Transactions C: Chemistry and Chemical Engineering
Vol. 17, No. 1, pp. 24–30
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# PEG-SO$_3$H as a New, Highly Efficient and Homogeneous Polymeric Catalyst for the Synthesis of Acylals from Aldehydes and Acetic Anhydride

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**Abstract.** *A highly efficient, simple and rapid method for the chemoselective preparation of acylals from aldehydes and acetic anhydride in the presence of a catalytic amount of poly(ethylene glycol)-bound sulfonic acid (PEG-SO$_3$H) (1.67 mol%) at room temperature is described. Ketones do not react under these reaction conditions.*

**Keywords:** *Poly (ethylene glycol)-bound sulfonic acid (PEG-SO$_3$H); Polymeric catalyst; Acylal; Aldehyde; Acetic anhydride.*

## INTRODUCTION

For many years, functionalized polymers have been employed as stoichiometric reagents and catalysts in organic synthesis [1,2]. However, their development and applications in organic synthesis are undergoing a tremendous renaissance at present, which is undoubtedly being fueled by the special requirements of combinatorial and green chemistry [1,2]. There are a number of key advantages that link functionalized polymers to synthetic chemistry including the ease of product isolation, the use of excess amounts of reagents to drive the reaction toward completion and the good stability of the catalyst [3,4]. Nevertheless, a large number of available functionalized polymers (especially major polymers) are insoluble in different solvents, being polystyrene based and possessing either low (merrifield resin) or high (macroporous resins) degrees of cross-linking [1,2]. Moreover, emerging problems associated with the application of insoluble polymeric derivatives under heterogeneous conditions, including lowered reactivities and site-site interactions, extended reaction times, diffusion-limited reactivity, reagent leaching and toxicity, have meant that soluble matrixes, [5] such as poly(ethylene glycol)s (PEGs) [6-9], fluorous supports [10], linear poly(styrene)s [11] and poly(ethylene)s [12] are receiving increasing attention, both for combinatorial synthesis and as supports to catalyze organic reactions in solution and solvent-free media. Among them, PEGs are inexpensive, readily functionalized are reagents and solvents with nontoxic properties are Phase Transfer Catalysts (PTC) [13], environmentally benign [14], commercially available in different molecular weights and have a broad solubility profile [15]. According to these excellent properties, PEGs are an important group of polymers and catalysts in several branches of chemistry and industry, such as organic synthesis [16]. Based on recent efforts to use eco-friendly and environmentally benign reagents in chemistry, PEGs are good candidates for these purposes [17].

The protection of carbonyl functional groups as acylals is an important strategy in organic synthesis [18]. Acylals are alternatives to acetals, and are important protecting groups in organic synthesis because of their stability under neutral and basic conditions, as well as under critically controlled acidic conditions [18]. They have several synthetic and

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*Received 28 October 2009; received in revised form 17 February 2010; accepted 10 April 2010*

industrial applications. Acylals have been utilized as cross linking reagents in cellulose and cotton industries, and as stain bleaching agents [19,20]. As synthons, they have been exploited in well-known reactions of organic chemistry like nitriles synthesis [21], Grignard reactions [22], Prins reactions [23], condensation reactions, such as Knoevenagel [24] and benzoin [25]. Because of their industrial, as well as synthetic, importance and their excellent properties as protective groups and synthons, finding a new strategy for the efficient and facile preparation of acylals is of current interest. Acylals are prepared from aldehydes and acetic anhydride using strong Brønsted or Lewis acidic catalysts, such as $H_6P_2W_{18}O_{62}.24H_2O$ [26], $H_3PW_{12}O_{40}$ supported MCM-41 molecular sieves [27], supported $H_3PMo_{12}O_{40}$ [28], $Ce(OTf)_4.xH_2O$ [29], $HClO_4/SiO_2$ [30], $P_2O_5/Al_2O_3$ [31], $In(OTf)_3$ [32], $ZrCl_4$ [33], $RuCl_3.xH_2O$ [34], $TiCl_3(OTf)$ [35]’ $NbCl_5$ [36] and zirconia-supported mixed oxide systems [37]. However, many of the reported methods have one or more of the following disadvantages:

(i) Lack of substrate tolerance and generality.
(ii) Long reaction time.
(iii) Low yield and selectivity.
(iv) The use of large amounts of reagent.
(v) Rigorous reaction conditions.
(vi) Application of expensive, non-available, corrosive, as well as moisture and air-sensitive, reagents.

Therefore, development of an efficient, general, low cost, selective and simple method for the conversion of aldehydes to acylals is still of interest.

Having the above facts in mind, and also as part of our ongoing program to develop more efficient methods in organic synthesis [38-46], we report here a new efficient method for the preparation of acylals via the acylation of aldehydes with acetic anhydride, using poly(ethylene glycol)-bound sulfonic acid (PEG-$SO_3H$) as a homogeneous catalyst at room temperature (Figure 1). Interestingly, our method has none of the above-mentioned disadvantages.

## RESULTS AND DISCUSSION

At first, the synthesis of acylal **1** from benzaldehyde (2 mmol) and acetic anhydride (8 mmol) was examined in the presence of different amounts of PEG-$SO_3H$ in $CH_2Cl_2$ (2 mL) at room temperature (Figure 1); the respective results are summarized in Table 1. As the data in Table 1 show, the best results were obtained when 0.2 g (1.67 mol%) of the catalyst was used. Increasing the amount of PEG-$SO_3H$ to 2.1 mol% did not improve the reaction results.

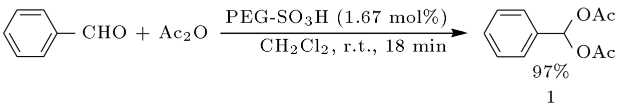


**Figure 1.** The acylation of benzaldehyde with acetic anhydride.

To select the appropriate solvent for the acylation reaction, the influence of various solvents was investigated on the reaction of benzaldehyde with acetic anhydride (Table 2). As the data in Table 2 indicate, a higher yield and a shorter reaction time were obtained when $CH_2Cl_2$ was used.

To assess the generality and scope of the method, acylals were synthesized from different aromatic/aliphatic aldehydes and acetic anhydride in the presence of PEG-$SO_3H$ in $CH_2Cl_2$ at room temperature; the respective results are displayed in Table 3. As clear from the data in Table 3, the method was highly efficient and general; using this method, all kinds of aldehydes, including benzaldehyde, aromatic aldehydes possessing electron-releasing substituents, electron-withdrawing substituents and halogens on their aromatic rings, 2-naphthaldehyde, acid-sensitive aldehyde (furfural), bis-aldehyde (terephthaldehyde) and aliphatic aldehydes were acylated in excellent yields and in short reaction times.

In another study, a competitive reaction for the preparation of acylal 1 from benzaldehyde in the presence of a ketone (acetophenone) using PEG-$SO_3H$

**Table 1.** Effect of different amounts of PEG-$SO_3H$ on the reaction of benzaldehyde (2 mmol) with acetic anhydride (8 mmol) in $CH_2Cl_2$ (2 mL) at room temperature.

| **Entry** | **Amount of PEG-$SO_3H$** | **Time (min)** | **Yield[a] (%)** |
|---|---|---|---|
| 1 | 0.1 g (~ 0.83 mol%) | 40 | 75 |
| 2 | 0.15 g (~ 1.25 mol%) | 30 | 86 |
| 3 | 0.2 g (~ 1.67 mol%) | 18 | 97 |
| 4 | 0.25 g (~ 2.1 mo%)[b] | 18 | 97 |

a: Isolated yield.

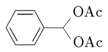
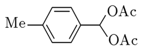
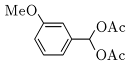
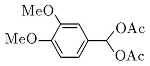
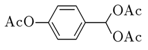
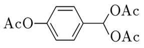
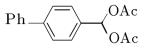
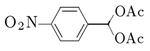
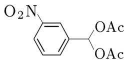
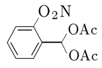
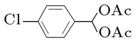
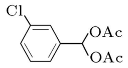
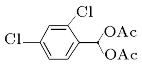
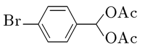
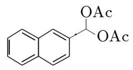
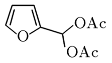
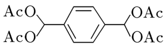
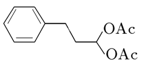
b: Increasing the amount of PEG-$SO_3H$ to 2.1 mol% did not improve the reaction results.

**Table 2.** The synthesis of acylal **1** from benzaldehyde and acetic anhydride using PEG-$SO_3H$ in different solvents at room temperature.

| **Entry** | **Solvent** | **Time (min)** | **Yield[a] (%)** |
|---|---|---|---|
| 1 | $CH_2Cl_2$ | 18 | 97 |
| 2 | $CHCl_3$ | 30 | 79 |
| 3 | THF | 25 | 82 |
| 4 | Ethyl acetate | 25 | 88 |

a: Isolated yield.

**Table 3.** The preparation of acylals from aldehydes and acetic anhydride using PEG-$SO_3H$ at room temperature.

| Product Number | Product | Time (min) | Yield[a] (%) | M.p. (°C) | |
|---|---|---|---|---|---|
| | | | | Found | Reported |
| 1 |  | 18 | 97 | 44-46 | 42-43 [31] |
| 2 |  | 16 | 96 | 83-85 | 81-82 [34] |
| 3 |  | 22 | 94 | Oil | Oil [31] |
| 4 |  | 26 | 90 | 61-63 | 64 [30] |
| 5 |  | 18 | 97 | 55-57 | 57 [30] |
| 6[b] |  | 18 | 95 | 55-57 | 57 [30] |
| 7 |  | 20 | 92 | 124-126 | 128-130 [33] |
| 8 |  | 23 | 96 | 122-124 | 125 [30] |
| 9 |  | 20 | 98 | 61-63 | 64-66 [32] |
| 10 |  | 23 | 92 | 87-89 | 85-86 [32] |
| 11 |  | 20 | 94 | 78-80 | 80 [30] |
| 12 |  | 20 | 95 | 61-63 | 65-66 [31] |
| 13 |  | 25 | 90 | 97-99 | 100-102 [30] |
| 14 |  | 20 | 91 | 83-85 | 84 [30] |
| 15 |  | 20 | 94 | 99-101 | 101 [30] |
| 16[c] |  | 30 | 89 | 50-52 | 51-52 [31] |
| 17[d] |  | 25 | 94 | 170-172 | 174-175 [30] |
| 18 |  | 30 | 86 | Oil | Oil [31] |

a: Isolated yield.

b: In this reaction, the starting aldehyde was *p*-hydroxybenzaldehyde in which the corresponding triacetate was produced.

c: This reaction was carried out using 1.25 mol% of PEG-$SO_3H$.

d: In this reaction, the aldehyde/$Ac_2O$ ratio (mol/mol) was 1/8, and 2.5 mol% of the catalyst was utilized.

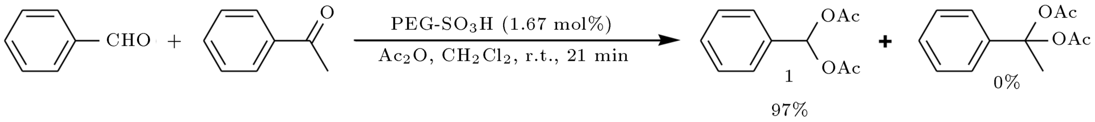


**Figure 2.** The competitive acylation of benzaldehyde in the presence of acetophenone.

as a catalyst was performed (Figure 2). It was observed that using this catalyst, an aldehyde could be selectively acylated in the presence of a ketone. Thus, the method is highly chemoselective.

## CONCLUSION

In summary, we have developed a new method for the chemoselective preparation of acylals from aldehydes and acetic anhydride. The advantages of this method are generality, efficiency, high yield, short reaction time, simplicity, low cost, cleaner reaction profile, ease of preparation of the catalyst and ease of product isolation.

## EXPERIMENTAL

All chemicals were purchased from Merck or Fluka Chemical Companies. All products were identified by comparison of their melting points and/or spectral data with those of the authentic samples. IR spectra were run on a Shimadzu FTIR-8300 spectrophotometer. The $^1$H NMR (250 MHz) was run on a Bruker Avance DPX-250 FT-NMR spectrometer ($\delta$ in ppm). Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes.

### Preparation of Polymeric Catalyst PEG-SO$_3$H

At 0°C, chlorosulfonic acid (10 mmol) was added to a solution of PEG-6000 (1 mmol) in $CH_2Cl_2$ (10 mL), and the resulting solution was stirred at room temperature overnight. Then, the solution was concentrated under a vacuum and ether (25 mL) was added to it. The resulting precipitate was filtered and washed with ether (10 mL) three times to afford PEG-SO$_3$H as a gummy solid [8,9].

### General Procedure for the Chemoselective Preparation of Acylals from Aldehydes and Acetic Anhydride

Aldehyde (2 mmol) was added to a mixture of acetic anhydride (0.817 g, 8 mmol), PEG-SO$_3$H (0.2 g, 0.033 mmol) and $CH_2Cl_2$ (2 mL) in a 10 mL round-bottomed flask, and the resulting mixture was stirred at room temperature for the times reported in Table 3. Afterward, the reaction mixture was diluted with $CH_2Cl_2$ (30 mL), washed with a saturated solution of $Na_2CO_3$ (2 × 30 mL) and, then, with $H_2O$ (2 × 30 mL). The organic layer was separated and dried over $Na_2SO_4$. The solvent was evaporated to afford the pure product or chromatographed on silica gel (petroleum ether/EtOAc) where necessary.

### Selected Spectral Data of the Products

Compound 1: IR (KBr): 3067, 2952, 1754, 1503, 1441, 1242, 1010, 951 cm$^{-1}$; $^1$H NMR ($CDCl_3$): $\delta$ 2.09 (s, 6H), 7.36-7.40 (m, 3H), 7.50-7.53 (m, 2H), 7.65 (s, 1H).

Compound 8: IR (KBr): 2961, 1757, 1625, 1536, 1349, 1234, 995 cm$^{-1}$; $^1$H NMR ($CDCl_3$): $\delta$ 2.13 (s, 6H), 7.76 (d, 2H, $J$ = 7.9 Hz), 8.25 (d, 2H, $J$ = 7.9 Hz), 7.71 (s, 1H).

Compound 16: IR (KBr): 3114, 1751, 1609, 1501, 1374, 1140, 960 cm$^{-1}$; $^1$H NMR ($CDCl_3$): $\delta$ 2.15 (s, 6H), 6.42 (m, 1H), 6.59 (m, 1H), 7.38 (m, 1H), 7.76 (s, 1H).

## ACKNOWLEDGMENTS

The authors thank Payame Noor University (PNU) and the Persian Gulf University Research Council for the financial support of this work.

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