**SHORT PAPER**

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# Facile preparation of 1,1-diacetates from aldehydes with acetic anhydride catalysed by $TiO_2/SO_4^{2-}$ solid superacid[†]

**Tong-Shou Jin*, Yan-Ran Ma, Xu Sun, Dan Liang and Tong-Shuang Li**

*Department of Chemistry, Hebei University, Baoding 071002, Hebei Province, P. R. China*

A facile and efficient synthesis of 1,1-diacetates in excellent yields from aldehydes with acetic anhydride catalysed by $TiO_2/SO_4^{2-}$ solid superacid.

1,1-Diacetates are synthetically useful as protecting groups for aldehydes due to their moderate stability and easy conversion into parent aldehydes.[1–6] These are also important building blocks for the synthesis of dienes for Diels–Alder cycloaddition reaction.[7] Usually, they are synthesized from aldehydes and acetic anhydride using strong proton acids and Lewis acids as catalysts, typically such as sulfuric acid, phosphoric acid, methanesulfonic acid,[8] Nafion-H,[9] zinc chloride,[10] ferric chloride[6] or phosporous trichloride.[11] These methods have not been entirely satisfactory, owing to such drawbacks as low yields (4% in the case of 4-nitrobenzaldehyde[11]), long reaction time (up to 120 h in the case of 2-furaldehyde[11]), emerging the problems of corrosivity, tedious workup, effluent pollution and non-recoverable catalysts. Consequently, it is necessary to develop alternative methods for the synthesis of 1,1-diacetates of aldehydes under mild and environmental friendly conditions. In recent years, β-zeolite,[12] sulfated zirconia,[13] montmorillonite clays,[14] expansive graphite,[15] trimethylchlorosilane and sodium iodide[16] or scandium triflate[17] were employed as catalysts for this purpose to obtain relatively better results. More recently, microwave irradiation has been applied to accelerate this condensation reaction.[18]

$TiO_2/SO_4^{2-}$ solid superacid has been used as a catalyst for organic reactions.[19–21] Herein we wish to report a fast and efficient procedure for the synthesis of 1,1-diacetates from aldehydes catalysed by $TiO_2/SO_4^{2-}$ solid superacid at room temperature.

As summarised in Table 1, when aldehydes **1** were treated with acetic anhydride **2** in the presence of $TiO_2/SO_4^{2-}$, the corresponding 1,1-diacetates **3** were obtained in excellent yields at room temperature except for 4-dimethylaminobenzaldehyde(**1o**, no reaction).

$$\underset{\mathbf{1}}{RCHO} + \underset{\mathbf{2}}{Ac_2O} \xrightarrow[85\text{–}99\%]{TiO_2/SO_4^{2-}\ \text{r.t. 2-20min}} \underset{\mathbf{3}}{RCH(OAc)_2}$$

**Scheme 1**

We were pleased to find that aromatic aldehydes containing electron-withdrawing groups or donor groups (**1d**–**1l**) and cinnamaldehyde (**1m**) gave the corresponding 1,1-diacetates in near quantitative yields in shorter time (less than 20 min) using $TiO_2/SO_4^{2-}$ than some of the report methods. The nature of the substituents on the aromatic ring seems to have no effect on the reaction system. Aliphatic aldehydes also gave good to excellent yield of the corresponding 1,1-diacetates.

Mention must be made here that phenol groups were also protected as acetates in hydroxyl containing aromatic aldehydes (**1g** and **1h**) under these conditions. It is also worth noting that ketones, such as cyclohexanone and acetophenone, did not give any 1,1-diacetates under the same reaction conditions and this suggested that chemoselective protection of an aldehyde in the presence of a ketone could be achieved. Additionally, 4-dimethylaminobenzaldehyde(**1o**) failed to give the corresponding 1,1-diacetate and the starting materials were quantitatively recovered under the same conditions. The explanation for this result may be due to the strong electron

**Table 1** 1,1-Diacetates from aldehydes using $TiO_2/SO_4^{2-}$ as catalyst

| Entry | Substrate | Solvent(t/min) | Isolated Yield(%) | Mp/°C or bp/torr Found | Reported |
|---|---|---|---|---|---|
| 1 | $C_2H_5CHO$ **1a** | none/5 | 88 | 122-125/30 | 115-118/8[4] |
| 2 | $CH_3CH{=}CHCHO$ **1b** | none/5 | 88 | 92-94/20 | 89-90/15[11] |
| 3 | $C_6H_5CHO$ **1c** | none/2 | 99 | 44-45 | 44-45[4] |
| 4 | $4\text{-}MeC_6H_4CHO$ **1d** | none/10 | 98 | 80-81 | 81-82[5] |
| 5 | $4\text{-}MeOC_6H_4CHO$ **1e** | none/10 | 98 | 64-65 | 64-65[5] |
| 6 | $3,4\text{-}(OCH_2O)C_6H_3CHO$ **1f** | $CH_2Cl_2$/5 | 97 | 79-80 | 79-80[14] |
| 7 | $2\text{-}HOC_6H_4CHO$ **1g** | none/15 | 95 | 104-105 | 103-104[14] |
| 8 | $3\text{-}MeO\text{-}4\text{-}HOC_6H_3CHO$ **1h** | $CH_2Cl_2$/10 | 94 | 90-91 | 90-91[14] |
| 9 | $3\text{-}ClC_6H_4CHO$ **1i** | none/5 | 98 | 65-66 | 65-66[14] |
| 10 | $4\text{-}ClC_6H_4CHO$ **1j** | $CH_2Cl_2$/10 | 96 | 81-82 | 81-81[14] |
| 11 | $3\text{-}O_2NC_6H_4CHO$ **1k** | $CH_2C_{l2}$/15 | 97 | 64-66 | 65-66[14] |
| 12 | $4\text{-}O_2NC_6H_4CHO$ **1l** | $CH_2Cl_2$/20 | 94 | 125-126 | 125[15] |
| 13 | $C_6H_5CH{=}CHCHO$ **1m** | none/5 | 97 | 84-85 | 84-86[4] |
| 14 | 2-furyl **1n** | $CH_2Cl_2$/10 | 85 | 51-53 | 52-54[12] |
| 15 | $4\text{-}Me_2NC_6H_4CHO$ **1o** | $CH_2Cl_2$/540 | no reaction | | |

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* To receive any correspondence. Fax: +86 312 5079361. E-mail: orgsyn@mail.hbu.edu.cn

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donating dimethylamino group in **1o** which will reduce the reactivity. A degree of tautomerisation may occur in **1o** with formation of quinoid structure and thus decreased reactivity of the aldehyde group.

The catalysts need not regeneration and could be reused ten times for the synthesis of benzaldehyde 1,1-diacetate **3c** without significant loss of activity.

In conclusion, we provide a rapid and efficient method for the preparation of 1,1-diacetates from aldehydes, because of its operational simplicity, high yields, short reaction time, non-corrosive, non-pollutive and employing a reusable catalyst. This method will be better than many existing ones.

## Experimental

Melting and boiling points are uncorrected. $^1$H NMR spectra were determined on a Varian VXR-300S spectrometer using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal reference. IR spectra were obtained on a Perkin–Elmer 983G spectrometer. The products were also characterised by comparison of their melting and boiling points with literature values. 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°C for 4 h, and powdering the precipitates below a 100 mesh. The hydroxide were treated with 2N $H_2SO_4$ for 4 h filtrating, drying, calcined in furnace at 475°C for 4 h, and finally stored in a desiccator until use.

*General procedure for the preparation of 1,1-diacetates*: A mixture of the 3-chlorobenzaldehyde **1i** (5.00 mmol), acetic anhydride **2** (15.0 mmol) and $TiO_2/SO_4^{2-}$ (100 mg) was stirred at room temperature for 5 min (Table 1). The progress of the reaction was monitored by TLC. After completion, $Et_2O$ (5 ml) was added to the reaction mixture and the catalyst was filtered off. The catalyst was washed with $Et_2O$ (2×5 ml) and then the filtrate was washed with 5% HCl (10 ml), 5% $NaHCO_3$ (10 ml) and brine (2×10 ml) successively and dried ($MgSO_4$). The solvent was evaporated under reduced pressure and the residue was chromatographied on silica gel (light petroleum–ether as eluent) to give 1,1-diacetate **3i** in 98% yield; mp 65 – 66°C.

For **3f** : $\nu_{max}$/cm$^{-1}$ 2950, 1755, 1605, 1490, 1440, 1395, 1365, 1235, 1200, 1150, 1105, 1040, 1005, 980, 950, 930, 870, 820, 795, 725; $\delta_H$ 2.02 [6H, s, $ArCH(O_2CC\mathbf{H}_3)_2$] 5.87 (2H, s, $OC\mathbf{H}_2O$), 6.65-6.93 (3H, m, $C_6\mathbf{H}_3$), 7.51 [1H, s, $ArC\mathbf{H}(OAc)_2$]. For **3g** : $\nu_{max}$/cm$^{-1}$ 2960, 1740, 1600, 1490, 1440, 1382, 1245, 1205, 1160, 1005, 985, 940, 920, 850, 800, 760; $\delta_H$ 2.09 [6H, s, $ArCH(O2CC\mathbf{H}_3)_2$], 2.33 (3H, s, 2-$C\mathbf{H}_3CO_2$), 7.05–7.69 (4H, m, $C_6H_4$ ), 7.89 [1H, s, $ArC\mathbf{H}(OAc_2)_2$].

For **3h** : $\nu_{max}$/cm$^{-1}$ 2950, 1765, 1745, 1605, 1510, 1465, 1430, 1375, 1325, 1250, 1160, 1115, 1070, 995, 950, 895, 835, 780; $\delta_H$ 2.11 [6H, s, $ArCH(O_2CC\mathbf{H}_3)_2$], 2.29 (3H s, 4-$C\mathbf{H}_3CO_2$),3.85 (3H, s, $OC\mathbf{H}_3$),7.00–7.10 (3H, m, $C_6H_3$), 7.65 [1H, s, $ArC\mathbf{H}(OAc)_2$].

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