

Poly (4-vinylpyridinium tribromide): an efficient catalyst for the synthesis of 1,1-diacetates from aldehydes

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Poly(4-vinylpyridinium tribromide) is an excellent catalyst for the protection of aldehydes as 1,1-diacetate derivatives, by using acetic anhydride under solvent-free conditions. This method has some advantages such as mild reaction conditions, good to excellent yields and use of non metallic catalyst.

Keywords: 1,1-Diacetate; Poly(4-vinylpyridinium tribromide); Acetic anhydride; Aldehyde; Acylal.

INTRODUCTION

1,1-diacetates are some of the essential carbonyl protecting groups because of their stability in neutral and basic media [1]. Diacetates of α,β -unsaturated aldehydes are important starting materials for synthesis of dienes in Diels–Alder reactions [2,3]; they are also useful intermediates in various transformations [4]. Moreover, acylals can be converted into other functional groups by reaction with suitable nucleophiles [5,6].

In the literature, many methods are reported for the preparation of 1,1-diacetates from aldehydes using acetic anhydride and various catalysts [7-8]. The catalysts have been used for these protection reactions to improve yields, reaction times and temperature. Some of the reported catalysts for the preparation of 1,1-diacetates from aldehydes and acetic anhydride include FeF_3 [9], 1,3-dibromo-5,5-dimethylhydantoin [10], $\text{FeCl}_3\text{-SiO}_2$ [11], PVC-FeCl_3 [12], $\text{SnCl}_4\text{-SiO}_2$ [13], amberlyst-15 [14], $\text{Zr(SO}_4)_2\cdot 4\text{H}_2\text{O-SiO}_2$ [15], $\text{P}_2\text{O}_5\text{-SiO}_2$ [16], $\text{H}_3\text{PW}_{12}\text{O}_{40}$ [17], N-bromosuccinimide [18], $\text{Zr(HSO}_4)_4$ [19], etc. Some of these reported methods suffer from at least one of the following drawbacks: reactions under oxidizing conditions, use of halogenated solvents, long reaction times, and high toxicity.

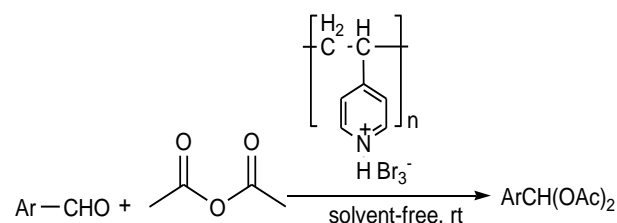
Polymer supported reagents used as catalysts have acquired wide interest in recent years [20-24] because of the ease of work-up and product purification and minimized environmental damages. Herein we report poly(4-vinylpyridinium tribromide) catalyzed rapid and mild synthesis of

1,1-diacetates from aldehydes under solvent free conditions.

RESULTS AND DISCUSSION

In continuation of our studies on the application of poly(4-vinylpyridinium tribromide) in organic reactions [25-27], we have found that the combination of acetic anhydride as acylating agent and catalytic amount of poly(4-vinylpyridinium tribromide) could be an efficient protocol for conversion of aldehydes into their corresponding 1,1-diacetates.

Initially, to find out an appropriate solvent, the reaction of 4-chlorobenzaldehyde was performed in different solvents, the results of which are summarized in Table 1. It was observed that solvent-free conditions are best for the synthesis of acylals. Therefore, we report a convenient method for the effective conversion of aldehydes to their corresponding 1,1-diacetates by using Ac_2O and catalytic amount of PVP-Br_3 under solvent-free conditions, as depicted in Scheme 1.



Scheme 1. Conversion of aldehydes to 1,1-diacetates

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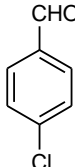
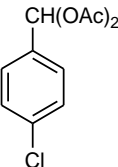
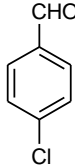
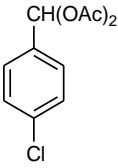
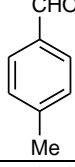
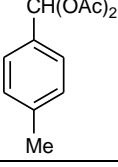
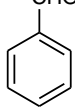
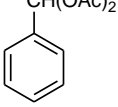
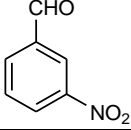
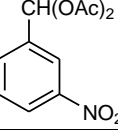
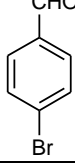
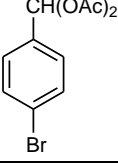
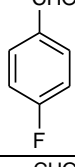
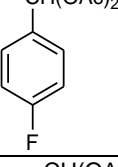
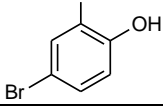
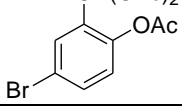
Table 1: Optimization of solvent for the synthesis of 4-chlorobenzene aldehyde 1,1-diacetate by acetic anhydride and catalytic amount of poly(4-vinylpyridinium tribromide) at room temperature.^a

Entry	Solvent	Time (h)	Yield (%) ^b
1	Ethylacetate	24	35
2	Chloroform	24	51
3	Dichloromethane	24	32
4	Acetonitrile	24	27
5	n-Hexane	24	30
6	Solvent-free	105 min	93 ^c

^a reaction condition; substrate: acetic anhydride: poly(4-vinylpyridinium tribromide): solvent (1mmol: 2mmol: 0.035g: 3mL).

^b yield isolated by short column chromatography . ^c isolated yield.

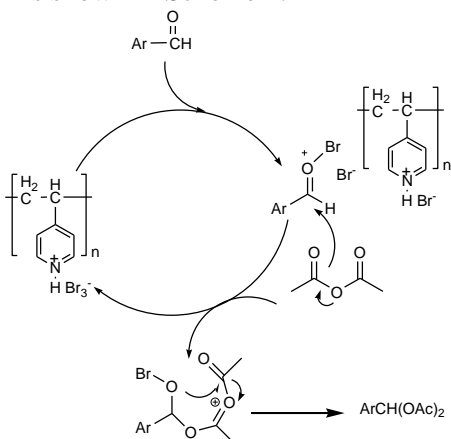
Table 2: PVP-Br₃-catalysed conversion of aldehydes to 1,1-diacetates with Ac₂O under solvent-free conditions.

Entry	Substrate	Product	Acetic anhydride (mmol)/ Catalyst (g)	Time (min)	Yield (%) ^a	
1			2	0.035	105	93
2			2	-- ^b	24 h	-- ^c
3			2	0.035	90	94
4			2	0.035	60	89
5			2	0.035	75	70
6			2	0.035	50	94
7			2	0.035	46	91
8			2	0.035	47	98

^a Isolated yield. ^b Reaction in the absence of catalyst. ^c No reaction.

The results of this study are summarized in Table 2. As shown in Table 2, various aromatic aldehydes were converted to corresponding acylals in high yields with short reaction times under solvent-free conditions. It should be noted that these acylation reactions did not proceed with the use of acetic anhydride alone even after 24 hours, and the presence of poly(4-vinylpyridinium tribromide) as catalyst is necessary. The result is presented in entry 2, Table 2.

A possible mechanism suggested for this reaction is shown in Scheme 2.



Scheme 2. Mechanism of the protection of aldehydes as 1,1-diacetates

In conclusion, herein we report a mild and efficient polymeric catalyst for the preparation of 1,1-diacetates from aldehydes in the presence of acetic anhydride under solvent-free conditions at room temperature. This method has some advantages such as rapid and inexpensive synthesis having a low environmental impact.

EXPERIMENTAL

General

Chemicals were purchased from Fluka, Merck and Aldrich chemical companies. The products were characterized by comparison of their spectral (^1H NMR, and ^{13}C NMR) and physical data with those of authentic samples.

Preparation of poly(4-vinylpyridinium tribromide)

In a 50 mL round-bottomed flask, 1 mL of HBr (47%) and 1.85 g of poly(4-vinylpyridine) were stirred for 1 h, then kept at 50 °C for 24 h to obtain dry poly(4-vinylpyridinium bromide). In the next step 1.2 mL of Br_2 was added to the resulting powder; this mixture was stirred for 2 h and an orange crystalline solid, poly(4-vinylpyridinium tribromide), was quantitatively obtained (Scheme 3) [18].

General procedure for the protection of aldehydes

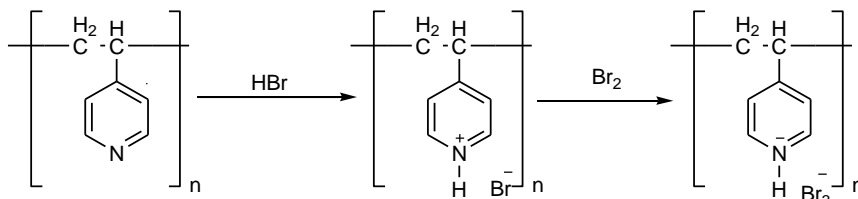
A mixture of aldehyde (1 mmol), acetic anhydride (2 mL) and poly(4-vinylpyridinium tribromide) (0.035 g) was stirred under solvent-free conditions at room temperature (the progress of the reaction was monitored by TLC). After reaction completion, the reaction was quenched with water (5 mL) and then washed with 5% NaHCO_3 (5 mL). The product was extracted with CH_2Cl_2 (4×5 mL). After separation of the organic layer, anhydrous Na_2SO_4 (1.5 g) was added to the solution and was filtered off after 20 min. Finally, dichloromethane was evaporated and pure acylals were obtained in good yields.

Selected ^1H NMR and ^{13}C NMR data

4-chlorobenzene aldehyde 1,1-diacetate: ^1H -NMR(CDCl_3 , 400MHz)= δ_{H} (ppm): 2.15 (s, 6H), 7.39 (d, $J=7.6$ Hz, 2H), 7.48 (d, $J=8.2$ Hz, 2H), 7.662 (s, 1H). ^{13}C -NMR(CDCl_3 , 100MHz)= δ_{C} (ppm): 20.8, 89.1, 128.2, 128.9, 134, 135.1, 168.7.

5-bromo-2-oxyacetatebenzaldehyde 1,1-diacetate: ^1H -NMR(CDCl_3 , 400MHz)= δ_{H} (ppm): 2.143 (s, 6H), 2.365 (s, 3H), 7.047 (d, $J=8.8$ Hz, 1H), 7.568 (d, $J=8.8$ Hz, 1H), 7.788 (d, $J=2.4$ Hz, 1H), 7.876 (s, 1H). ^{13}C -NMR(CDCl_3 , 100MHz)= δ_{C} (ppm): 20.7, 20.8, 84.4, 119.3, 124.9, 129.8, 130.9, 133.7, 147.2, 168.3, 169.1.

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Scheme 3. Preparation of poly(4-vinylpyridinium tribromide)

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ПОЛИ (4-ВИНИЛПИРИДИН ТРИБРОМИД): ЕФЕКТИВЕН КАТАЛИЗАТОР ЗА СИНТЕЗАТА НА 1,1-ДИАЦЕТАТИ ОТ АЛДЕХИДИ

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(Резюме)

Поли (4-винилпиридин трибромид)-ът е отличен катализатор за защита на алдехиди като 1,1-диацетат'ови производни с помощта на оцетен анхидрид в отсъствие на разтворител. Методът има предимства: меки реакционни условия, добри до отлични добиви и използване на неметален катализатор.