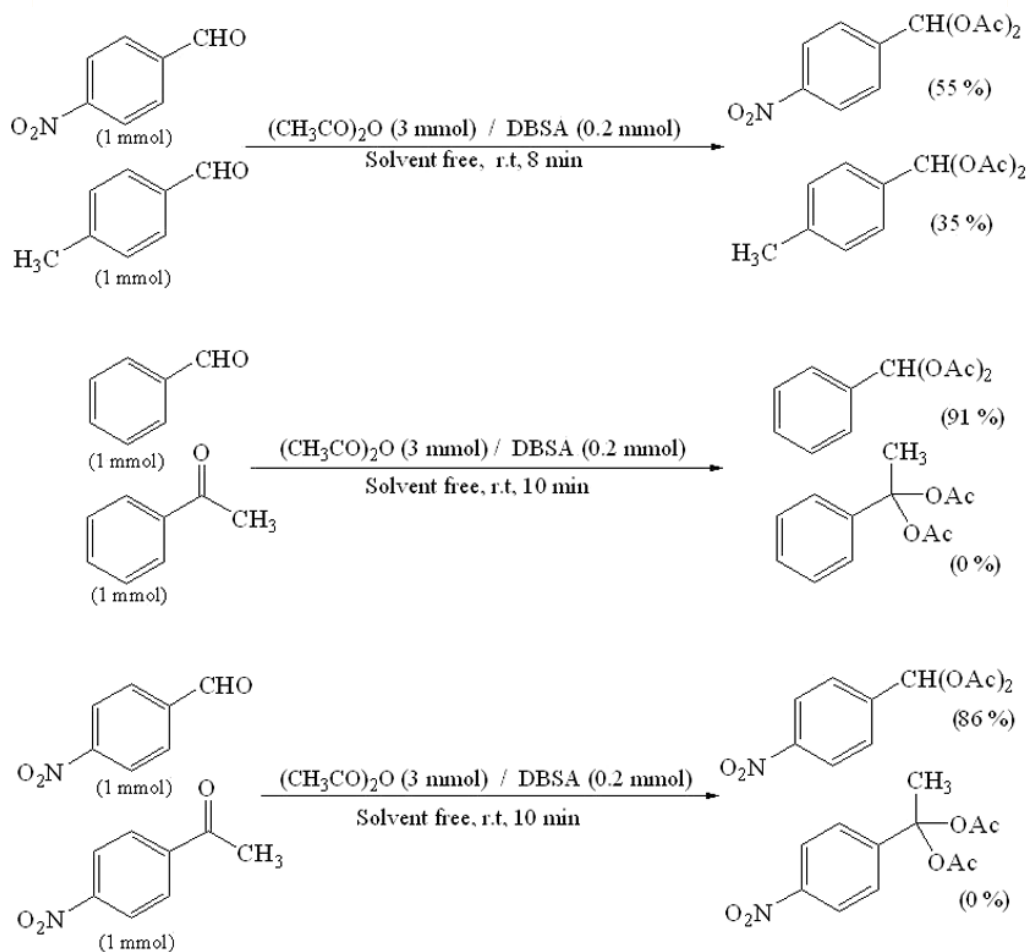
8			6	91	63-65 (65-66)	[22]
9			7	90	124-126 (125-27)	[22]
10			7	86	64-66 (66-67)	[46]
11			10	83	51-53 (52-53)	[22]
12			8	93	83-85 (84-85)	[46]
13			4	92	Oil	---
14			5	93	Oil	---
15			30	NR	---	---
16			30	NR	---	---
17			30	NR	---	---

^a Reaction condition: aromatic and aliphatic aldehydes (1 mmol), acetic anhydride (3 mmol), DBSA (0.2 mmol) at room temperature under solvent-free condition

^b The yields refer to the isolated pure products

The results indicated that the substitute groups of aromatic aldehyde, whether they were electron-donating or electron-withdrawing groups, had less effect on the efficiency of reaction (Table 3). Heterocyclic, α,β -unsaturated and Aliphatic aldehydes produced acylals in good yields (Table, entries 10-14). Acid-sensitive compounds such as 2-furylaldehyde, 2-thiophenecarboxaldehyde, and cinnamaldehyde are also protected as 1,1-diacetates in high yields without any side products (Table 3, entry 10-12). Under these reaction conditions, many functional groups such as methyl ether, bromo, nitro, and olefins are unaffected. Another advantage

of this protocol is that it does not require dry or inert reaction conditions. Ketones remain unreacted under these reaction conditions. Therefore, aldehydes can be chemoselectivity protected in the presence of ketones. To check the chemoselectivity of this reaction, an equimolar mixture of 4-nitrobenzaldehyde and 4-methyl benzaldehyde, benzaldehyde and acetophenone, and also 4-nitrobenzaldehyde and 4-nitroacetophenone were added to acetic anhydride (3 mmol) in the presence of DBSA (0.2 mmol) and stirred at room temperature for the appropriate time (Scheme 2).



Scheme 2. Competitive acylal formation reactions using Ac_2O in the presence of DBSA catalyst

Exclusively 1,1-diacetates of benzaldehyde and 4-nitrobenzaldehyde were obtained, and acetophenone and 4-nitroacetophenone remained because of the electron-donating ability and the steric effect of the methyl group (Scheme 2).

Comparing different aldehydes diacetylation reactions in the presence of acid catalysts indicates that the performance of these reactions in the presence of DBSA is much better compared to other acid catalysts because the key factor in such

chemical transformations is not the acid power, but it is the acid catalyst and activating the molecule surface that plays an important role in accelerating reactions. Also, the existence of polar and nonpolar hydrophobic groups in DBSA catalyst compared to similar catalysts such as PEG-supported sulfonic acid, saccharin Sulfonic acid, silica-bonded *s*-sulfonic acid, silica sulfuric acid and silica phosphoric acid caused these substances to be used as cleaner, emulsifier and activator of the molecule

surface [44]. Analyzing the reactions on Lewis acids such as sulphated zirconia, $\text{Fe}(\text{CH}_3\text{SO}_3)_2 \cdot 4\text{H}_2\text{O}$, β -zeolite, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and chloroacetylated polystyrene-supported Zinc

complexes lead to harsh conditions, long times and using organic solvents to produce the desired products (Table 4).

Table 4. Comparison of DBSA with the reported catalysts for the diacetylation of Benzaldehyde

Entry	Catalyst	Solvent	Temp.(°C)	Time(min)	Yield(%) ^a	Ref.
1	DBSA	Solvent-free	rt	5	94	Present work
2	P-TSA	Solvent-free	rt	8	92	Present work
3	PEG - Supported Sulfonic Acid (0.1 mmol)	Solvent-free	rt	35	92	[26]
4	Saccharin Sulfonic Acid (0.2 mmol)	Solvent-free	rt	48	90	[27]
5	Silica-bonded S-sulfonic acid (0.005 g)	Solvent-free	rt	4	84	[28]
6	Silica sulfuric acid (200 mg, 0.52 mol%)	Solvent-free	rt	30	84	[29]
7	1-H-3-methyl-imidazolium hydrogen sulfate (3.8 mol%)	Solvent-free	rt	25	90	[47]
8	Silica Phosphoric Acid (2.5 mol%)	Solvent-free	rt	35	88	[30]
9	$\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{MCM-41}$ (20 wt %)	Solvent-free	60 °C	120	84	[31]
10	$(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ (0.5 mol%)	Solvent-free	rt	90	98	[48]
11	$\text{Fe}(\text{CH}_3\text{SO}_3)_2 \cdot 4\text{H}_2\text{O}$ (3 mol%)	Solvent-free	rt	60	97	[49]
12	Sulphated Zirconia (25 mg)	Solvent-free	0 °C	360	97	[50]
13	Chloroacetylated Polystyrene-Supported Zinc Complexes (5 mol%)	Solvent-free	rt	60	87	[51]
14	β -Zeolite (50 wt %)	Solvent-free	60 °C	120	92	[25]
15	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (10 mol %)	CH_3CN	rt	90	87	[18]

^a Yields refer to the isolated pure products

Also, analyzing the data in Table 4 reveals that completion of these reactions in the presence of PEG - Supported sulfonic acid, saccharin sulfonic acid, silica sulfuric acid, silica phosphoric acid and heteropolyacids such as $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{MCM-41}$ leads to longer time for these reactions to be done. Using silica-bonded S-sulfonic acid catalyst, the data leads to lower yields for the reactions.

4. Conclusion

In conclusion, a simple, efficient and rapid procedure for the preparation of geminal diacetates was established. The advantages of this method are short reaction times, excellent yields, high selectivity, no solvent, low catalyst loading and does not need rigorous reaction conditions. Further

investigation on the application of DBSA discloses several unique properties of DBSA, such as commercial availability, stability, act as a combined Brønsted acid-surfactant-catalyst (BASC) and a surfactant to increase the concentration of organic reactants by forming micellar aggregates [33] make DBSA useful for catalytic applications [34, 52].

Acknowledgments

We gratefully acknowledge the support of this work by Shiraz University Research Council.

References

- [1] Green, T. W. & Wuts, P. G. M. (1999). *Protective groups in organic synthesis*. 3rd ed., New York: Wiley-Interscience.
- [2] 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. *J. Org. Chem.*, 48, 1765-1767.
- [3] Chakarabarti, A. K., Thilagavathi, R. & Kumar, R. (2004). Copper (II) tetrafluoroborate-catalyzed formation of aldehyde-1,1-diacetates. *Synthesis*, 6, 831-833.
- [4] Karimi, B. & Maleki, J. (2003). Lithium trifluoromethanesulfonate (LiOTf) as a recyclable catalyst for highly efficient acetylation of alcohols and diacetylation of aldehydes under mild and neutral reaction conditions. *J. Org. Chem.*, 68, 4951-4954.
- [5] Whitesell, J. K. (1989). Enantioselective lewis acid catalysts of the early transition metals. *Chem. Rev.*, 89, 1581-1590.
- [6] Sandberg, M. & Sydnes, L. K. (2000). The chemistry of acylals. 3. Cyanohydrin esters from acylals with cyanides reagents. *Org. Lett.*, 2, 687-689.
- [7] Ghribi, A., Alexakis, A. & Normant, J. F. (1984). Reactivity of RCuBF_3 and $\text{R}_2\text{CuLiBF}_3$ towards allylic acetals and ethers. *Tetrahedron Lett.* 1984, 25, 3079-3082.
- [8] 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.
- [9] Trost, B. M. & Vercauteren, J. (1985). Allylic geminal diacetates. Unusual carbonyl substitutes via metal-catalyzed reactions. *Tetrahedron Lett.*, 26, 131-134.
- [10] Michie, J. K. & Miller, J. A. (1981). Phosphorus trichloride as catalyst in the preparation of 1,1-diacetates from aldehydes. *Synthesis*, 8, 824-825.
- [11] Wang, W. B., Shi, L. L. & Huang, Y. Z. (1999). An efficient SbCl_3 -metal system for allylation, reduction and acetalization of aldehydes. *Tetrahedron*, 46, 3315-3320.
- [12] Knoevenagel, E. (1914). Acetylation of organic compounds. *J. Liebigs Ann. Chem.* 402, 111-115.
- [13] Wang, C. & Li, M. (2002). A novel and efficient conversion of aldehydes to 1,1-diacetates catalyzed with $\text{FeCl}_3/\text{SiO}_2$ under microwave irradiation. *Synth. Commun.*, 32, 3469-3474.
- [14] Fry, A. J., Rho, A. K., Sherman, L. R. & Sherwin, C. S. (1991). Cobalt (II)-catalyzed reaction of polycyclic aldehydes and acetic anhydride: Formation of acylals, not 1,2-diketones. *J. Org. Chem.*, 56, 3283-3286.
- [15] Karimi, B., Ebrahimian, G. R. & Seradj, H. (2002). Highly efficient and chemoselective conversion of aldehydes to acylals catalyzed with tungsten hexachloride (WCl_6). *Synth. Commun.*, 32, 669-673.
- [16] Yadav, J. S., Subba Reddy, B. V. & Srinivas, C. (2002). Indium trichlorides-catalyzed chemoselective conversion of aldehydes to gem-diacetates. *Synth. Commun.*, 32, 1175-1180.
- [17] Chandra, K. L., Saravanan, P. & Singh, V. K. (2000). An efficient method for diacetylation of aldehydes. *Synlett*, 3, 359-360.
- [18] 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.
- [19] Aggarwal, V. K., Fonquerna, S. & Vennall, G. P. (1998). $\text{Sc}(\text{OTf})_3$, an efficient catalyst for formation and deprotection of geminal diacetates (acylals), chemoselective protection of aldehydes in presence of ketones. *Synlett*, 8, 849-850.
- [20] Carrigan, M. D., Eash, K. J., Oswald, M. C. & Mohan, R. S. (2001). An efficient method for the chemoselective synthesis of acylals. *Tetrahedron Lett.*, 42, 8133-8135.
- [21] Sumida, N., Nishioka, K. & Sato, T. (2001). Conversion of aldehydes into geminal dicarboxylates (acylals) catalyzed by lithium tetrafluoroborate. *Synlett*, 12, 1921-1922.
- [22] Jin, T. S., Sun, G., Li, Y. W. & Li, T. S. (2002). An efficient and convenient procedure for the preparation of 1,1-diacetates from aldehydes catalyzed by $\text{H}_2\text{NSO}_3\text{H}$. *Green Chem.*, 4, 255-256.
- [23] Freeman, F. & Karchefski, E. M. (1977). Preparation and spectral properties of benzylidene diacetates. *J. Chem. Eng. Data*, 22, 355-357.
- [24] Pereira, C., Gigante, B., Marcelo-Curto, M. J., Carreyre, H., Perrot, G. & Guisnet, M. (1995). Diacetates from aldehydes in the presence of zeolites. *Synthesis*, 9, 1077-1078.
- [25] Kumar, P. V., Hegde, R. & Kumar, T. P. (1995). An efficient synthesis of diacetates from aldehydes using beta zeolite. *Tetrahedron Lett.*, 36, 601-602.
- [26] Wang, Q. Y., Sheng, S. R., Wei, M. H., Xie, Z. L. & Liu, X. L. (2007). PEG-Supported sulfonic acid as an efficient and recyclable catalyst for the synthesis of 1,1-diacetates under solvent-free conditions. *Synth. Commun.*, 37, 1019-1026.
- [27] Shirini, F., Mamaghani, M. & Abedini, M. (2010). Saccharin sulfonic acid as an efficient catalyst for the preparation and deprotection of 1,1-diacetates. *Bull. Korean Chem. Soc.*, 31, 2399-2401.
- [28] Niknam, Kh., Saberi, D. & Nouri Sefat, M. (2009). Silica-bonded S-sulfonic acid as a recyclable catalyst for chemoselective synthesis of 1,1-diacetates. *Tetrahedron Lett.*, 50, 4058-4062.
- [29] Desai, U. V., Thopate, T. S., Pore, D. M. & Wadgaonkar, P. P. (2006). An efficient, solvent-free method for the chemoselective synthesis of acylals from aldehydes and their deprotection catalyzed by silica sulfuric acid as a reusable solid acid catalyst. *Catal. Commun.*, 7, 508-511.
- [30] Zhang, F., Liu, H., Zhang, Q. J., Zhao, Y. Z. & Yang, F. L. (2010). Silica phosphoric acid: An efficient and recyclable catalyst for the solvent-free synthesis of acylals and their deprotection in MeOH. *Synth. Commun.*, 40, 3240-3250.
- [31] Nagy, N. M., Jakab, M. A., Konya, J. & Antus, S. (2002). Convenient preparation of 1,1-diacetates from aromatic aldehydes catalysed by zinc-montmorillonite. *Appl. Clay Sci.*, 21, 213-216.
- [32] Reddy, A. V., Ravinder, K., Reddy, V. L. N., Ravikanth, V. & Venkateswarlu, Y. (2003). Amberlyst-15-catalyzed efficient synthesis of 1,1-

- diacetates from aldehydes. *Synth. Commun.*, *33*, 1531-1536.
- [33] Shrikhande, J. J. (2007). p-Dodecylbenzenesulfonic acid: A Brønsted acid-surfactant-combined catalyst. *Res J. Chem. Envir.*, *11*, 82-83.
- [34] Jin, T. S., Liu, L. B., Liu, L. B., Yin, Y., Zhao, Y. & Li, T. S. (2006). Clean synthesis of 14-alkyl and 14-aryl-14-H-dibenzo[a,j]xanthenes. *Lett. Org. Chem.*, *3*, 591-596.
- [35] Prasad, D., Preetam, A. & Nath, M. (2012). Microwave-assisted green synthesis of dibenzo [a,j]xanthenes using p-dodecylbenzenesulfonic acid as an efficient Brønsted acid catalyst under solvent-free conditions. *C. R. Chim.*, *15*, 675-678.
- [36] Peng, Y. Y., Zhang, Q. L., Yuan, J. J. & Cheng, J. P. (2008). A facile aqueous synthesis of bis(indol-3-yl)alkanes catalyzed by dodecylbenzenesulfonic acid. *Chinese J. Chem.*, *26*, 2228-2232.
- [37] Manabe, K., Mori, Y. & Kobayashi, S. (2001). Three-component carbon-carbon bond-forming reactions catalyzed by a Brønsted acid-surfactant-combined catalyst in water. *Tetrahedron*, *57*, 2537-2544.
- [38] Hatakeyama, T., Chisaka, Y. & Kuroda, C. (2009). Alkyl-group selection in an acidic-surfactant-promoted reaction of homoallyl alcohols and aldehydes in water. *Helv. Chim. Acta*, *92*, 1333-1340.
- [39] Hota, S. K., Chatterjee, A., Bhattacharya, P. K. & Chattopadhyay, P. (2009). A green chemical approach for the N-alkylation of aldoximes to form nitrones in organized aqueous media and their *in situ* cycloaddition with olefins. *Green Chem.*, *11*, 169-176.
- [40] Jin, T. S., Zhao, R. Q. & Li, T. S. (2006). An one-pot three-component process for the synthesis of 6-amino-4-aryl-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazoles in aqueous media. *Arkivoc*, *11*, 176-182.
- [41] Manabe, K., Lumura, S., Sun, X. M. & Kobayashi, S. (2002). Dehydration reactions in water. Brønsted acid-surfactant-combined catalyst for ester, ether, thioether, and dithioacetal formation in water. *J. Am. Chem. Soc.*, *124*, 11971-11978.
- [42] Chai, Y., Dong, D., Ouyang, Y., Liang, Y., Wang, Y., Li, M. & Liu, Q. (2007). Thia-Michael addition reactions in water using 3-[bis(alkylthio) methylene] pentane-2,4-diones as odorless and efficient thiol equivalents. *Lett. Org. Chem.*, *4*, 281-284.
- [43] Jermy, B. R. & Pandurangan, A. (2008). Synthesis of geminal diacetates (acylals) using heterogeneous H₃PW₁₂O₄₀ supported MCM-41 molecular sieves. *Catal. Commun.*, *9*, 577-583.
- [44] 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*, 1677-1678.
- [45] Ghosh, R., Maiti, S., Chakraborty, A. & Halder, R. (2004). Indium triflate: a reusable catalyst for expeditious chemoselective conversion of aldehydes to acylals. *J. Mol. Catal. A.*, *215*, 49-53.
- [46] Yadav, J. S., Reddy, B. V. S., Venugopal, C. & Ramalingam, T. (2002). LiBF₄-mediated conversion of aldehydes to gem-diacetates. *Synlett*, *4*, 604-606.
- [47] 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. *Catal. Commun.*, *9*, 89-96.
- [48] Jitendra, R. S. & Radha, V. J. (2008). (NH₄)₃PW₁₂O₄₀ as an efficient and reusable catalyst for the synthesis and deprotection of 1,1-diacetates. *Synth. Commun.*, *38*, 595-602.
- [49] Wang, M., Tian, G. F., Song, Z. G. & Jiang, H. (2009). Ferrous methanesulfonate as an efficient and recyclable catalyst for chemoselective synthesis of 1,1-diacetate from aldehydes. *Chinese Chem Lett.*, *20*, 1034-1038.
- [50] Laura Nadxieli, P. G., Deysi, C. G., Leticia, L. R., Eduardo, G. Z., Gerardo, U. & Guillermo, N. S. (2009). Sulphated zirconia as an eco-friendly catalyst in acylal preparation under solvent-free conditions, acylal deprotection assisted by microwaves, and the synthesis of anhydro-dimers of o-hydroxybenzaldehydes. *Molecules*, *14*, 4065-4078.
- [51] Wang, L. & Cai, Ch. (2009). Preparation and characterization of chloroacetylated polystyrene-supported zinc complexes and evaluation of their catalytic activities for the synthesis of 1,1-diacetates. *J. Appl. Polym. Sci.*, *112*, 2087-2093.
- [52] Luo, S., Xu, H., Li, J., Zhang, L., Mi, X., Zhenga, X. & Cheng, J. P. (2007). Facile evolution of asymmetric organocatalysts in water assisted by surfactant Brønsted acids. *Tetrahedron*, *63*, 11307-11314.