SHORT PAPER

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TiO_2/SO_4^{2-}: a facile and efficient catalyst for deprotection of 1,1-diacetates[†]

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A facile and efficient method for the selective deprotection of 1,1-diacetates to the corresponding aldehydes in the presence of TiO_2/SO_4^{2-} solid superacid in excellent yield is described.

Selective protection and deprotection of functional groups are of great importance in synthetic organic chemistry. In the course of the last decade, 1,1-diactates 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 reactions.[13,14]

A number of methods have been documented for the conversion of 1,1-diacetates to corresponding aldehydes namely (1) alcoholic sulfuric[1] or hydrochloric acid,[2] (2) either sodium hydroxide or potassium carbonate in aqueous THF overnight,[3] (3) boron triiodide-N,N-diethylaniline complex,[15] (4) ceric ammonium nitrate coated on silica gel in dichloromethane,[16] (5) neutral alumina under microwave irradiation,[17] (6) potassium phenoxides,[18] (7) montmorrillonite K10[19] or KSF[20] under microwave irradiation. Some of the reported methods feature strong proton acids,[1,2] long reaction time,[3] low yield (<60%)[16] and require the use of a microwave oven and only one compound was studied.[17] More recently, expansive graphite[21] and aluminium chloride[22] were applied as catalysts for the purpose of obtaining relatively better results.

TiO_2/SO_4^{2-} solid superacid has been used as a catalyst for organic reactions.[23–25] Herein we wish to describe an efficient and facile deprotection of 1,1-diacetates under catalysis of TiO_2/SO_4^{2-} in refluxing dichloromethane or benzene.

$$\underset{\mathbf{1}}{RCH(OAc)_2} \xrightarrow[]{\begin{array}{l}TiO_2/SO_4^{2-}, H_2O\\ Ch_2Cl_2 \text{ or } C_6H_6\\ \text{reflux,5-10min}\\ 96\text{-}99\%\end{array}} \underset{\mathbf{2}}{RCHO + CH_3COOH}$$

Scheme 1

When 1,1-diacetates **1** are heated in refluxing dichloromethane or benzene in the presence of TiO_2/SO_4^{2-}, the corresponding aldehydes **2** are obtained in excellent yield (Table 1).

The reaction takes a longer time at room temperature. For example, complete conversion of phenylmethanediol diacetate (**1a**) to the corresponding aldehyde(**2a**) needs 5h in dichloromethane under catalysis of TiO_2/SO_4^{2-}. Nitro derivatives (**1d** and **1e**) provide lower conversion rate (<70%) in refluxing dichloromethane for 3h whereas 98% yields are obtained in refluxing benzene after 5 min and 10 min, respectively. The reactions of nitro derivatives were performed in the presence of TiO_2/SO_4^{2-} (100 mg), whereas other compounds required only 50 mg, possibly due to the strongly electron withdrawing nitro substituent.

Table 1 Deprotection of 1,1-diacetates in the presence of TiO_2/SO_4^{2-}

Entry	R	Solvent	Time (min)	Yield (%)
a	C_6H_5	CH_2Cl_2	5	99
b	$4\text{-}ClC_6H_4$	C_6H_6	5	98
c	$3\text{-}ClC_6H_4$	C_6H_6	10	98
d	$4\text{-}NO_2C_6H_4$	C_6H_6	5	98
e	$3\text{-}NO_2C_6H_4$	C_6H_6	10	96
f	2-furyl	CH_2Cl_2	5	97
g	$4\text{-}CH_3C_6H_4$	C_6H_6	5	96
h	$C_6H_5CH{=}CH$	C_6H_6	5	98
i	$4\text{-}MeOC_6H_4$	CH_2Cl_2	5	99
j	$3,4\text{-}(OCH_2O)C_6H_3$	C_6H_6	7	98

The catalysts need no regeneration and could be reused ten times for the deprotection of 1,1-diactates without significant loss of activity.

In conclusion, we have a rapid and efficient method for the selective deprotection of aryl aldehyde diacetates to the corresponding aldehydes, featuring operational simplicity, high yields, short reaction time, non-corrosive, non-polluting and employing a reusable catalyst.

Experimental

The catalyst TiO_2/SO_4^{2-} solid superacid was prepared as follows. $Ti(OH)_4$ was obtained by hydrolysing $TiCl_4$ with aqueous ammonium hydroxide, washing the precipitates, drying them at 120^0C for 4 h, and powdering the precipitates below a 100 mesh. The hydroxide was treated with 2N H_2SO_4 for 4 h, the filtered off, dried calcined in furnace at 475^0C for 4 h, and finally stored in a desiccator until use. 1,1-Diacetates **1** were synthesized as described previously. The products were characterized by ^{1}H 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** (1.00 mmol), dichloromethane or benzene (6 mL), H_2O (2.00 mmol) and TiO_2/SO_4^{2-} (50 mg) was stirred at reflux temperature for the length of time indicated in Table 1. The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was cooled and TiO_2/SO_4^{2-} was filtered off. The catalyst was washed with dichloromethane and then the filtrate was washed with brine two times and dried ($MgSO_4$). The solvent was evaporated under reduced pressure and the residue was chromatographed on silica gel (petroleum-ether, 4:1 as eluent) to give the corresponding aldehydes **2** in the yield of 96-99% (Table 1).

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