Polyvinylpolypyrrolidonium Tribromide as an Efficient Catalyst for the Acetylation of Alcohols and Phenols

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Abstract: An efficient and versatile procedure for the acetylation of alcohols and phenols using acetic anhydride in the presence of a catalytic amount of polyvinylpolypyrrolidonium tribromide has been successfully developed. Primary, secondary, and tertiary alcohols, as well as a selection of the phenolic compounds, have been successfully acetylated according to this procedure, with good to high yields being achieved over short reaction times.

Key words: alcohol; phenol; polyvinylpolypyrrolidonium tribromide; acetylation; acetic anhydride

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The acetylation of alcohols and phenols is one of the most widely used transformations in organic synthesis. Organic esters represent an important family of intermediates and they are frequently employed in the synthesis of fine chemicals, perfumes, drugs, food preservatives, plasticizers, and pharmaceuticals [1–5]. Further to this, the acetylation of the hydroxyl group is often used as a protection technique in organic synthesis because of the ease of formation as well as the mild conditions required for the subsequent deprotection [6]. Acid anhydrides and acid halides are usually used as acetylating agents in the presence of an appropriate catalyst or activator [7–12].

Although many synthetic methods have been reported for the acetylation of the hydroxyl group, these approaches are invariably limited by the formation of undesired by-products, the requirement for harsh reaction conditions, low product yields, and long reaction times. With this in mind, the development of a general, mild, and novel procedure is required to prepare *O*-acetylated compounds in the presence of an appropriate catalyst.

Polymer-supported reagents have received considerable attention in recent years in the development of novel organic reaction methodologies [13–17] because of their heterogeneous nature, which enables reactions to be conducted under mild conditions and for the organic products to be isolated with relative ease from the reaction media. Furthermore, these systems show low toxicity. Taken together, the special properties associated with polymeric reagents prompted us to investigate their application in organic synthesis.

1 Experimental

All of the chemicals used in the current study were purchased from the Fluka, Merck, and Aldrich chemical companies. The acetylated products were characterized by comparison of their spectral (IR, ^1H NMR, and ^{13}C NMR) and physical data with those of the authentic samples. Polyvinylpolypyrrolidonium tribromide was prepared according to a procedure previously reported by our group [13].

Polyvinylpolypyrrolidonium tribromide (0.011 g) was added to a stirred solution of 4-*iso*-propylbenzyl alcohol (0.15 g, 1 mmol) and acetic anhydride (0.255 g, 2.5 mmol) in acetonitrile (5 ml) and the resulting mixture was stirred at room temperature for 15 min. Upon completion of the reaction, as determined by TLC analysis, water (5 ml) was added to the mixture with stirring and the product mixture was extracted with CH_2Cl_2 (5 ml $\times$ 4). The combined organic extracts were dried over anhydrous Na_2SO_4 (1.5 g) and concentrated to dryness by evaporated to give the desired product (0.186 g, 97% yield).

3-Fluorobenzyl acetate. ^1H NMR (400 MHz, CDCl_3): δ 7.40–7.46 (m, 1H), 7.14–7.21 (m, 3H), 5.10 (s, 2H), 2.07 (s, 3H); ^{13}C NMR (100.6 MHz, CDCl_3): δ 170.68, 162.6 (d, $J_{\text{C-F}} = 968$ Hz), 139.6 (d, $J_{\text{C-F}} = 32$ Hz), 130.9 (d, $J_{\text{C-F}} = 32$ Hz), 122.5 (d, $J_{\text{C-F}} = 12$ Hz), 114.9–115.3 (2C), 65.0, 21.1.

2 Results and discussion

We developed a particular interest in the application of polyvinylpolypyrrolidonium tribromide (Scheme 1) [18],

Scheme 1. Structure of polyvinylpolypyrrolidonium tribromide.

as an efficient, green, and versatile polymeric catalyst for the protection of alcohols and phenols as the corresponding acetyl esters.

In a continuation of our ongoing efforts to develop novel applications of polymeric reagents or catalysts in organic reactions [19–24], polyvinylpolypyrrolidonium tribromide was investigated as a green catalyst for the preparation of *O*-alkyl and aryl acetylated compounds.

Polyvinylpolypyrrolidonium tribromide was prepared via the combination of polyvinylpolypyrrolidone with hydrobromic acid followed by the reaction of resulting salt with bromine [18].

To identify an appropriate solvent for the transformation, a screening process was conducted involving the acetylation of 2-phenylethanol in several different solvents. The results of the screening process have been summarized in Table 1. The results in Table 1 clearly show that acetonitrile was the best solvent, in terms of reactivity, for the polyvinylpolypyrrolidonium tribromide catalyzed acetylation reaction of 2-phenylethanol with acetic anhydride. Acetonitrile was therefore applied as the solvent for all of the subsequent

Table 1 Acetylation of 2-phenylethanol with acetic anhydride in the presence of a catalytic amount of polyvinylpolypyrrolidonium tribromide in different solvents

Solvent	Time (min)	Yield ^a (%)
Chloroform	300	81
Acetonitrile	25	91
<i>n</i> -Hexane	1440	66 ^b
Dichloromethane	270	92
Ethyl acetate	100	95
Acetone	180	86

Reaction conditions: substrate 1 mmol, catalyst 0.011 g, acetic anhydride 2.5 mmol.

^aIsolated yield.

^bProduct purified by short-column chromatography.

acetylation reactions.

Having established the best solvent for the procedure, we proceeded to investigate the scope polyvinylpolypyrrolidonium tribromide catalyzed acetylation reaction. Consequently, herein we disclose a novel catalytic protocol for the acetylation of primary, secondary, and tertiary alcohols, as well as a selection of phenolic compounds, using acetic anhydride and a catalytic amount of polyvinylpolypyrrolidonium tribromide under mild and heterogeneous conditions at room temperature (Table 2).

Table 2 Acetylation of alcohols and phenols using acetic anhydride in the presence of a catalytic amount of polyvinylpolypyrrolidonium tribromide in acetonitrile at room temperature

Entry	Substrate	Product	Time (min)	Yield ^a (%)	Ref.
1			60	91	[10]
2			15	97	[28]
3			30	96	[26]
4			20	91	[10]
5			15	94	[26]
6			5	96	[10]
7			5	86	—
8			5	98	[10]
9			30	86	[2]
10			25	91	[10]
11 ^b			1440	— ^c	[10]

(To be continued)

Table 2 (Continued)

Entry	Substrate	Product	Time (min)	Yield ^a (%)	Ref.
12			140	85	[9]
13			45	96	[29]
14			20	92	[4]
15			210	84	[10]
16			1440	68 ^d	[10]
17			210	92	[26]
18			40	93	[25]
19			90	99	[27]

Reaction conditions: substrate 1 mmol, catalyst 0.011 g, acetic anhydride 2.5 mmol.

^aIsolated yield. ^bIn the absence of catalyst. ^cNo reaction. ^dProduct purified by short column chromatography.

The acetylation of alcohols and phenols was easily achieved by the mixing 1 mmol of the alcohol or phenol with 0.011 g of polyvinylpyrrolidonium tribromide and 2.5 mmol of acetic anhydride in acetonitrile, with the resulting mixture then being stirred at room temperature for the appropriate time period (Table 2). Upon completion of the reaction, the mixture was quenched by the addition of water and the pure products isolated with relative ease via the extraction of the reaction mixture with dichloromethane. It is clear from Table 2 that unhindered alcohols reacted faster than the hindered ones. To highlight the catalytic role of polyvinylpyrrolidonium tribromide in the described reaction system, 2-phenylethanol was subjected to the acetylation procedure in the absence of the catalyst (Table 2, entry 11). The result clearly demonstrates the catalytic role of polyvinylpyrrolidonium tribromide in the reaction of 2-phenylethanol with acetic anhydride, as the reaction in the absence of the catalyst gave none of the desired product following a 24 h reaction period.

A possible mechanism for this polyvinylpyrrolidonium tribromide-catalyzed transformation is depicted in Scheme 2.

3 Conclusions

A novel polyvinylpyrrolidonium tribromide catalyzed procedure for the acetylation of alcohols and phenols with acetic anhydride was successfully developed. The procedure employs a polymeric catalyst and provides a simple and effective procedure for the preparation of alkyl and aryl

Scheme 2. Possible mechanism for acetylation of alcohols.

acetates in good to excellent yields with high purity. This procedure is characterized by heterogeneous and mild reaction conditions, non-toxic content and an easy reaction work-up, making it ideal for both laboratory and large-scale preparations.

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