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A Fast and Efficient Deprotection of Aldehydes from Acylals Using a Wells-Dawson Heteropolyacid Catalyst ($H_6P_2W_{18}O_{62} \cdot 24H_2O$)

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A Fast and Efficient Deprotection of Aldehydes from Acylals Using a Wells-Dawson Heteropolyacid Catalyst ($\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62} \cdot 24\text{H}_2\text{O}$)

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3909

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ABSTRACT

A rapid and efficient method for the deprotection of aldehyde 1,1-diacetates is described. The reaction was carried out using a Wells-Dawson type catalyst supported on silica. The catalyst, used in 1% molar quantity, is easily recoverable and reusable and maintains the activity after its use in four consecutive reaction batches. The yield of the deprotection was 92–100% (15 examples including nitrobenzaldehyde 1,1-diacetates). Reaction conditions involve short times and the use of toluene as the solvent; isolation is simple and the products are nearly pure.

Key Words: Acylal; Aldehyde; 1,1-Diacetate; Heteropolyacid; Protecting group; Wells-Dawson catalyst.

INTRODUCTION

Aldehydes are conveniently and selectively protected as 1,1-diacetates (acylals) as an alternative to the formation of acetals;^[1,2] moreover, some acylals are compounds of technological interest, and have been applied e.g., as synthetic precursors of functionalized butadienes for Diels Alder reactions.^[3] Formation of acylals is involved in some preparation methods for substituted aldehydes from toluenes.^[4]

The main reported procedures for performing the cleavage of 1,1-diacetates to the corresponding aldehydes were accounted recently.^[5] These procedures involve catalysis by mineral acids, alkaline bases, boron triiodide-diethylaniline complex, CAN coated on silica gel, neutral alumina under microwave irradiation, Montmorillonite K-10 and expansive graphite. In addition, bismuth (III) chloride,^[6] type Y zeolite (HSZ-360),^[7] and scandium triflate^[8] have been used. More recently, a method using of CBr_4 ^[9] was reported.

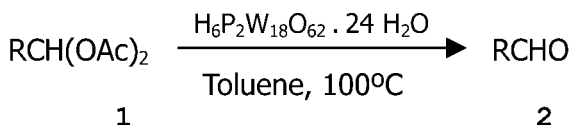
The problems associated with both the handling and disposal of conventional inorganic acids have raised the interest in the development of alternative clean processes and technologies involving the use of solid acid catalysts. Wells-Dawson (WD) type heteropolyacid ($\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62} \cdot 24\text{H}_2\text{O}$) showed to be useful and versatile for the catalysis of a number of reactions. Among these are the preparation of MTBE from methanol and isobutylene,^[10] epoxidation of alkenes and alkenols,^[11] deprotection of MOM-ethers of phenols,^[12] protection of alcohols and phenols as THP-acetals and their deprotection,^[13] protection of aldehydes as acylals,^[2] and a Michael reaction involving alkylation of cyclohexanone with alcohols.^[14]

Wells-Dawson acid was prepared as described elsewhere^[10] from an aqueous solution of α/β $K_6P_2W_{18}O_{62} \cdot 10H_2O$ salt, which was treated with ether and concentrated (37%) HCl solution. Silica-supported WD acid containing 20% by weight was attained by wet impregnation of Grace-Davidson silica (Grade 59, specific area = $250\text{ m}^2/\text{g}$) with an aqueous solution of the WD acid. After the impregnation, samples were dried at room temperature in a vacuum desiccator for 8 h. WD acid can be utilized both in bulk or supported forms, and both homogeneous and heterogeneous catalysis are possible. Structure of WD heteropolyacid was already studied.^[10]

DISCUSSION

In line with our previous article^[2] a simple and rapid procedure to deprotect aldehydes from 1,1-diacetates is reported here, as a result of a research project for developing environmentally friendly organic reactions. We use WD acid as the deprotection catalyst, performing the cleavage (Sch. 1) in solvent toluene and using 1,1-diacetates **1a–1o** as the substrates; their structure and the results are displayed in Table 1. Phenylmethanediol diacetate (**1a**) was selected for optimizing the reaction conditions; effects of the temperature, time, and aggregation state of the catalyst were examined. Wells-Dawson acid was tested as bulk and solid-supported samples; in the latter case silica gel was used as the support.

When aldehyde 1,1-diacetates (**1**) are heated at 50°C in the presence of 1% (mol) of WD acid in toluene, the corresponding aldehydes (**2**) are obtained, requiring 45–90 min to attain very good to excellent yields. Substrates **1a–1f** and **1i–1o** showed this behavior in such mild conditions. Nitrophenylmethanediol diacetates (**1g**, **1h**) yielded 85% and 75% aldehyde, respectively after 6 h. But if the reaction is carried out at 100°C and while other reaction conditions are kept unchanged, most of the 1,1-diacetates are deprotected with excellent yields in 5 min. For example, arylmethanediol diacetates **1a**, **1g**, **1j**, **1k**, and **1l** gave aldehydes quantitatively, see Table 1; other examples, even the chloro-substituted **1d** and **1e** are deprotected with very good to excellent yields, showing that most of the chosen substituents



Scheme 1. Deprotection of aldehydes from aldehyde 1,1-diacetates.

Table 1. Catalytic conversion^a of acylals in aldehydes **2a–o**^b using WD acid.

Entry	Acylals 1a–o	R	Time (min)	Yield (%)
1	a	C ₆ H ₅	5	100
2	b	4-CH ₃ C ₆ H ₄	5	97
3	c	4-CH ₃ SC ₆ H ₄	5	95
4	d	4-ClC ₆ H ₄	5	95 ^c
5	e	2-ClC ₆ H ₄	5	95
6	f	3-C ₆ H ₅ OC ₆ H ₄	5	94
7	g	4-NO ₂ C ₆ H ₄	10	98
8	h	2-NO ₂ C ₆ H ₄	10	97
9	i	2-Cl-6-FC ₆ H ₃	5	93
10	j	1-C ₁₀ H ₇	5	99
11	k	2-C ₁₀ H ₇	5	100
12	l	C ₆ H ₅ -CH=CH	5	99
13	m	2-Furyl	5	96
14	n	C ₇ H ₁₅	5	93
15	o	C ₁₀ H ₂₁	5	92

^aReactions were carried out in toluene, at 100°C.

^bAll the yields were calculated from isolated products, being their purity better than 97% by GLC.

^cThe used catalyst was recovered and reused three times yielding 96%, 94%, and 94%, respectively.

at the phenyl ring have no considerable effect on the reaction. Likewise, nitrophenyl ones deprotect almost quantitatively but require double the time.

All the deprotected aldehydes were identified by comparison (TLC, GLC, and physical constants) with authentic samples. All the yields were calculated from isolated products, and GC was used to establish their purities; being better than 97% in all of the examples.

GENERAL PROCEDURE FOR THE DEPROTECTION OF ALDEHYDES FROM 1,1-DIACETATES

A mixture of a 1,1-diacetate (**1**, 0.5 mmol), toluene (1 mL) and Wells-Dawson catalyst (solid supported, 20% by weight; 1% mmol, ca. 20 mg) was stirred by the indicated period of time and temperature, see Table 1. The catalyst was then removed by filtration and washed twice with toluene (0.5 mL each). The organic solution was washed twice with water (3 mL each) and then it was dried over anhydrous Na₂SO₄. The crude products are better than 97%, as revealed by GLC. Evaporation of the solvent under

reduced pressure and flash column chromatography of the residue on silica gel gave the practically pure aldehyde **2**.

CONCLUSIONS

The deprotection of acylals using Wells-Dawson catalyst is a clean, general, and inexpensive reaction; their workup is very simple; and the yields are very good to excellent. The use of these solid catalysts allows replacement of the usual soluble inorganic acids, contributing in this way to the reduction of wastes.

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