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Original Research Article

Chemoselective synthesis of 1,1-diacetates (acylals) using 1,1'-butylenebispyridinium hydrogen sulfate as a new, halogen-free and environmental-friendly catalyst under solvent-free conditions

Sobhan Rezayati^{a,*} , Rahimeh Hajinasiri^b , Zinatossadat Hossaini^b , Sima Abbaspour^c

^a Department of Chemistry, Payame Noor University, 19395-4697 Tehran, Iran

^b Chemistry Department, Qaemshahr Branch, Islamic Azad University, P. O. Box 163, Qaemshahr, Iran

^c School of Chemistry, Shahrood University of Technology, Shahrood, Iran

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KEYWORDS

(Bbpy)(HSO₄)₂

Acylals

Protection

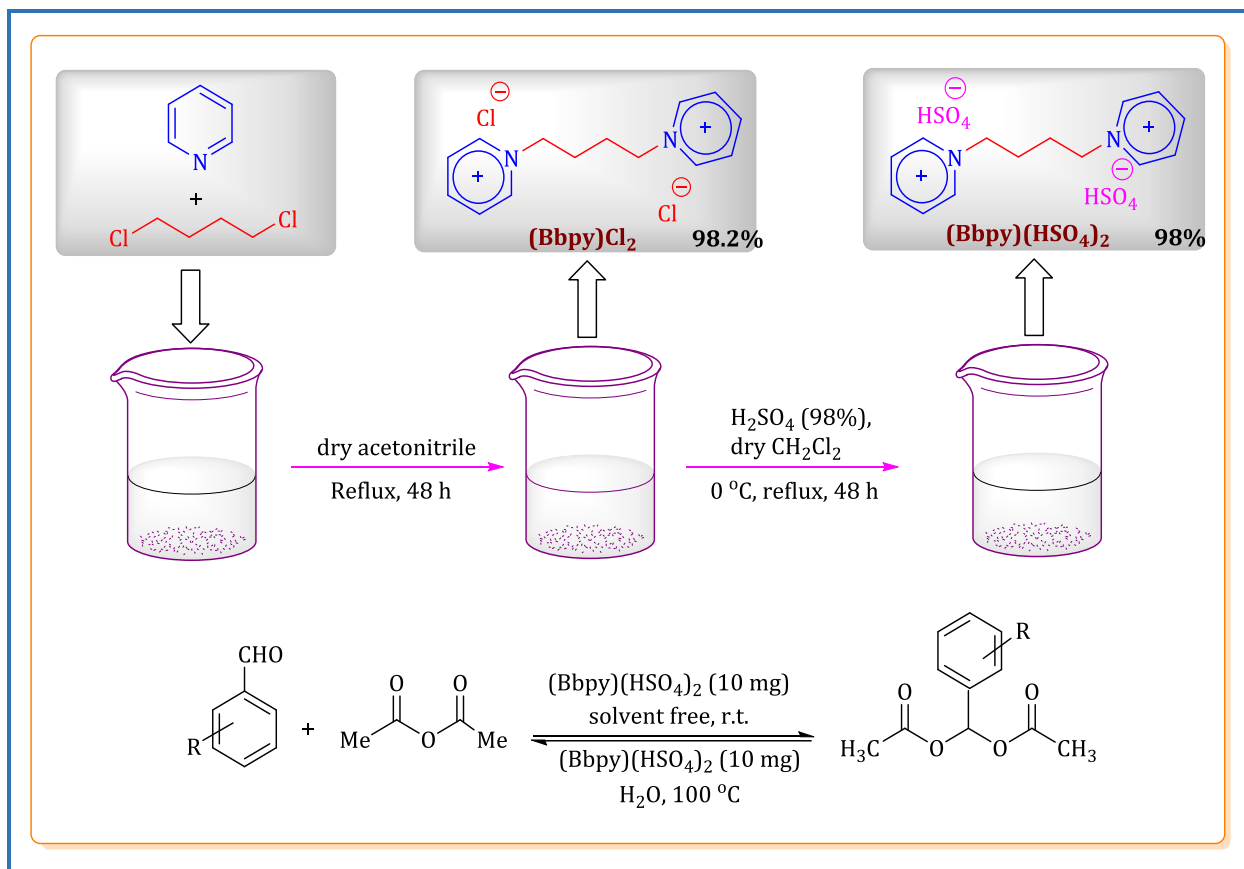
Deprotection

Brønsted acidic ionic liquid

ABSTRACT

In this study, an efficient and simple procedure is reported for the chemoselective acetylation of various aldehydes (aromatic and aliphatic) with acetic anhydride by 1,1'-butylenebispyridinium hydrogen sulfate (Bbpy)(HSO₄)₂ as a green and halogen-free catalyst under solvent-free conditions at room temperature. The selective conversion of the aldehydes was observed in the presence of ketones, and the deprotection of 1,1-diacetates has also been achieved using (Bbpy)(HSO₄)₂ in water as a green solvent in reflux conditions. This procedure has valuable advantages including short reaction times, simple workup, high yields of products, absence of solvent, and use of commercially available and non-toxic reagents.

Graphical Abstract



Introduction

The formation of 1,1-diacetates (Acylals) through protection carbonyl groups of aromatic and aliphatic aldehydes is of great importance in synthetic organic chemistry and also it is extremely important steps in modern organic chemistry, because of the stability of corresponding products and their easy conversion back to the parent compounds [1]. Acylals are synthetically important precursors for the preparation of α , β -unsaturated for Diels–Alder reactions, which are useful intermediates in industries, as chiral allylic esters and also as cross linking reagents for the cellulose in cotton [2–5]. Therefore, the methods for their synthesis have received considerable attention. Usually, preparation of the 1,1-diacetates has been achieved by reaction of the aldehydes with acetic anhydride in the presence of different catalysts, under the microwave irradiation such as H-mordenite zeolite [6], $\text{Fe}_3\text{O}_4/\text{SiO}_2$ [7], PEG- SO_3H [8], poly(4-vinylpyridinium) perchlorate [9], dipyridine cobalt chloride [10], *N*-sulfonic acid poly(4-vinylpyridinium) hydrogen sulfate [11], $\text{NaHSO}_4\text{-SiO}_2$ [12], silica-supported boron sulfonic acid (SBSA) [13], selectfluorTM [14], 1,3-dibromo-5,5-dimethylhydantoin [15], silica-supported functional ionic liquid (Si-[SbSipim][PF₆]) [16], γ -

$\text{Fe}_2\text{O}_3\text{@HAp-Ni}^{2+}$ [17], amberlyst-15 [18], 1-methyl-3-(2(sulfooxy)ethyl)-1*H*-imidazol-3-ium chloride [19], bismuth triflate [20], and *N*-propylsulfamic acid supported onto magnetic Fe_3O_4 nanoparticles (MNPs-PSA) [21]. Although some of these methods 1,1-diacetates are obtained in good to high product yields suffer from some disadvantages such as long reaction time, require high temperature, tedious work-up procedure, the use of homogenous catalysts or harmful solvents, high cost, and highly toxic catalysts and involve strongly acidic or oxidizing conditions.

Ionic liquids (ILs), known as molten salts (Consisting only of cations and anions) with melting point under 100–150 °C or room temperature ionic liquids, have attracted an increasing attention in the context of green synthesis in recent years. ILs were introduced as an alternative green media due to their unique properties including low vapor pressure being non-volatile, high thermal stability (Up to about 300 °C), wide liquid temperature range, low volatility, highly polar, non flammability, large electrochemical window, miscible with certain organic solvents and/or water and good solubility of organic and inorganic materials, chemically inert [22–26].

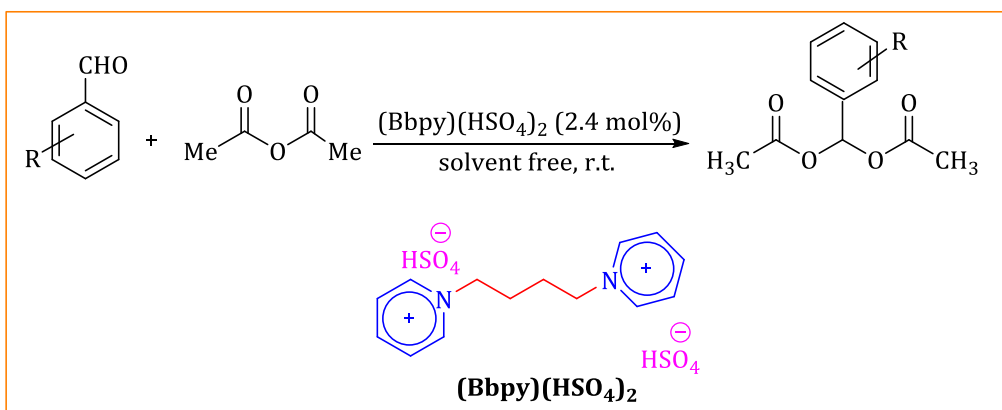
(Bbpy)(HSO_4)₂ is a low-cost available readily acidic material. Recently, (Bbpy)(HSO_4)₂ has been used as a versatile mediator or an efficient Brønsted acidic ionic liquid catalyst for the one-pot multi component synthesis of unsymmetrical polyhydroquinoline derivatives, that for the first time has been reported by Ghaffari Khaligh [27].

In continuation of our previous works on synthesis of the solid acids and organic reactions environmentally [28–33], herein, we report a simple and efficient procedure for the preparation of the 1,1-diacetates using a reaction between the aromatic and aliphatic aldehydes and acetic anhydride in the presence of the (Bbpy)(HSO_4)₂ as a halogen-free and recyclable catalyst under the solvent free conditions at room temperature (Scheme 1).

Experimental

Materials and methods

All the solvents and the reagents were purchased from Merck and Fluka with a high-grade quality. The nuclear magnetic resonance (^1H NMR) spectra were recorded using the CDCl_3 at 400 MHz, on a BRUKER DRX-400 AVANCE (Germany). The chemical shifts are denoted in δ units (ppm) relative to TMS ($\delta=0.00$) for protons ^1H : singlet (s), broad singlet (br), doublet (d), double doublet (dd), triplet (t), and multiplet (m). Melting points were taken on an electrothermal capillary melting point apparatus (UK) and are uncorrected. Monitoring the reactions and the purity check of the final products were carried out by thin layer chromatography (TLC) analysis using the silica gel precoated aluminium sheets (60–120 mesh; Merck) and visualization with ultraviolet light at 365 and 254 nm.



Scheme 1. Schematic synthesis of diacetate using catalyst $(\text{Bbpy})(\text{HSO}_4)_2$ under solvent-free conditions.

Synthesis of 1,1'-butylenebispyridinium hydrogen sulfate $(\text{Bbpy})(\text{HSO}_4)_2$

In this study, Pyridine (0.95 g, 12.01 mmol), 1,4-dichlorobutane (0.80 g, 6.30 mmol), and dry acetonitrile (10 mL) were added into a two-neck 100 mL round bottomed flask equipped with a reflux condenser and magnetic stirrer. The mixture was refluxed for 48 h. After the reaction, the solvent was removed under the vacuum, and the residue was washed with dichloromethane and dried at 60 °C under the vacuum to give 1,1'-butylenebispyridinium dichloride $(\text{Bbpy})\text{Cl}_2$ as a white solid (1.68 g, 98.2%). To a stirred solution of the $(\text{Bbpy})\text{Cl}_2$ (1.40 g, 4.91 mmol) in 25 mL dry CH_2Cl_2 at 0 °C was added dropwise 98% H_2SO_4 (0.53 mL, 9.82 mmol) over 10 min. The resulting solution was refluxed for 48h, and then the solution was washed with a mixture of ethanol and water (50%, 2×5 mL). The solvent was distilled off under the reduced pressure to give $(\text{Bbpy})(\text{HSO}_4)_2$ as a darkish viscous liquid (1.96 g, 98%) [27, 33].

General procedure for the preparation of 1,1-diacetates

A mixture of the aldehyde (1 mmol), freshly distilled AC_2O (2 mmol), and $(\text{Bbpy})(\text{HSO}_4)_2$ (10 mg, 2.4 mol%) was stirred at room temperature for appropriate time (As shown in Table 3) with the progress of the reaction monitored by TLC. After completion of the reaction the catalyst was isolated by a simple filtration and washed with ethyl acetate. The filtrate was washed twice with a 10% solution of sodium bicarbonate, and the organic layer was dried over anhydrous sodium sulfate and evaporated under a reduced pressure. The residue was purified by crystallization and by flash column chromatography and afforded the corresponding 1,1-diacetates in 76–91% yield. The $(\text{Bbpy})(\text{HSO}_4)_2$ was reused immediately after washed with ethyl acetate and dried at 50 °C for 2 h. All the compounds were characterized by ^1H NMR, ^{13}C NMR, and IR use of physical data.

Results and discussion

The preparation and characterization of (Bbpy)(HSO₄)₂

1,1'-butylenebispyridinium hydrogen sulfate (Bbpy)(HSO₄)₂ was prepared readily in the two-step process as detailed in the literature (Scheme 2).

The FT-IR spectrum of the (Bbpy)(HSO₄)₂ (Figure 1) was recorded using the KBr disc technique. The O=S=O asymmetric and symmetric stretching modes of the sulfonic acid functional groups were found at the range of 1020 and 1060 cm⁻¹, respectively, and that of the S–O stretching mode at 1227 cm⁻¹. Also, one absorptions at 1637 for C=N cm⁻¹ and 1400 cm⁻¹ for C=C group. The spectrum also showed a broad OH stretching absorption around 3144 and 3465 cm⁻¹ [33].

Optimization the reaction condition

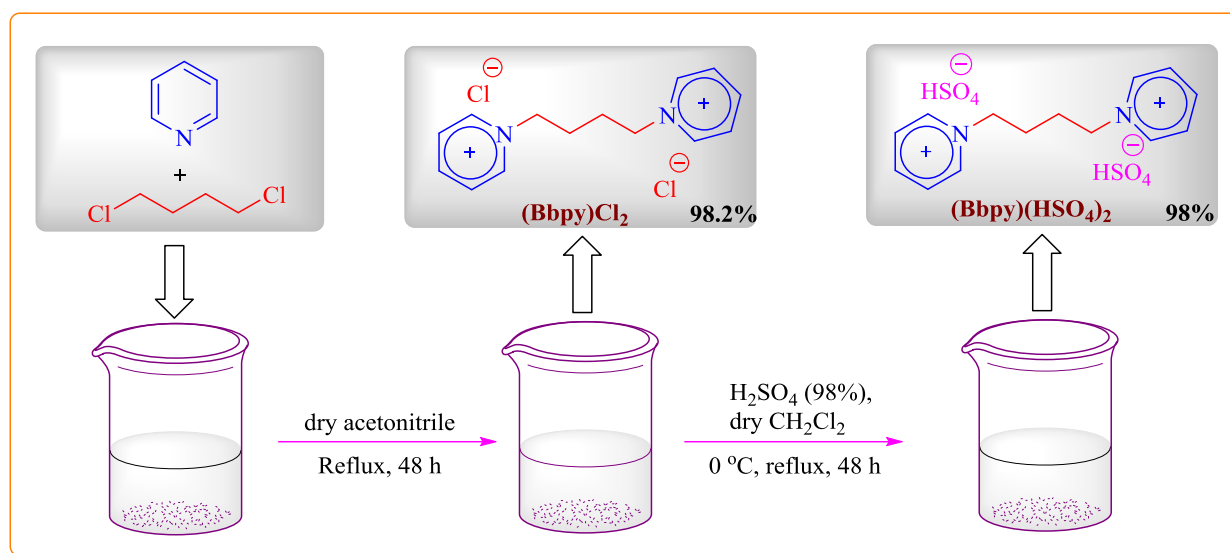
In the first step, to optimize the amount of catalyst-loading in the model reaction between the benzaldehyde (1 mmol) and acetic anhydride (2 mmol) in the presence of different amount (Bbpy)(HSO₄)₂ as catalyst under solvent-free conditions at room temperature (Table 1). Without using any catalyst, the reaction was slow and showed no yield even after 24 h. We observed that the best results were obtained using 15 mg of catalyst under the solvent-free conditions at room temperature (Table 1, entry 5). The obtained results were recored based on time and yield.

In the second step, to compare the efficiency of the solvent-free procedure versus solvent conditions, the reaction between the benzaldehyde (1 mmol) and acetic anhydride (2 mmol) in the presence of (Bbpy)(HSO₄)₂ (15 mg) was studied in various solvents under reflux conditions. The results are summarized in Table 2. As can be seen in Table 2, long reaction time and low yields of the product were obtained in the solvent conditions.

Using the optimal conditions for the reaction

To assess the efficiency and the scope of the (Bbpy)(HSO₄)₂ in the chemoselctive acetylation of the various aromatic aldehydes (Including aldehydes possessing electron-releasing substituents, electron-withdrawing substituents and halogens on their aromatic ring) were reacted with the acetic anhydride in the optimal reaction conditions to produce the desired products in high yields and in short reaction times. The results are displayed in Table 3.

In this reaction sequence, the alcoholic group is also acylated apart from the acylal formation in more than 90% yield and 25 min (Scheme 3). All the products were characterized by comparison (TLC and physical constants) with the authentic samples prepared by the conventional method, using the (Bbpy)(HSO₄)₂.



Scheme 2. Synthesis of 1,1'-butylenebispyridinium hydrogen sulfate $(\text{Bbpy})(\text{HSO}_4)_2$

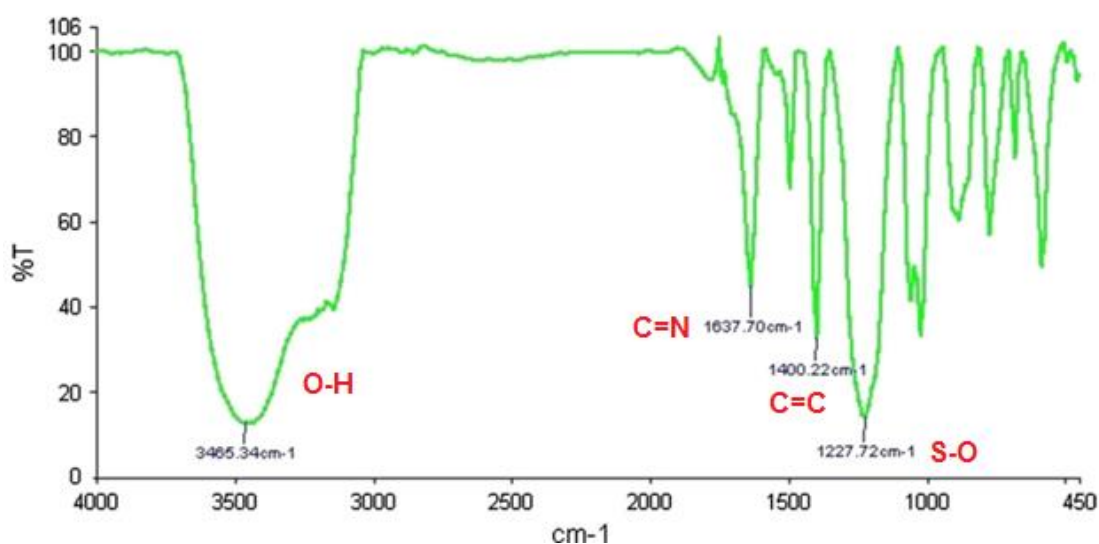


Figure 1. The FT-IR spectrum of 1,1'-butylenebispyridinium hydrogen sulfate

Table 1. Optimization of amount of catalyst-loading for the synthesis of 1,1-diacetates under solvent-free conditions at room temperature

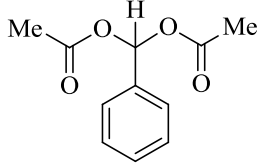
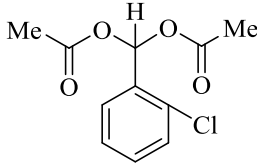
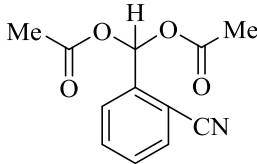
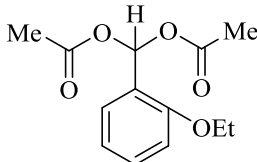
Entry	Catalyst (mg)	Time (min)	Yield (%) ^a
1	-	24 h	Trace
2	1	60	55
3	5	60	78
4	10	35	86
5	15	25	94

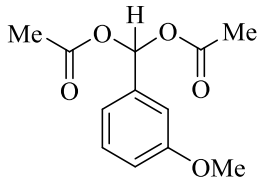
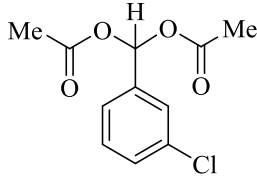
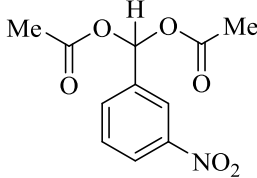
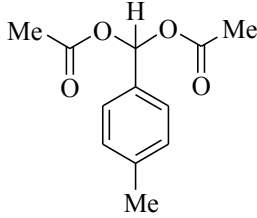
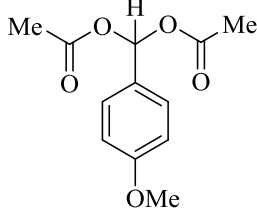
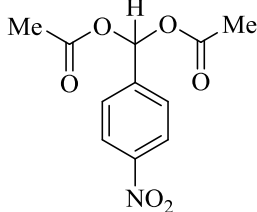
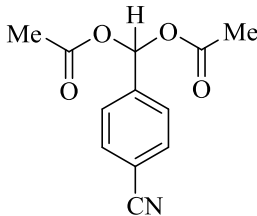
6	20	25	94
7	25	30	91

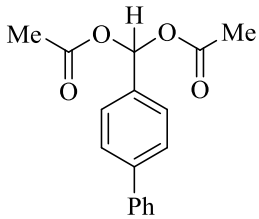
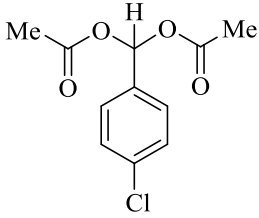
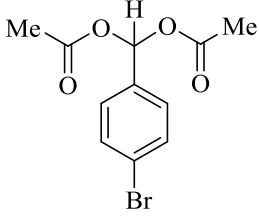
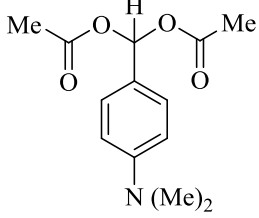
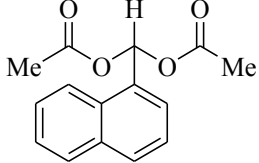
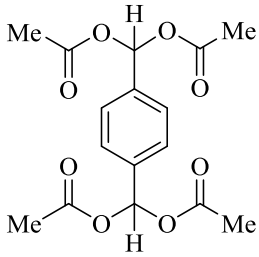
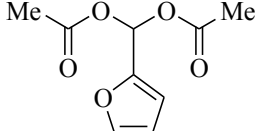
^aYield of isolated products**Table 2.** Optimization of various solvent for the synthesis of 1,1-diacetates under reflux conditions

Entry	Solvent (5 mL)	Time (min)	Yield (%) ^a
1	CH ₂ Cl ₂	60	42
2	EtOH	60	40
3	EtOAc	60	35
4	CHCl ₃	60	30
5	H ₂ O	60	35

^aYield of isolated products**Table 3.** Conversion of aldehydes to acylals using (Bbpy)(HSO₄)₂ under solvent-free conditions at ambient temperature

Entry	Product	Time (min)	Yield (%)	M.p. (°C) [lit.]
1		25	94	44-46 44-45 [14]
2		35	92	56-58 57-58 [14]
3		40	93	78-80 79-80 [14]
4		40	92	82-83 84-86 [14]

5		40	91	Oil	Oil [14]
6		30	90	65-67	64-65 [14]
7		30	89	89-90	91-92 [14]
8		25	89	82-84	80-82 [14]
9		35	91	64-65	63-64 [14]
10		30	92	44-46	44-45 [14]
11		35	89	103-104	100-102 [14]

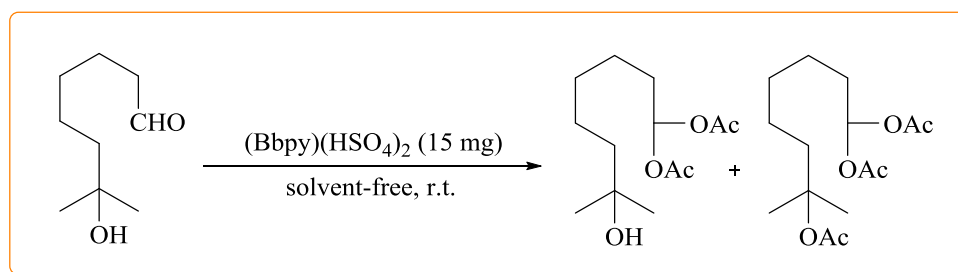
12		25	90	127-128	129-128 [14]
13		30	92	79-81	80-82 [14]
14		30	91	94-95	92-94 [14]
15		24 h	Trace	–	–
--16		30	93	102-104	101-102 [14]
17		35	92	173-175	174-176 [14]
18		30	88	52-53	50-52 [14]

19		40	88	Oil	Oil [14]
20		40	89	184-186	183-185 [14]

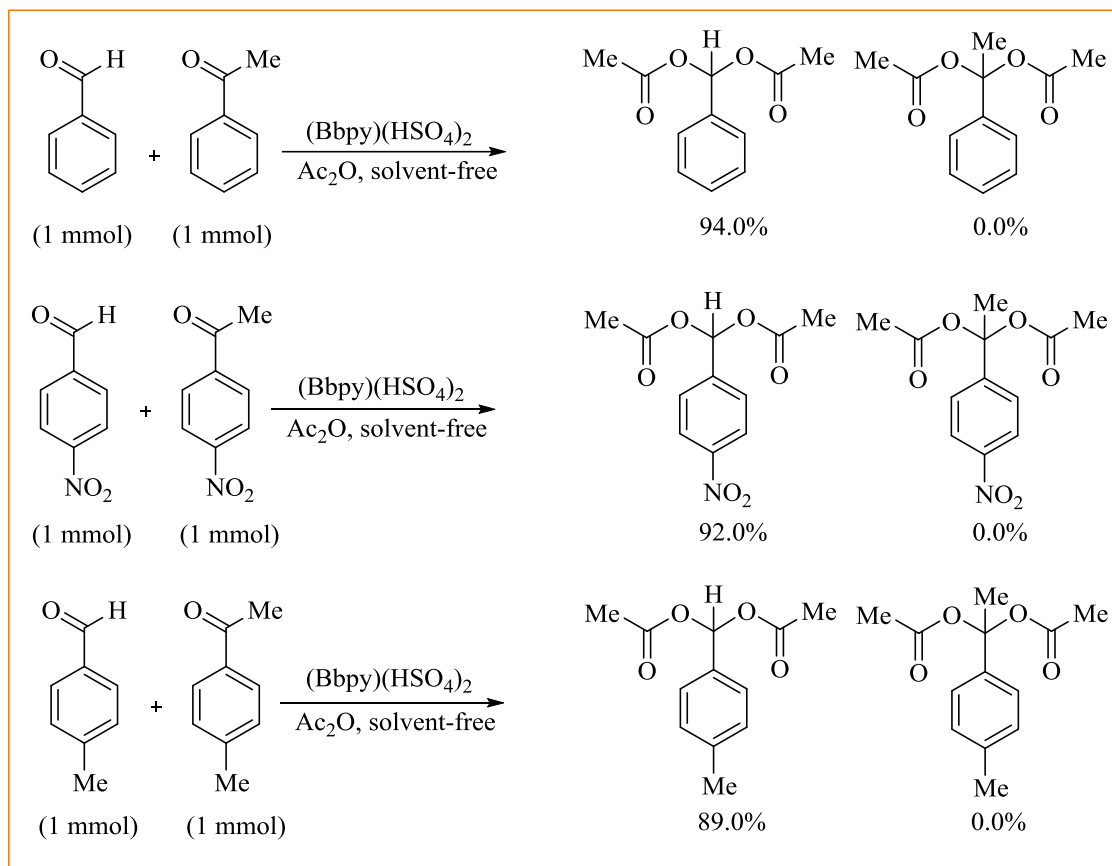
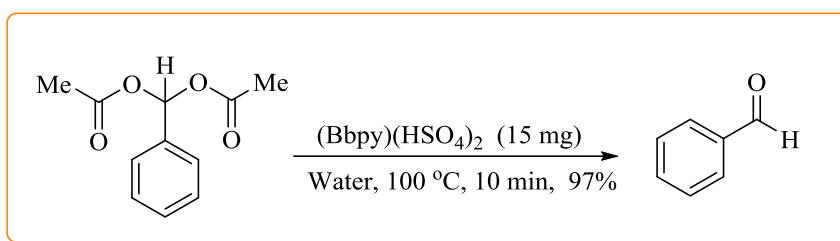
^a Yield of isolated products

In addition, we investigated the application of the $(\text{Bbpy})(\text{HSO}_4)_2$ as catalyst for deprotection of the 1,1-diacetates to their corresponding aldehydes. For this purpose, after the completion of the reaction for the formation of the phenyl ethylene diacetate from the benzaldehyde and acetic anhydride, water as a green solvent was added to the mixture reaction and the reaction temperature increased to 100 °C. By this procedure, the related acylals was completely transformed into the benzaldehyde in short reaction time and high yields (Scheme 4).

Finally, to show the high chemoselectivity of the method, a competitive reaction between the mixtures of some aldehydes and the ketones such as benzaldehyde and acetophenone, 4-nitro benzaldehyde and 4-nitro acetophenone, and 4-methyl benzaldehyde and 4-methyl acetophenone, with acetic anhydride (2 mmol) in the presence of $(\text{Bbpy})(\text{HSO}_4)_2$ (15 mg) under solvent-free condition at room temperature was studied. The results are shown in Scheme 5 that aldehydes were converted to the corresponding acylals, but the ketones remained practically intact.



Scheme 3. Acetylation of alcoholic group using Ac_2O in the presence of $(\text{Bbpy})(\text{HSO}_4)_2$ under solvent-free conditions.

Scheme 4. Deprotection of phenyl ethylene diacetate in the presence**Scheme 5.** Chemoslective acetylation of various aldehydes in the presence of ketones

Conclusion

In summary, the $(\text{Bbpy})(\text{HSO}_4)_2$ is a highly efficient and chemoselective catalyst for gem-diacetate synthesis from both the aromatic and aliphatic aldehydes under solvent-free conditions at room temperature. The advantages of this methodology over the other methods is its low cost, excellent chemoselectivity, exceptionally fast reactions, applicability to large-scale reactions, short reaction time, and operational simplicity without need of any solvent.

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Disclosure statement

No potential conflict of interest was reported by the authors.

Orcid

Sobhan Rezayati  0000-0001-8940-292

Rahimeh Hajinasiri  0000-0002-8219-101X

Zinatossadat Hossaini  0000-0001-7193-1759

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