

Efficient and Selective *N*-, *S*- and *O*-Acetylation in TEAA Ionic Liquid as Green Solvent. Applications in Synthetic Carbohydrate Chemistry

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Received April 15, 2015; Revised December 18, 2015; Accepted December 30, 2015

Abstract: Background: The ionic liquid triethylammonium acetate (TEAA) was found to be an efficient solvent in the acetylation of alcohols, amines, oximes and thiols to their corresponding acetyl compounds using only a 10% excess of acetic anhydride under mild conditions. Moreover TEAA is not only an inexpensive and recyclable solvent but also an anomeric selective catalyst in the per-*O*-acetylation of sugar moieties.

Methods: Simple and effective organic synthesis protocols were provided for the selective acetylation of several substrates. The products were fully characterized by ^1H and ^{13}C NMR spectroscopy and the anomeric ratios were obtained from the ^1H spectra.

Results: Structurally diverse alcohols, phenols, thiols, amines, carbohydrates and oximes underwent acylation under mild conditions by this procedure to provide the corresponding acetates in excellent yields. TEAA ionic liquid is unique in its capability to act as both, solvent and high selective catalyst. As expected, the reaction proceeds with high *b* anomeric selectivity for sugars derivatives. Moreover, the ionic liquid was regenerated, recycled and reused for three times without apparent loss of reactivity and selectivity in all cases.

Conclusions: The present procedure provides a powerful and versatile acylation method for alcohols, phenols, thiols, amines, oximes and carbohydrates. This protocol is endowed with several unique merits: selectivity, cost-efficiency, atom-economy and mild reaction conditions tolerable to acid sensitive functionalities. With these features, this method may be considered as a better alternative for the acetylation of a wide range of substrates.

Keywords: Acylation, carbohydrates, green chemistry, triethylammonium acetate (TEAA).

INTRODUCTION

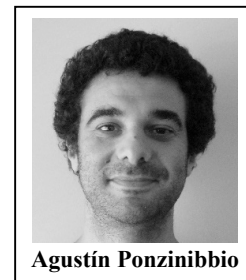
The acylation of hydroxyl, thiol and amino groups is one of the most frequently used transformations in organic synthesis as it provides an efficient protocol during multistep synthetic procedures [1]. In addition, hydroxyl group *O*-acetylation is used extensively in carbohydrate chemistry as a protection strategy and for the isolation and identification of various natural products containing carbohydrate substructures [2]. Acetylation is usually carried out by treatment of an alcohol, thiol or amine with an excessive amount of acetic anhydride or acetyl chloride in the presence of either acid [3] or base [4] catalysts. Although various acetylation methods are available, most protocols to date possessed inherent drawbacks including long reaction times, harsh conditions, tedious work-up procedures, moisture-sensitivity and high cost of the acid or base catalysts. The solvents commonly chosen for these reactions are methylene chloride, acetonitrile and tetrahydrofuran. Moreover these procedures using chlorinated hydrocarbons or toxic substances as solvents also do not satisfy the requirements of green synthesis [5].

More efficient alternative methods are developed in recent years using microwave [6] and ultrasonic activation [7], solid supports [8], solid protic acids [9], enzymes [10] and ionic liquids [11]. Ionic liquids are commonly used as reusable 'green' solvents. In addition to solvent, ILs may have multiple functions in catalytic reactions. They may act as catalyst, co-catalyst, support or ligands. The application of ionic liquids as novel media may provide convenient solutions to both the solvent emission and catalyst reuse problem. A great deal of attention has been given to imidazolium based ionic liquids, however industrial application is limiting because of their high price and low recyclability [12].

Triethylammonium acetate (TEAA) is an easily accessible and inexpensive room temperature ionic liquid recently used in organic synthesis and catalysis as an environment friendly solvent [13]. This ionic liquid is air and water stable and easy to synthesize from triethylamine and acetic acid, which are relatively cheap. We report here that TEAA ionic liquid is not only effective solvent for a wide variety of alcohols, thiols, amines and saccharides but also active catalyst for their selective acetylation.

RESULTS AND DISCUSSION

Structurally diverse alcohols, phenols, thiols, amines and oximes underwent acylation under mild conditions by this



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Table 1. Acetylation reaction in TEAA with 1.10 equiv. of Ac₂O at room temperature.

Entry	Compound Structure: R=H → R=Ac ^a	Time ^b	Yield% ^c
1		3	74
2		3	71
3		3	68
4		3	69
5		3	70
6		4	65
7		3	72
8		1	66
9		1	67
10		1.5	73
11		2	65

^a All products were known and their identities were confirmed by comparing their spectral data with those available in the literature. (ref. 3)

^b Time (hours) for 100% conversion by TLC monitoring.

^c Isolated yields

procedure to provide the corresponding acetates in excellent yields. In a typical experiment, 0.2 mmol of the substrate was dissolved, under stirring, in 2 ml of TEAA. Then 1.10 equiv of acetic anhydride per reactive group was added to the medium and the reaction was monitored by TLC. The desired compounds obtained by extraction with diethyl ether are of high purity and do not require further purification as seen by ¹H and ¹³C NMR spectroscopy. The acylations are, in general reasonably fast and clean as seen in Table 1.

It's well known that nucleophilic functionalities have different reactivity patterns for the acylation reaction. This difference in activity persuaded us to investigate the feasibility of selective protections of hydroxyl groups in the presence of phenols in more complex substrates. As expected the use of 1.1 equiv. of acetic anhydride and moderate reaction conditions leads to the monoacetylated product. Similar results were obtained when 4-aminophenol was used as substrate to afford exclusively N-(4-hydroxyphenyl) acetamide (paracetamol), a widely used analgesic drug. The results shown in

Table 2 clearly illustrate the high chemoselectivity of our protocol.

In view of our ongoing efforts in the development of environmentally friendly catalytic processes for the synthesis of biologically active carbohydrate derivatives [14], we decided to investigate the use of TEAA as both solvent and catalyst for the per-O-acetylation of sugars. Acetylation of saccharides were usually carried out in the presence of pyridine [15], sodium acetate [16], zinc chloride [17], sulfuric acid [18], or perchloric acid as catalysts [19]. Most of the methods suffer from some drawbacks such as low anomeric selectivity, unpleasant odors, difficulties in workup, and use of toxic and/or corrosive reagents. Recently, several triflate derivatives have been shown to be effective for per-O-acetylation of carbohydrates [20]. However the cost, availability and toxicity can limit the widespread application of these catalysts. Thus, introduction of new efficient methodologies for per-O-acetylation reactions of sugars is still in strong demand. Encouraged by the results obtained we in-

Table 2. Selective acetylation of various functional groups in TEAA with 1.1 equiv of Ac₂O in 3 h at room temperature.

Entry	Substrate	Product ^a	Yield% ^b
1			75
2			67
3			73

^a All products were known and their identities were confirmed by comparing their spectral data with those available in the literature. (ref. 3)

^b Isolated yields

investigated the feasibility of our synthetic protocol for the acetylation of carbohydrates moieties.

At first we examined the solubility of sugars in TEAA ionic liquid. Glucose is soluble in this liquid to greater than 10 weight percent at room temperature. The TEAA ionic liquid appears to be of great value in carbohydrate chemistry among other families of ionic liquids, in presenting high solubility to saccharides. In contrast, for example butyl methyl imidazolium cations with chloride, hexafluorophosphate and tetrafluoroborate anion offer low to very low solubility [10b].

A set of initial experiments carried out using D-glucose as substrate revealed that 1.1 mol equiv per OH was optimal for the complete acetylation. The mixture was stirred at 50°C until completion of reaction (indicated by disappearance of α -D-glucose on TLC). Under these conditions a facile reaction took place leading to the formation of the desired product in excellent yields. The solid obtained was pure peracetylated glucose in 18:82 α/β ratio. The product was fully characterized by ¹H and ¹³C NMR spectroscopy and the anomeric ratio was obtained from the ¹H spectra.

Table 3 summarizes the results on a range of saccharides using TEAA and acetic anhydride as reactants. All hydroxyl groups were successfully acetylated, indicating the generality of this reaction. Most of the assays were carried out beyond saturation limits of the substrate, the reaction mixture became completely homogenous as the reaction proceeds. This approach allowed the use of minimal amounts of TEAA ionic liquid.

We observed that the reactions described above proceed rapidly with no added catalyst. Since sodium acetate has been reported as a catalyst for acetylation of carbohydrate derivatives [21], is likely and not surprising that TEAA may play a catalytic role. In order to investigate these facts the acetylation of α -D-glucose was carried out using only 0.5 eq. of TEAA in DMF. As expected, α -D-glucose was fully acetylated and obtained in 65% yield (15:85 α/β ratio).

In most examples of Lewis acid promoted acetylations, the cleavage of acid-labile functionalities has been reported [22]. Interestingly, the acid-labile groups such as acetals and

O-glycosides survived the present reaction conditions and the yields of acetylated products were excellent as seen in entries 7 and 8 in Table 3. No formation of fully acetylated sugars was detected.

TEAA ionic liquid is unique in its capability to act as both, solvent and high selective catalyst. As expected, the reaction proceeds with high β anomeric selectivity [21]. In addition, more of the acetic acid formed as product remains in the ionic liquid and could be used in the regeneration process of TEAA by the addition of triethylamine. It is noteworthy that the entire process is selective, rapid, cheap and atom-economic.

The long reaction times and lower yields in the organic solvents illustrate the usefulness of TEAA as reaction promoter compared to more traditional solvents. Moreover, the ionic liquid was regenerated, recycled and reused for three times without apparent loss of reactivity and selectivity. After five cycles, a slight drop in yields by about 10-15 % was found with the recycled IL after dried in vacuum. It is possible that this decrease values could be due to partial decomposition of the IL during the reaction as in NMR spectra appeared some minor unknown peaks.

Further work expanding on the scope of the substrates and on the suitability of the protocol to prepare thioglycosides in a one-pot reaction is under way in our laboratory.

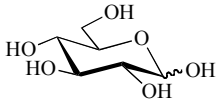
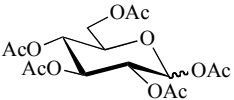
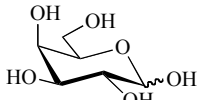
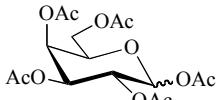
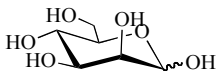
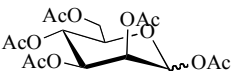
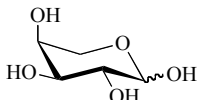
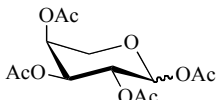
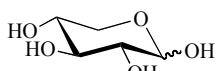
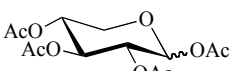
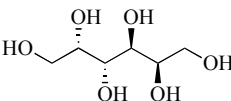
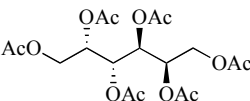
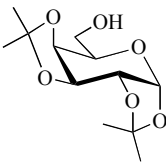
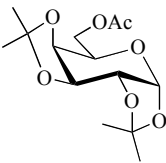
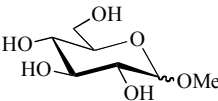
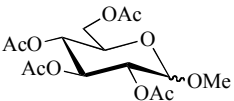
CONCLUSION

The present procedure provides a powerful and versatile acylation method for alcohols, phenols, thiols, amines, oximes and carbohydrates. This protocol is endowed with several unique merits: selectivity, cost-efficiency, atom-economy and mild reaction conditions tolerable to acid sensitive functionalities. With these features, this method may be considered as a better alternative for the acetylation of a wide range of substrates.

EXPERIMENTAL

All reagents were obtained from commercial sources and used without further purification. Preparation of all sugar

Table 3. Peracetylation of saccharidic compounds promoted by TEAA.

Entry	Substrate	Product ^a	Ratio α : β ^b	Yield% ^c
1			18:82	65
2			12:88	69
3			20:80	67
4			--- ^d	70
5			--- ^d	67
6			---	72
7			---	65
8			---	64

^a ¹H and ¹³C NMR spectra of the products were in total accordance with literature (ref. 21).

^b anomeric ratios were obtained from ¹H NMR spectra.

^c isolated yields.

^d not determined as a mixture of pyranose and furanose forms were obtained.

derivatives followed the already known methods described in literature. Thin layer chromatography (TLC) was performed on Merck 60 F₂₅₄ plates. Reactions were monitored by TLC on silica gel, with detection by UV light (254 nm) or by charring with sulfuric acid. Flash chromatography was performed using silica gel (230-400 mesh). ¹H and ¹³C NMR spectra were recorded on a Bruker Avance II 500 MHz using Me₄Si as the internal standard in CDCl₃. HSQC and COSY spectra were used to establish peak assignments in ¹H and ¹³C NMR.

Modified Procedure of Triethylammonium Ionic liquid Synthesis [12]

The synthesis of TEAA was carried out under argon atmosphere in a two necked 250 cm³ round-bottomed flask equipped with a reflux condenser and a dropping funnel with pressure compensation. Acetic acid (1.5 mol) was dropped into freshly distilled triethylamine (1 mol) at 70°C within 1 hour. After the addition, the mixture was stirred for 2 hours

at 80°C. The reaction mixture was then diluted and evaporated twice with 5 ml of toluene. The residue was then dried at 80°C in high vacuum (0.1 mm Hg) until the weight of TEAA remained constant. Yield: 92%. ¹H NMR: (500 MHz, CDCl₃) δ =9.18 (s, 1H), 3.08 (q, J = 7.3 Hz, 6H), 1.99 (s, 3H), 1.24 (t, J=7.4 Hz, 9H). ¹³C NMR: (125 MHz, CDCl₃) δ 176.35, 45.03, 22.19, 8.35.

Typical Procedure: Acetylation of 2-naphthol

To a stirred solution of 2-naphthol (0.2 mmol) in TEAA (2 ml), was added acetic anhydride (0.22 mmol). The solution was stirred for 3 hours at room temperature. After consumption of starting material (TLC monitoring, ethyl acetate/hexane, 2:8), the product formed was diluted with 1 ml H₂O and extracted with 3 x 2 ml ether. The combined organic layer was separated, dried (Na₂SO₄), and evaporated under reduced pressure to afford the desired product. ¹H and ¹³C NMR spectra were in full accordance with the structure proposed. The water in the aqueous layer was distilled under

reduced pressure leaving behind the TEAA which was further recycled.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

ACKNOWLEDGEMENTS

Authors wish to thank Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CICPBA), UNLP and CONICET for their financial support to the present work. A. P. is member of CIC of CONICET.

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