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Dodecatungstophosphoric Acid ($H_3PW_{12}O_{40}$): A Novel and Efficient Recyclable Catalyst for Synthesis of 1,1-Diacetates from Aromatic Aldehydes in Solvent-Free System and Their Deprotection

Majid M. Heravi [a], Fatemeh Derikvand [a] & Fatemeh F. Bamoharram [b]
[a] Department of Chemistry, School of Science, Azzahra University, Vanak, Tehran, Iran
[b] Department of Chemistry, Azad University of Mashhad, Mashad, Iran

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Dodecatungstophosphoric Acid ($H_3PW_{12}O_{40}$): A Novel and Efficient Recyclable Catalyst for Synthesis of 1,1-Diacetates from Aromatic Aldehydes in Solvent-Free System and Their Deprotection

Majid M. Heravi and Fatemeh Derikvand
Department of Chemistry, School of Science, Azzahra University, Vanak,
Tehran, Iran

Fatemeh F. Bamoharram
Department of Chemistry, Azad University of Mashhad, Mashad, Iran

Abstract: A facile and efficient method for the formation of 1,1-diacetates from a variety of aldehydes in the presence of a catalytic amount of $H_3PW_{12}O_{40}$ and acetic anhydride was achieved in good yields at room temperature. The deprotection of the resulting acylals is achieved using the same catalyst in acetone.

Keywords: Acylals, dodecatungstophosphoric acid, 1,1-diacetate, heteropolyacid, $H_3PW_{12}O_{40}$, Keggin-type heteropolyacid

1,1-Diacetates are suitable protecting groups for aldehydes because of their stability and easy conversion into parent aldehydes.[1–3] In addition they can be converted into other useful functional groups by reaction with appropriate nucleophiles[4] and used as carbonyl surrogates for asymmetric synthesis.[5] The synthesis of optical aldehydes by lipase-catalyzed resolution of the corresponding 1,1-diacetates has been reported.[6] They are also

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Address correspondence to Majid M. Heravi, Department of Chemistry, School of Science, Azzahra University, Vanak, Tehran, Iran. E-mail: mmh1331@yahoo.com

important building blocks in the synthesis of dienes for the Diels–Alder cycloaddition reaction.[7] Acetic anhydride is the most used commonly reagent for acylal formation, and a long list of catalysts is available for this reaction, including H_2NSO_3H,[8] $(NH_4)_2Ce(NO_3)_6$,[9] $ZrCl_4$,[10] $AlPW_{12}O_{40}$,[11] $Zn(BF_4)_2$,[12] $InCl_3$,[13] NBS,[14] PCl_3,[15] and several inorganic heterogeneous catalysts such as Nafion-H,[16] Zeolites,[17] and Montmorillonite.[18]

The use of solid acid catalysts has received considerable attention in different areas of organic synthesis, because of their environmental compatibility, reusability, greater selectivity, experimental simplicity, low cost, and ease of isolation of the products.

Heteropolyacids (HPAs) have many advantages that make them economically and environmentally attractive in both academic and industrial significance; they are useful acid and oxidation catalysts in various reactions because their catalytic features can be varied at a molecular level.[19] HPAs possess superacidity and a remarkable stability both in solution and in solid state.[20] Many typical acid-catalyzed reactions are effective in the presence of a suitable heteropolyacid.[21–24]

In continuation of our program to develop reactions in ecofriendly conditions[21–25] and our interest in the synthesis of 1,1-diacetates,[26,27] in this communication we report an efficient and convenient procedure for the preparation of 1,1-diacetates from aromatic aldehydes and their deprotection catalyzed by dodecatungstophosphoric acid ($H_3PW_{12}O_{40}$).

When an appropriate aldehyde was stirred with acetic anhydride in the presence of a catalytic amount of $H_3PW_{12}O_{40}$ at room temperature, the corresponding 1,1-diacetate was obtained in excellent yield (Scheme 1). The results are shown in Table 1.

By using this catalyst, benzaldehyde, aromatic aldehydes containing electron-withdrawing or electron-donating groups, and cinamaldehyde gave the corresponding 1,1-diacetate in almost quantitative yields in short reaction times (5–60 min). It is noteworthy to mention that this catalyst is not suitable for the preparation of acylals from aldehydes carrying amino groups such as 4-N,N-dimethylaminobenzaldehyde and ketones. To show the high selectivity of the method, we studied competitive reactions for acylation of aldehydes in the presence of ketones using $H_3PW_{12}O_{40}$ as catalyst. Ketones such as acetophenone did not produce any acylal under the same condition (Table 1, entry 10); this suggested that chemoselective protection of aldehydes in the presence of ketones could be achieved with this process (Scheme 2).

Scheme 1.

Table 1. Synthesis of 1,1-diacetates using a catalytic amount of $H_3PW_{12}O_{40}$

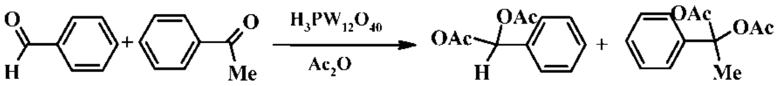
Entry	Substrate	Time (min)	Yield (%)[a]	Mp(°C) Found	Mp(°C) Reported[lit]
1	Benzaldehyde	4	98	44	44–45[2]
2	4-Methyl-benzaldehyde	5	97	81–81	81–82[3]
3	2-Methoxy-benzaldehyde	4	99	70	70–71[31]
4	4-Methoxy-benzaldehyde	15	98	63–64	64–65[32]
5	4-Chloro-benzaldehyde	9	97	81	81–82[33]
6	2-Nitro-benzaldehyde	20	99	89	90[34]
7	3-Nitro-benzaldehyde	20	98	65–66	64–66[32]
8	4-Nitro-benzaldehyde	60	99	125–126	125–126[32]
9	Cinamaldehyde	5	93	87–86	84–86[2]
10	Acetophenone	12 h	0	—	—
11	4-N,N-Dimethyl-benzaldehyde	12 h	0	—	—

[a] Yields were analyzed by GC.

A few methods are reported in the literature for the conversion of acylals to the corresponding aldehydes.[28–30] We use this catalyst in the deprotection of 1,1-diacetates to the corresponding aldehydes by treatment of acylals with a catalytic amount of $H_3PW_{12}O_{40}$ in acetone as solvent. Under this condition, aldehydes were obtained in quantitative yields (Scheme 1). The results are shown in Table 2.

In conclusion, we established a facile, mild, and efficient method for preparation of 1,1-diacetates from aromatic aldehydes and acetic anhydride at room temperature and deprotection of the obtained acylals to the corresponding aldehydes in acetone in the presence of $H_3PW_{12}O_{40}$ in high yields. Some of the major advantages of this procedure are operational simplicity, high yields, short reaction times, and high selectivity. In addition, as a nonhygroscopic, noncorrosive, and water-stable compound, the handling of $H_3PW_{12}O_{40}$ is easy, which makes this catalyst suitable for the large-scale operation.

HPAs are not soluble in organic reactions, and they could be separated by a simple filtration. The filtered catalyst was washed with diethyl ether and reused. The results of the first experiment and our subsequent experiment were almost consistent in yield for the synthesis of 1,1-diacetate from benzaldehyde (Entry 1, Table 1). The obtained results are comparable with those



Scheme 2.

Table 2. Deprotection of acylals catalyzed by $H_3PW_{12}O_{40}$

Entry	R	Time (min)	Yield (%)
1	Phenyl-	30	95
2	4-Me-Phenyl-	5	98
3	2-Metoxy-Phenyl-	15	95
4	4-Metoxy-phenyl-	5	98
5	4-Chloro-Phenyl-	15	94
6	2-Nitro-phenyl-	40[a]	99
7	3-Nitro-phenyl-	15[a]	97
8	4-Nitro-Phenyl-	40[a]	94
9	Cinamyl-	15	94

[a] The reaction was carried out in refluxing acetone.

reported using $AlPW_{12}O_{40}$, but it should be noted that $H_3PW_{12}O_{40}$ is the precursor of $AlPW_{12}O_{40}$.

EXPERIMENTAL

All products were known and characterized by comparison of their physical and spectral data with those reported.[2,3,31–34]

Preparation of 1,1-Diacetate: General Procedure

A mixture of an appropriate aldehyde (5.0 mmol), acetic anhydride (15.00 mmol), and HPA (0.5 mol%) was stirred at room temperature for the indicated time (Table 1). The progress of the reaction was monitored by thin-layer chromatoarphy (TLC) using petroleum ether–ethyl acetate as eluent. After completion of the reaction, diethyl ether (5 mL) was added to the mixture, and the catalyst was filtered off. The catalyst was washed with diethyl ether (5 mL), and then the filtrate was washed with 5% HCl (10 mL), 5% $NaHCO_3$ (10 mL), and brine (10 mL) successively and dried over $MgSO_4$. The solvent was evaporated under reduced pressure to yield the pure product. The filtered catalyst was washed with diethyl ether and reused.

Deprotection of Acylals: General Procedure

A mixture of acylal (1 mmol) and HPA (0.4 mol%) was stirred in acetone (5 mL) at room temperature for the indicated time (Table 1). For the acylal with electron-drawing groups, the mixture was refluxed. The progress of the reaction was monitored by TLC using petroleum ether–ethyl acetate as eluent. After completion of the reaction, the catalyst was filtered off and washed with diethyl ether. The combined organic layer was washed with 5% $NaHCO_3$ (10 mL) and brine (10 mL) and dried over $MgSO_4$. The solvent was evaporated under reduced pressure to yield the product. The filtered catalyst was washed with diethyl ether and reused.

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