SHORT PAPER

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A facile and efficient procedure for deprotection of 1,1-diacetates catalysed by H_2NSO_3H[†]

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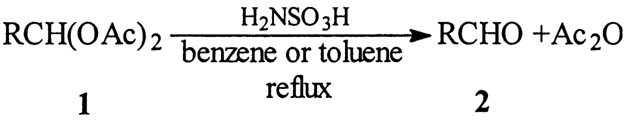
A rapid, efficient and high yield method of the deprotection of 1,1-diacetates is described which occurs under catalysis of H_2NSO_3H.

Keywords: 1,1-diacetates, H_2NSO_3H, deprotection

The selective protection and deprotection of functional groups is of great importance in synthetic organic chemistry. During the last decade 1,1-diacetates have been received increasing attention, since these compounds are stable to oxidants,[1, 2] easily prepared,[3-11] and can serve as an alternative to acetals for the selective protection of aldehydes[3-12] and as starting materials for Diels–Alder cycloaddition reaction.[13,14]

Recently, a number of methods have been documented for the conversion of 1,1-diacetates to corresponding aldehydes: (a) alcoholic sulfuric[1] or hydrochloric acid,[2] (b) either sodium hydroxide or potassium carbonate in aqueous THF overnight,[3] (c) boron triiodide: N,N-diethylaniline complex,[15] (d) ceric ammonium nitrate coated on silica gel in dichloromethane,[16] (e) neutral alumina under microwave irradiation,[17] (f) potassium phenoxides,[18] (g) montmorillonite K10[19] or KSF[20] under microwave irradiation. These methods have their merits and some shortcomings. Some of methods have not been satisfactory, owing to drawbacks such as long reaction time,[3] low yield,[16] expensive catalysts which were not easily obtained,[15] use of a microwave oven and only one compound was studied.[17] More recently, expansive graphite,[21] aluminum chloride[22] and TiO_2/SO_4^{2-} solid super acid[23] were used as catalysts for the purpose of obtaining relatively better results.

H_2NSO_3H has been extensively used as efficient catalyst for a variety of organic reactions.[24-26] Herein we wish to describe an efficient and facile method for the deprotection of 1,1-diacetates under catalysis with H_2NSO_3H in refluxing benzene or toluene (Scheme 1).



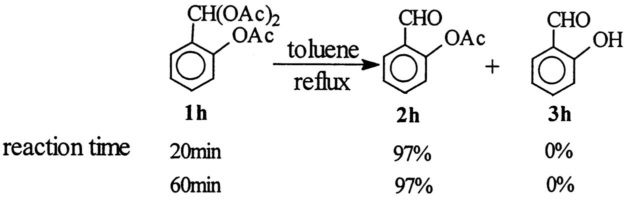
$$\underset{\mathbf{1}}{RCH(OAc)_2} \xrightarrow[\text{benzene or toluene, reflux}]{H_2NSO_3H} \underset{\mathbf{2}}{RCHO} + Ac_2O$$

Scheme 1

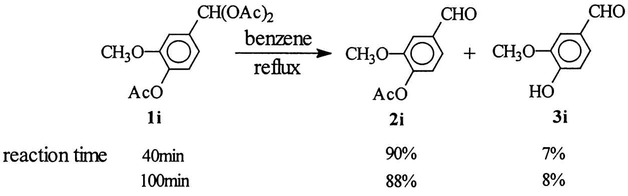
When 1,1-diacetates **1** are heated and stirred in refluxing benzene or toluene in the presence of H_2NSO_3H, the corresponding aldehydes **2** are obtained in good yields (Table 1). No additional water is needed for the reaction.

It is noteworthy that the reaction takes a longer time at room temperature. For example, complete conversion of **1a** and **1b** to the corresponding aldehydes **2a** and **2b** need 7h under catalysis of H_2NSO_3H at room temperature. **1k** and **1l** were not deprotected in refluxing benzene and even in refluxing toluene gave only provide poor conversion rate (<50%) for 2h, possibly due to the strong electron withdrawing nitro substituent.

It should be noticed that the phenolic acetate function in **1h** was unaffected even in a longer time (Scheme 2). As to the phenolic acetate function in **1i**, only a small portion was deprotected and the amount of the deprotected product increased very little when the reaction proceeded a longer time (Scheme 3). Therefore the present procedure affords a selective deprotection of aldehyde diacetates to aryl aldehydes in the presence of a phenolic acetate.



Scheme 2



Scheme 3

In summary, we have developed a rapid, efficient and selective method for the deprotection of 1,1-diacetates. Because of its operational simplicity, high yield, short reaction time and the inexpensive catalyst, this method is better than many other existing ones.

Experimental

1,1-Diacetates **1** were synthesised as described previously.[27] The products were characterised by ^1H NMR spectra and comparison of their melting or boiling points with authentic samples.

General procedure for the deprotection of 1,1-diacetates: A mixture of 1,1-diacetate **1** (1.00mmol), benzene or toluene (3ml), and H_2NSO_3H (100mg) was stirred at reflux temperature for the time indicated in Table 1. The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was cooled and H_2NSO_3H was filtered off. The catalyst was washed with dichloromethane and then the filtrate was washed with brine twice and dried with $MgSO_4$. The solvent was evaporated under reduced pressure and residue was chromatographed on silica gel (petoleum-ether as eluent) to give the corresponding aldehydes **2** (Table 1).

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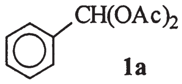
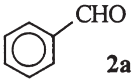
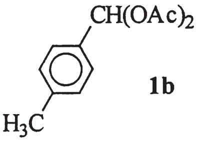
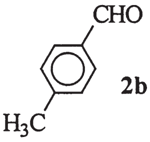
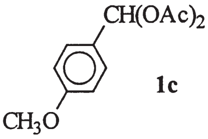
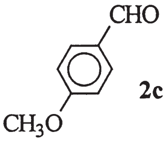
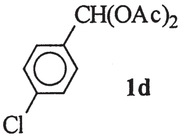
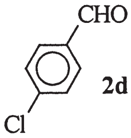
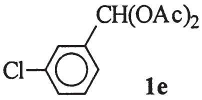
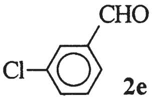
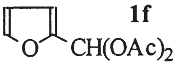
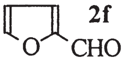
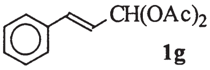
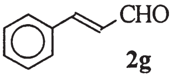
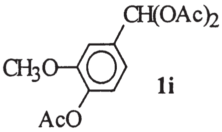
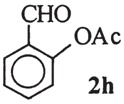
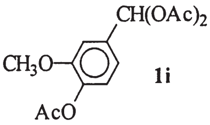
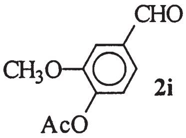
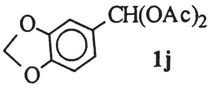
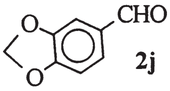
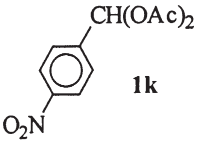
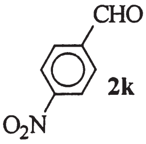
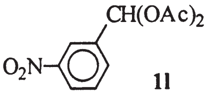
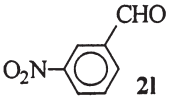
[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 Deprotection of 1,1-diacetates catalysed by H_2NSO_3H.

Entry	Substrate	Product	Solvent	Time	Yield	B.p./ torr or M.p. (°C)	
				min	%[a]	Found	Reported
1	 **1a**	 **2a**	Toluene	5	96	78–80/25	62/10[28]
2	 **1b**	 **2b**	Toluene	5	98	112–114/20	106/10[28]
3	 **1c**	 **2c**	Toluene	5	97	138–140/18	134–135/12[28]
4	 **1d**	 **2d**	Benzene	15	95	46–48	47[28]
5	 **1e**	 **2e**	Benzene	10	92	100–102/20	213–214/760[28]
6	 **1f**	 **2f**	Benzene	14	95	72–74/30	90/6528
7	 **1g**	 **2g**	Benzene	15	96	132–134/20	130/20[29]
8	 **1i**	 **2h**	Toluene	20	97	38–39	38–39[28]
9	 **1i**	 **2i**	Benzene	40	90	101–102	102–103[29]
10	 **1j**	 **2j**	Benzene	10	98	37–39	37[28]
11	 **1k**	 **2k**	Toluene	120	45	105–106	106[28]
12	 **1l**	 **2l**	Toluene	120	37	58–59	58[28]

[a] Yields refer to isolated products.

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