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$[B(OH)_3]_{0.78}[B(OH)_2(OSO_3H)]_{0.22}$ as a new, cheap and eco-friendly catalyst for synthesis of acylals at room temperature under solvent free conditions

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ABSTRACT

$[B(OH)_3]_{0.78}[B(OH)_2(OSO_3H)]_{0.22}$ or (BSA) was simply prepared by addition of chlorosulfonic acid to commercial boric acid at room temperature. This cheap and green solid acid was used as an efficient catalyst for synthesis of acylals from aldehydes under solvent-free conditions at room temperature.

***Keywords**: $[B(OH)_3]_{0.78}[B(OH)_2(OSO_3H)]_{0.22}$, Acylal, Protecting group, Aldehyde, BSA.*

1. Introduction

Acylals or 1,1-diacetates, as alternative to acetals, are synthetically useful as aldehyde protecting groups, due to their stability towards aqueous acids and mild bases. Some catalysts such as acid functionalized MCM-41 (MCM-SO_3H) [1], poly(4-vinylpyridinium)hydrogen sulfate salt (PVPHS) [2], SiO_2-Pr-SO_3H [3], high-valent titanium(IV)salophen [Ti^{IV}(salophen)$(OTf)_2$] [4], *N*-sulfonic acid poly(4-vinylpyridinum) chloride (NSPVPC) [5], rice husk supported $FeCl_3$ nanoparticles ($FeCl_3$-RiH) [6], ZSM-5-SO_3H [7], $Mg(CH_3SO_3)_2$-HOAc [8], $NaHSO_4$-SiO_2 [9], stannum (IV) phosphomolybdate [10], silica-bonded propyl-diethylene-triamine-*N*-sulfamic acid [11], cerium(IV) sulfate [12], polyaniline (PANI), polypyrrole (PPY), poly-(3,4-ethylenedioxythiophene) (PEDOT) salts [13], host (nanocavity of zeolite-Y)-guest (molybdophosphoric acid) [14], HSO_3-pmim CH_3SO_3 [15], $Fe(NO_3)_3$. $9H_2O$ [16], $SnCl_2$. $2H_2O$, $Ni(OAc)_2.4H_2O$ [17], carbon-silica composites bearing sulfonic acid [18], polystyrene-supported, $Al(OTf)_3$ [19], [bmpy]HSO_4 [20], silica chromate (SiO_2-O-CrO_2-O-SiO_2) [21], silica phosphoric acid [22], PEG-SO_3H [23], saccharin sulfonic acid [24], cobalt(II) bromide [25], H_2SO_4 [26], $LiHSO_4/SiO_2$ [27], $Al(HSO_4)_3$ [28], $Fe(CH_3SO_3)_2.4H_2O$ [29], Ruthenium(III) chloride [30], SO_4^{2-}/SnO_2 [31], Silica sulfuric acid [32], zirconium hydrogen sulfate [33], $HClO_4$-SiO_2 [34] and silica-bonded S-sulfonic acid (SBSSA) [35] have been used for acylal formation by acetic anhydride. At present, considerable efforts are being made to find suitable, recyclable and eco-friendly solid acid catalysts which can successfully carry out for acylal formation from aldehydes.

Previously, Kiasat and coworkers, have reported the synthesis of $B(OSO_3H)_3$ as a grayish solid material by addition of`5 ml of chlorosulfonic acid to 1.55 g of boric acid and then washing with diethyl ether [36]. At this work, $[B(OH)_3]_{0.78}[B(OH)_2(OSO_3H)]_{0.22}$ (BSA) was prepared *via* reaction of 4 g of boric acid with 2 ml of chlorosulfonic acid and used for synthesis of acylals from aldehydes at room temperature.

2. Experimental

2.1. General procedure

FT-IR (ATR) spectra were run on a Bruker, Eqinox 55 spectrometer, while ^{1}H-NMR spectra were obtained using a Bruker Avance 400 MHz DRX spectrometer. Melting points were determined without correction using a Buchi melting point B-540 B.V.CHI apparatus. The X-ray diffraction (XRD) patterns of materials were prepared by employing a Philips Xpert MPD diffract meter equipped with a Cu Kα anode (λ=1.54 Å) in the 2θ range from 5 to 80°. The thermal gravimetric analysis (TGA) was done with "NETZSCH TG 209 F1 Iris" instrument.

2.2. Preparation of BSA

In a ventilated cabinet, 2 ml of chlorosulfonic acid was added drop-wise to 4 g commercial boric acid with

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vigorously mixing at room temperature. After addition of chlorosulfonic acid, the mixing was continued for 60 minutes. Then, 50 ml of diethyl ether was added to mixture to obtain white solid. The solid was filtered and washed with diethyl ether and dried at room temperature. The BSA was obtained with 95 % yield.

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

In a mortar, a mixture of aldehyde (1 mmol), acetic anhydride (2.5 mmol), and BSA (0.018 g) was pulverized for 2-10 minutes. The reaction progress was followed by TLC. After completion of the reaction, 0.5 g of K_2CO_3 and 5 ml of ethanol was added and the heterogeneous mixture was filtered. After evaporation of solvent, the product was crystallized by ethanol and water. For more purification, the products were recrystallized in chloroform.

Selected spectral data

1,1- Diacetoxy-1-(4-methoxycarbonylphenyl) methane (Table 2, Entry 10):

FT-IR (Neat ART): $\bar{\nu}$ = 2916, 1761, 1722, 1435, 1372, 1278, 1234 cm^{-1}. ^{1}HNMR (400 MHz, $CDCl_3$): δ= 8.05 (d, *J*=8 Hz, 2H), 7.69 (s, 1H), 7.56 (d, *J*=8 Hz, 2H), 3.90 (s, 3H), 2.12 (s, 6H).

1,1-Diacetoxy-1-(4-carboxyphenyl) methane (Table 2, Entry 19):

FT-IR (Neat ART): $\bar{\nu}$ = 2922, 1730, 1712, 1432, 1373, 1267, 870 cm^{-1}. ^{1}HNMR (400 MH_Z, $CDCl_3$): δ = 10.85 (s, 1H), 8.15 (d, *J*=8 Hz, 2H), 7.74 (s, 1H), 7.63 (d, J=8 Hz, 2H), 2.1 (s, 6H).

3. Results and Discussion

The FT-IR (ATR) spectra of boric acid and BSA are shown in Fig. 1. In boric acid FT-IR spectrum (Fig. 1-a), many peaks at 600-700 cm^{-1} formed by bending vibration of O-B-O group and the peak at 1413 cm^{-1} formed via asymmetric B-O stretching vibration. In BSA spectrum (Fig. 1-b) in addition to above mentioned peaks for boric acid, the peaks at 1050 and 1150 and a very broad peak at 2500-3000 cm^{-1} verify the -SO_3H group on boric acid.

The acidity of BSA was determined by titration by NaOH and the acidic capacity was 2.77 meq/g H+. So the n value was calculated (n= 0.22) and the$[B(OH)_3]0.78[B(OH)_2(OSO_3H)]0.22$ formula proposed for the catalyst.

TGA diagram of BSA is shown in Fig. 2. The catalyst is stable until 83 °C and only 5.3% of its weight was reduced. By heating the catalyst between 83 to 123 °C, the reduced weight increased to 25%. Only 18% of the catalyst weight was reduced between 123-513 °C.

Fig. 3 shows the XRD pattern of BSA. As shown in this figure, incorporation of $ClSO_3H$ leads to some changes in XRD pattern of boric acid. In XRD pattern of boric acid, sharp reflex at 2θ= 28° was moved to 28-29° after modification by $ClSO_3H$. The sharp peaks at 2theta 25.5°, 47° and 48° were disappeared but one peak at 55.5° was appeared. The broadness of some peaks implies that the crystalline size of BSA is decreased after reaction with $ClSO_3H$.

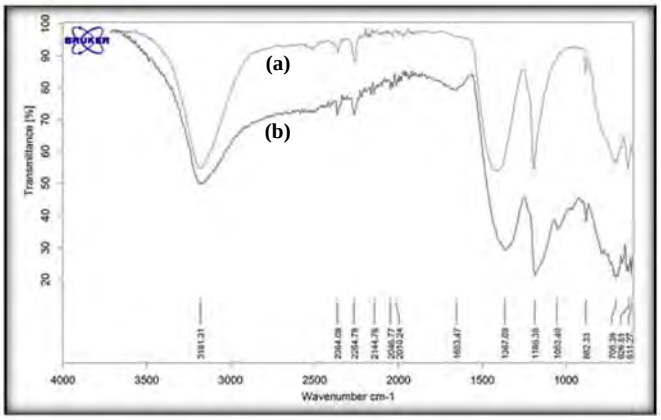


Fig. 1. FT-IR (ATR) spectra of (a) boric acid and (b) BSA.

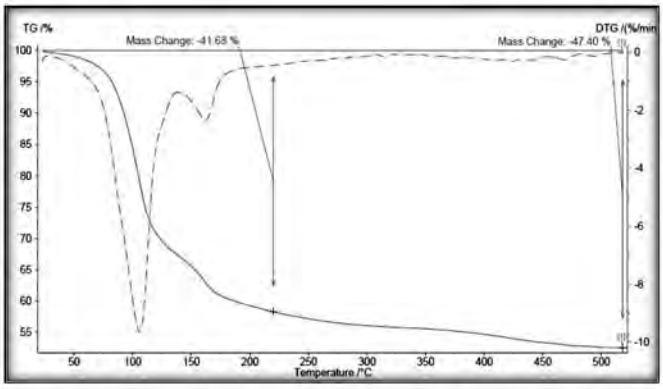


Fig. 2. TGA diagram of BSA.

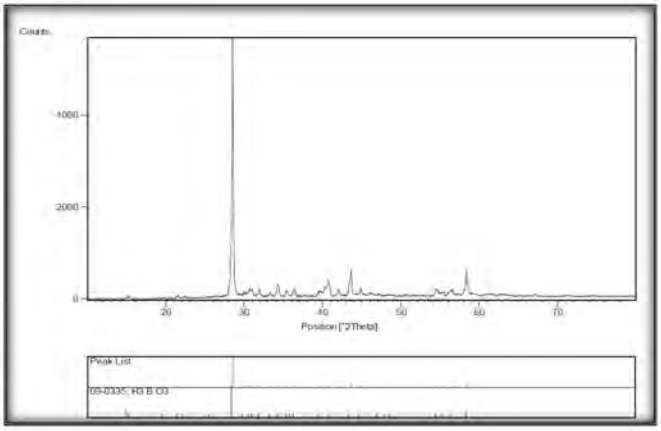


Fig. 3. XRD pattern of BSA.

A comparison between this work with the others in conversion of 3-nitrobenzaldehyde to corresponding acylal is shown in Table 1.

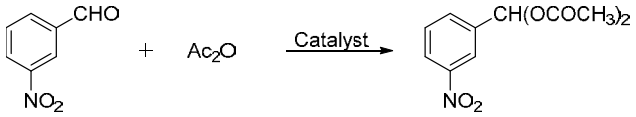
For examining the efficiency of catalyst, different aldehydes with electron-withdrawing and electron-releasing groups were tested and the corresponding 1,1-diacetates were obtained in good to excellent yields (Table 2). The results showed that the yield were higher for aldehydes with electron-withdrawing groups, while aldehydes containing electron releasing groups produced the lower yield.

OH group in salicylaldehyde, 4-hydroxybenzaldehyde and vaniline have also been acylated with acetic anhydride in the presence of catalyst (Table 2, Entries 5, 12 and 18).

Likewise, 4-(dimethylamino)benzaldehyde failed to give the expected acylal under grinding condition at room temperature or reflux. The explanation for this result may be due to the strong electron donating dimethyl amino group which will reduce the reactivity.

In terephthalaldehyde, the both aldehyde groups were converted to acylal groups (Table 2, Entry 7). Trioxane was used as formaldehyde source and produces the 1,1-diacetoxymethane with good yield.

Table 1. Comparison between this work with the others in conversion of 3-nitrobenzaldehyde to corresponding acylal.[a]



Entry	Catalyst (g)	Conditions	Time (min)	Yield (%)	Ref.
1	H_3BO_3 (0.02)	S.F./ R.T.	2	10	-
2	BSA(0.02)	S.F./ R.T.	2	98	-
3	BSA(0.02)	S.F./ 60 °C	15	70	-
4	BSA (0.018)	S.F./ R.T.	2	98	-
5	BAS (0.025)	S.F./ R.T.	2	96	-
6	BSA (0.03)	S.F./ R.T.	2	85	-
7	BSA (0.018)	EtOAc/ Reflux	120	85	-
8	BSA (0.018)	n-Hexane/ Reflux	120	44	-
9	BSA (0.018)	EtOAc/ M.W.	10	60	-
10	BSA (0.018)	S.F./ M.W.	10	67	-
11	PVPHS (0.005)	S.F./ Sonication	32	93	[2]
12	$[Ti^{IV}(salophen)(OTf)_2]$ (0.012)	CH_2Cl_2/ R.T.	1	94	[4]
13	NSPVPC (0.01)	S.F./ R.T.	15	92	[5]
14	$FeCl_3$-RiH (0.02)	S.F./ R.T.	35	94	[6]
15	ZSM-5-SO_3H (0.02)	S.F./ R.T.	4	96	[7]
16	SiO_2-O-CrO_2-O-SiO_2 (0.25)	S.F./ R.T.	30	95	[21]
17	SO_4^{2-}/SnO_2 (0.015)	S.F./ R.T.	30	83	[31]
18	$Al(HSO_4)_3$ (0.046)	S.F./ R.T.	5	80	[28]
19	Ruthenium(III) chloride (0.006)	S.F./ R.T.	5	88	[30]
20	Silica sulfuric acid (0.02)	S.F./ R.T.	15	96	[32]
21	$HClO_4$-SiO_2 (0.05)	S.F./ R.T.	2	95	[34]
22	zirconium hydrogen sulfate (0.02)	S.F./ R.T.	5	86	[33]
23	Silica-bonded S-sulfonic acid (SBSSA) (0.005)	S.F./ R.T.	2	87	[35]

[a]3-nitrobenzaldehyde (mmol): acetic anhydride (mmol) is 1: 2.5.

Table 2. Conversion of aldehydes to corresponding acylals by BSA as catalyst under solvent-free conditions at room temperature.[a]

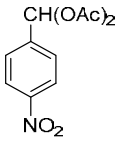
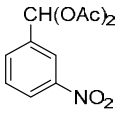
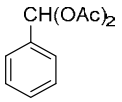
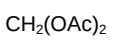
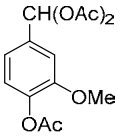
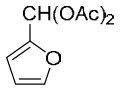
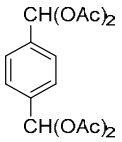
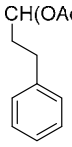
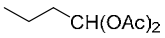
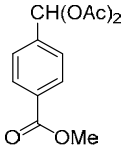
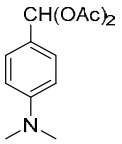
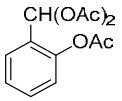
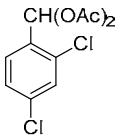
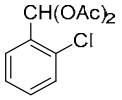
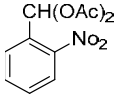
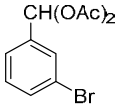
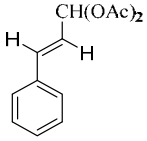
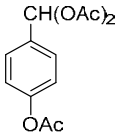
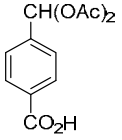
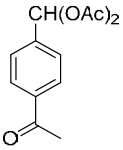
Entry	Substrate	Product	Time (min)	Yield[b,c](%)	m.p. ˚C		Ref.
					Found	Reported	
1	4-Nitrobenzaldehyde		5	96	125-126	124-125	[7]
2	3-Nitrobenzaldehyde		2	98	65-66	64-65	[7]
3	Benzaldehyde		5	88	45-46	44-45	[7]
4	Trioxane		7	89	Oil	-	-
5	Vanillin		10	84	93-94	90-91	[30]
6	Furfural		9	83	51-52	50-52	[9]
7	Terphthaldialdehyde		6	86	173-175	173-174	[35]
8	3-Phenylpropionaldehyde		7	85	Oil		[30]
9	Butyraldehyde		7	94	Oil		[9]
10	Methyl-4-formylbenzoate		9	87	68-69	-	-
11	4-(Dimethylamino)benzaldehyde		10	0	-	-	-
12	Salicylaldehyde		7	92	102-103	101-102	[21]
13	2,4-Dichlorobenzaldehyde		5	95	94-95	93	[33]

Table 2. *(Continued).*

14	2-Chlorobenzaldehyde		5	92	57-58	58-60	[7]
15	2-Nitrobenzaldehyde		5	84	89-91	90-91	[7]
16	3-Bromobenzaldehyde		6	83	83-85	83	[34]
17	Cinnamaldehyde		6	88	84-85	85-86	[32]
18	4-Hydroxybenzaldehyde		8	92	90-91	90-92	[30]
19	4-Carboxybenzaldehyde		5	97	88-89	-	-
20	4-Acetylbenzaldehyde		5	95	56-58	57	[33]

[a]The ratio of Substrate (mmol)/ BSA (g)/ Acetetic anhydride(mmol) is 1/ 0.018/ 2.5.
[b]All products were known and characterized from their spectral (IR and ^{1}H-NMR) and comparison to authentic samples.
[c]Yields refer to isolated pure products.

4-Nitroacetophenone, 4-acetyl benzaldehyde and acetal were also checked for the acylal formation. The acetal groups of these compounds have not reacted at room temperature. It is suggested that chemoselective protection of aldehydes in the presence of ketones or acetals can be achieved by this method (Scheme 1).

A proposed mechanism for preparation of acylals from aldehydes is shown in Scheme 2.

4. Conclusions

In conclusion, we have demonstrated a simple method for the synthesis of acylals with using BSA as a commercial based, cheap, eco-friendly and efficient catalyst. Short reaction times, high yields, a clean process, simple methodology, easy work-up and green conditions are advantages of this protocol.

Acknowledgment

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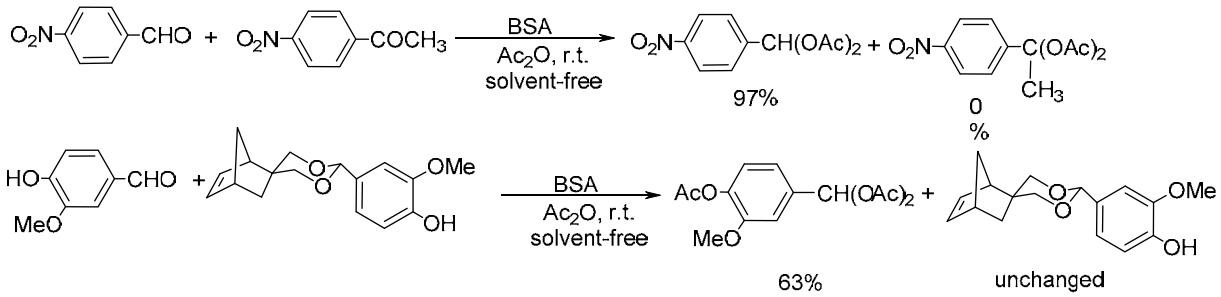
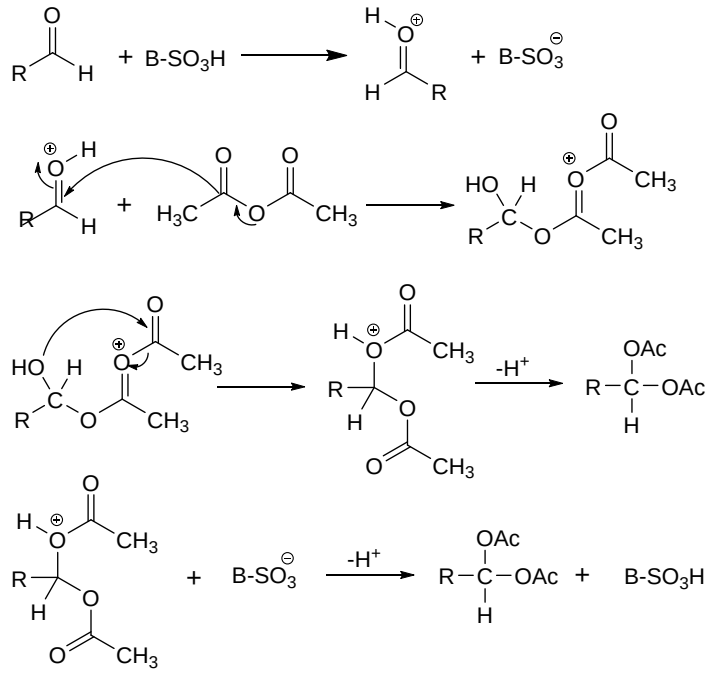


Scheme 1. Chemoselective protection of aldehydes in the presence of ketones or acetals catalyzed by BSA.



$[B(OH)_3]0.78[B(OH)_2(OSO_3H)]0.22 = B\text{-}SO_3H$

Scheme 2. Proposed mechanism for preparation of acylals from aldehydes.

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