Pergamon

SCIENCE DIRECT®

Tetrahedron Letters 44 (2003) 1301–1303

TETRAHEDRON
LETTERS

Solvent-free catalytic preparation of 1,1-diacetates from aldehydes using a Wells–Dawson acid ($H_6P_2W_{18}O_{62}\cdot 24H_2O$)

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Received 4 November 2002; revised 2 December 2002; accepted 2 December 2002

This work is dedicated to the memory of Emeritus Professor Dr. Jorge J. Ronco, at the first anniversary of his death (October 3rd, 2001)

Abstract—Aromatic and aliphatic aldehydes are transformed in 1,1-diacetates (acylals) in mild conditions, by a treatment with acetic anhydride and a Wells–Dawson acid ($H_6P_2W_{18}O_{62}\cdot 24H_2O$). *gem*-Diacetylation proceeds in Ac_2O with a little as 1% mol Wells–Dawson acid at room temperature and under solventless conditions, obtaining very good to excellent yields (88–98%) of 1,1-diacetates (19 examples). Neither 4-dimethylaminobenzaldehyde nor ketones react under the same conditions. © 2003 Elsevier Science Ltd. All rights reserved.

The use of protecting groups is greatly significant in organic synthesis,[1a] being often the key of the success of many synthetic enterprises. Acylals have interest as an alternative to acetals for the protection of aldehydes because of their stability to basic and neutral media, and some 1,1-diacetates were used, e.g. for the synthesis of dienes for Diels–Alder reactions.[2]

Preparation of 1,1-diacetates from aldehydes and acetic anhydride involves the use of strong protonic acids as sulfuric, methanesulfonic or phosphoric acids,[2,3] or Lewis acids e.g. ferric chloride,[1c] zinc chloride and phosphorus trichloride;[2] Nafion-H has been also used.[4] In some cases, these methods are not entirely satisfactory because of low yields, long reaction times and some environmental problems.[5] Several catalysts have been employed more recently, e.g. iodine,[6a] expansive graphite,[5a] zeolites,[1b,2] tungstosilicic acid and HZSM-5,[6b] Fe^{+3} on montmorillonite,[6c] PVC–$FeCl_3$ complex[5b] and Zirconium sulfophenyl phosphonate.[6d]

The environmental problems, mainly associated with the handling and disposal of the inorganic acids, and their potential hazards, have attracted the chemist's attention to the development of alternative processes using novel catalysts. Heteropolycompounds are useful and versatile to a number of transformations because of their redox and superacidic properties.[7] The molecular structure of the Wells–Dawson (WD) heteropolyacid catalyst ($H_6P_2W_{18}O_{62}\cdot 24H_2O$) shows two identical 'half units' PW_9 linked through the oxygen atoms;[8] and consists in a close-packed framework of W(VI)–oxygen octahedra WO_6 surrounding a central P(V) atom.

We have recently applied the WD acid for performing the tetrahydropyranylation of alcohols and phenols and their detetrahydropyranylation,[9] and to the cleavage of MOM–ethers of phenols.[10] Besides, some of us have explored the use of a Keggin heteropolyacid catalyst in the tetrahydropyranylation reaction.[11]

$$\underset{\textbf{1}}{RCHO} + Ac_2O \xrightarrow[\text{r. t., 30 min}]{H_6P_2W_{18}O_{62}\,.\,24\,H_2O} \underset{\textbf{2}}{RCH(OAc)_2}$$

Scheme 1. Preparation of acylals.

Keywords: protecting group; aldehyde; 1,1-diacetate; acylal; heteropolyacid; Wells–Dawson catalyst.

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PII: S0040-4039(02)02817-4

As a part of an ongoing research project to develop environmentally amicable organic reactions, we report here a rapid preparation of 1,1-diacetates of aldehydes using the WD acid, being tested as a homogeneous catalyst. The protection reaction (Scheme 1) was studied using aldehydes **1a**–**1s** as the substrates.[†] Their structure and the obtained results are shown in Table 1. Benzaldehyde (**1a**) was chosen for optimizing the reaction conditions: temperature, time, concentration of the solutions and molar ratio of the WD acid to substrate were checked.

The selected experiments were carried out at 20°C in 1 M solutions and varying the reaction times and the amount of catalyst used. When 1% (mmol) WD acid was added, the higher yield of 1,1-diacetate **1a** was attained at 30 min reaction at room temperature, shorter and longer times gave lower yields. Besides, using 5% catalyst and keeping unchanged other reaction conditions, yields were 1–5% higher than the ones recorded in Table 1, and when a reduction to a half on the amount of solvent was tried (other conditions as described below in general procedure) yields fell by 2–4%. Both benzaldehydes (**1a**–**1l**) and naphthaldehydes (**1n**,**1o**) gave excellent yields of the corresponding acylals. For example 4-nitrobenzaldehyde (**1e**) gave 4-nitrophenylmetanediol diacetate (**2e**) in 92% and 1-naphthaldehyde (**1n**) gave 1-naphthylmetanediol diacetate in 98% (**2n**). The nature of the substituent on the aromatic ring seems to have no relevant effect on the reaction, see e.g. entries 4, 8, 10 and 11; but hydroxyaldehydes **1h**, **1i** and **1k** gave the corresponding triacetates. Aliphatic aldehydes were also protected with very good yields (entries 17–19).

Table 1. Catalytic conversion of aldehydes in acylals using WD acid

Entry	Aldehydes **1a**–**s**	R	Acylals **2a**–**s** yield (%)[a]
1	**a**	Ph	95
2	**b**	2-ClC$_6$H$_4$	93
3	**c**	4-ClC$_6$H$_4$	93
4	**d**	2-O$_2$NC$_6$H$_4$	92
5	**e**	4-O$_2$NC$_6$H$_4$	92
6	**f**	3-PhOC$_6$H$_4$	93
7	**g**	4-MeSC$_6$H$_4$	97
8	**h**	2-HOC$_6$H$_4$	94[b]
9	**i**	3-HOC$_6$H$_4$	95[b]
10	**j**	2-Cl-6-FC$_6$H$_3$	96
11	**k**	3-MeO-4-HOC$_6$H$_3$	92[b]
12	**l**	2-Br-3,4-(OMe)$_2$C$_6$H$_2$	90
13	**m**	PhCH=CH	98
14	**n**	1-C$_{10}$H$_7$	98
15	**o**	2-C$_{10}$H$_7$	97
16	**p**	2-Furyl	88
17	**q**	*n*-C$_3$H$_7$	89
18	**r**	*n*-C$_5$H$_{11}$	90
19	**s**	*n*-C$_9$H$_{19}$	95

[a] Reactions were performed at 20°C and 30 min reaction time, using 1% (mmol) of WD acid. Yields are expressed from crystallized products (see text).

[b] Compounds **2h**, **2i** and **2k** are triacetates of **1h**, **1i** and **1k**, respectively.

Some aliphatic and aromatic ketones were also checked for the reaction: acetone, butanone, acetophenone and ethyl *n*-butyl ketone, they have not reacted under the described experimental conditions. Likewise, 4-dimethylaminobenzaldehyde failed to give the expected 1,1-diacetate.

All the products were characterized by comparison (GLC, TLC and physical constants) with authentic samples prepared by the conventional method,[3b] using sulfuric acid as the catalyst. All the yields were calculated from crystallized products, their purity was established by GLC, being better than 98%. The WD acid ($H_6P_2W_{18}O_{62}\cdot 24H_2O$) was prepared as described elsewhere[8] 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.

Studies are in progress in our laboratory in relation to the use of recoverable, supported catalysts.

General procedure for the protection of aldehydes

A mixture of aldehyde **1** (1 mmol), acetic anhydride (1 mL) and WD catalyst (1% mmol, ca. 45 mg) was stirred at room temperature for 30 min and then ethyl ether (10 mL) was added to the reaction mixture. The resulting solution was successively washed with 1 M NaOH and water, dried over anhydrous Na$_2$SO$_4$, and filtered. The solution was then concentrated, and the solid crude product was recrystallized from petroleum ether yielding each of the pure acylals **2**.[‡]

Conclusions

The above described procedure provides a useful alternative for the preparation of 1,1-diacetates from aldehydes, being general, rapid, selective and inexpensive, and having a low environmental impact.

Acknowledgements

Financial support from CONICET (Argentina), and Universidad Nacional de La Plata is gratefully acknowledged. H.J.T., G.P.R. and G.T.B. are members of CONICET.

[†] Starting aldehydes were commercial, they were initially purified to match the reported physical data.

[‡] As an example, spectroscopic data for the novel compound **2l** are given: ^{1}H NMR (CDCl$_3$) δ 7.87 s (1H), 7.04 s (1H), 7.03 s (1H), 3.91 s (3H), 3.88 s (3H), 2.14 (6H). ^{13}C NMR (CDCl$_3$) δ 168.2, 150.6, 148.6, 126.8, 115.6, 113.0, 110.5, 89.4, 56.23, 56.16, 20.71.

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