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# Synthesis of 1,1-diacetates from aromatic aldehydes using cerium(IV) sulfate tetrahydrate as catalyst under solvent-free conditions

**Min Zhang and Yi-Qun Li***

*Department of Chemistry, Jinan University, Guangzhou 510632, P. R. China.*

Aromatic aldehydes can be converted into the corresponding 1,1-diacetates rapidly in the presence of catalytic amounts of $Ce(SO_4)_2{\cdot}4H_2O$ at room temperature in excellent yield under solvent-free conditions. The catalyst can easily be recovered and reused at least 4 times.

**Keywords:** 1,1-diacetate, catalyse, cerium(IV) sulfate tetrahydrate

1,1-Diacetates are efficient protecting groups for aldehydes as they are generally stable in neutral and basic media.[1] Usually they are prepared from aldehydes and acetic anhydride in the presence of strong protic acids[2] such as $H_2SO_4$, $H_3PO_4$ or $CH_3SO_3H$ and Lewis acids such as $ZnCl_2$,[3] $FeCl_3$[4] as a catalyst. Recently, $I_2$,[5] $Sc(OTf)_3$,[6] $Cu(OTf)_3$,[7] $LiBF_4$,[8] $Zn(BF_4)_2$,[9] $Cu(BF_4)_2$,[10] $Zr(SO_4)_2/SiO_2$[11] have been introduced for this purpose. These methods have drawbacks such as low yields, long reaction time, cumbersome experimental process, use of organic solvents, moisture sensitive and costly catalysts. We report a novel catalyst for the synthesis of 1,1-diacetates from aldehydes under mild and environmental friendly conditions.

As a continuation of our research work in using $Ce(SO_4)_2{\cdot}4H_2O$ as a mild, efficient and heterogenous catalyst in organic synthesis, we wish to report an efficient and simple methodology for the rapidly synthesis of 1,1-diacetates under mild and solvent-free conditions catalysed by $Ce(SO_4)_2{\cdot}4H_2O$ (Scheme 1).

When a mixture of the aromatic aldehyde (5 mmol), acetic anhydride (7.5 mmol) and a catalytic amount of $Ce(SO_4)_2{\cdot}4H_2O$ (0.2 mmol, 4.0mol%) was stirred in a round flask at ambient temperature, an exothermic reaction took place immediately. The TLC showed the completion of the reaction at this stage. The reaction mixture cooled down to room temperature and the mixture solidified. Diethyl ether was added to the mixture to extract the product. The catalyst remained as a solid to be reused without further treatment. After removal of the organic solvent, the corresponding diacetates were obtained in excellent yields. Although the products were found to be practically pure, further purification was carried out by recrystallisation with the mixed solvent of petroleum ether and ethyl acetate. The results were shown in Table 1.

$$\underset{\mathbf{1}}{RCHO} + \underset{\mathbf{2}}{Ac_2O} \xrightarrow[\text{solvent-free, r.t.}]{Ce(SO_4)_2.4H_2O\ (4.0\ mol\%)} \underset{\mathbf{3}}{RCH(OAc)_2} \qquad (1)$$

As shown in Table 1, aromatic aldehydes containing both electron donor groups or withdrawing groups gave the desired products in good to excellent yields in the reaction time ranging from 3 to 15 min. Deactivated aldehydes such as *p*-nitrobenzaldehyde and *m*-nitrobenzaldehyde required a little longer reaction time possibly due to the electron withdrawing groups (Table 1, entry j–k). Moreover, the steric hindrance seems to have no significant effects on the reaction yields (Table 1, entry b, f and h). A blank reaction of aromatic aldehyde, acetic anhydride without the catalysts failed even after 8h of stirring at room temperature.

Note that a hydroxyl group on the aromatic ring such as 2-hydroxy-, 4-hydroxy-, and 3-methoxy-4-hydroxy-benzaldehyde were also acetylated to afford the corresponding triacetates when the use of 1.5 eq. $Ac_2O$ in the presence of catalytic amount of $Ce(SO_4)_2{\cdot}4H_2O$ (Table 1, entry b–d) (Scheme 2).

The reuse of the catalyst is highly preferable. In this work, we examined the possibility of recovery and reuse of $Ce(SO_4)_2{\cdot}4H_2O$. After the first reaction had been completed,

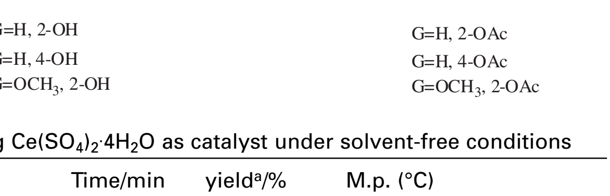
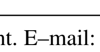
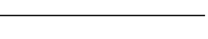


**Table 1** Preparation of 1,1-diacetates from aromatic aldehydes using $Ce(SO_4)_2{\cdot}4H_2O$ as catalyst under solvent-free conditions

| Entry | Aldehyde | Product | Time/min | yield[a]/% | M.p. (°C) | |
|---|---|---|---|---|---|---|
| | | | | | Found | Reported |
| a | $4\text{-MeO-}C_6H_4CHO$ | $4\text{-MeO-}C_6H_4CH(OAc)_2$ | 2 | 86 | 63–64 | 64–65[2] |
| b | $2\text{-HO-}C_6H_4CHO$ | $2\text{-AcO-}C_6H_4CH(OAc)_2$ | 5 | 87 | 101–103 | 103–104[11] |
| c | $4\text{-HO-}C_6H_4CHO$ | $4\text{-AcO-}C_6H_4CH(OAc)_2$ | 5 | 93 | 90–92 | 89–90[2] |
| d | $4\text{-HO-3-MeO-}C_6H_3CHO$ | $4\text{-AcO-3-MeO-}C_6H_3CH(OAc)_2$ | 8 | 89 | 82–84 | 79–80[2] |
| e | $C_6H_5CHO$ | $C_6H_5CH(OAc)_2$ | 8 | 95 | 41–43 | 41–41.5[2] |
| f | $2\text{-Cl-}C_6H_4CHO$ | $2\text{-Cl-}C_6H_4CH(OAc)_2$ | 5 | 92 | 55–57 | 56–57[2] |
| g | $4\text{-Cl-}C_6H_4CHO$ | $4\text{-Cl-}C_6H_4CH(OAc)_2$ | 3 | 96 | 77–79 | 79–80[2] |
| h | $2,4\text{-}Cl_2\text{-}C_6H_3CHO$ | $2,4\text{-}Cl_2\text{-}C_6H_3CH(OAc)_2$ | 3 | 96 | 99–101 | 101–102[11] |
| i | $4\text{-Br-}C_6H_4CHO$ | $4\text{-Br-}C_6H_4CH(OAc)_2$ | 3 | 98 | 90–92 | 91–92[2] |
| j | $3\text{-}NO_2\text{-}C_6H_4CHO$ | $3\text{-}NO_2\text{-}C_6H_4CH(OAc)_2$ | 15 | 95 | 63–65 | 63–64[2] |
| k | $4\text{-}NO_2\text{-}C_6H_4CHO$ | $4\text{-}NO_2\text{-}C_6H_4CH(OAc)_2$ | 10 | 84 | 124–126 | 124–125[2] |
| l |  |  | 3 | 84 | 49–51 | 50–51[2] |

[a] Isolated yield.

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* Correspondent. E–mail: tlyq@jnu.edu.cn

diethyl ether was added to the reaction mixture to separate the product. The remaining solid catalyst was directly used in the next run without further purification under the same conditions with using *p*-bromobenzaldehyde as model substrate. This procedure was repeated 5 times and the results obtained are shown in Table 2. The yields are still very close to the initial value in the previous four cycles. Unfortunately, the yield decreased to 82% from 98% at the case of the fifth cycle. Hence the catalyst can be efficiently recycled for at least 4 times without loss in activity.

In conclusion, we have provided an alternative preparation of 1,1-diacetates from aromatic aldehydes with the advantages of high yields, fast reaction, simple operation and minimal environmental impact.

## Experimental

Melting points were measured by X6 micro-melting point apparatus and were uncorrected. Infrared spectra were recorded using KBr pellet on a Bruker Equinox 66 spectrometer. $^1$H NMR spectra were recorded in CDCl$_3$ on a Bruker AVANCE 300 (300 MHz) instrument with the residue CHCl$_3$ as an internal standard at δ 7.24 ppm. Furyl aldehyde and benzaldehyde were purified by distillation. All other chemicals used were of commercial grade without further purification.

*General procedure for the preparation of 1,1-diacetates*: A mixture of the aromatic aldehyde (5 mmol), acetic anhydride (7.5 mmol) and Ce(SO$_4$)2.4H$_2$O (0.2 mmol) was stirred at ambient temperature. While the stirring continued, the mixture solidified completely. After completion of the reaction (monitored by TLC), diethyl ether (10 ml × 5) was added to extract the product and the catalyst remained as a solid. The recovered wet catalyst was used for recycling directly. The organic layer was washed 5% NaHCO$_3$, saturated NaHSO$_3$, brine and dried over anhydrous Na$_2$SO$_4$. The solvent was removed in vacuo to afford the practically pure product which was further purified by recrystallisation with the mixed solvent of petroleum ether and ethyl acetate.

## Spectroscopic data of selected products

**3c:** $^1$H NMR (CDCl$_3$, 300MHz) δ: 2.13 (s, 6H, 2CH$_3$CO), 2.31 (s, 3H, CH$_3$CO), 7.15 (d, *J* = 6.6 Hz, 2H, ArH), 7.55 (d, *J* = 6.6 Hz, 2H, ArH), 7.68 (s, 1H, CH); IR (KBr) δ: 1764, 1741, 1368, 1241, 1205, 1008 cm$^{-1}$.

**3d:** $^1$H NMR (CDCl$_3$, 300MHz) δ: 2.14 (s, 6H, 2CH$_3$CO), 2.33 (s, 3H, CH$_3$CO), 3.87 (s, 3H, CH$_3$O), 7.08–7.33 (m, 3H, ArH), 7.17 (d, *J* = 1.6 Hz, 1H, ArH), 7.66 (s, 1H, CH); IR (KBr) δ: 1762, 1611, 1375, 1244, 1206, 1014 cm$^{-1}$.

**Table 2** The reuse of the catalyst

| Run | Substrate | Reaction time /min | Isolated yield/% |
|---|---|---|---|
| 1 | 4-Br-C$_6$H$_5$CHO | 3 | 96 |
| 2 | 4-Br-C$_6$H$_5$CHO | 5 | 98 |
| 3 | 4-Br-C$_6$H$_5$CHO | 12 | 94 |
| 4 | 4-Br-C$_6$H$_5$CHO | 15 | 94 |
| 5 | 4-Br-C$_6$H$_5$CHO | 30 | 82 |

**3g:** $^1$H NMR (CDCl$_3$, 300MHz) δ: 2.14 (s, 6H, 2CH$_3$CO), 7.40 (d, *J* = 6.8 Hz, 2H, ArH), 7.46 (d, *J* = 6.8 Hz, 2H, ArH), 7.65(s, 1H, CH); IR (KBr) δ: 1755, 1379, 1247, 1202, 1089, 1065, 1010 cm$^{-1}$.

**3h:** $^1$H NMR (CDCl$_3$, 300MHz) δ: 2.16 (s, 6H, 2CH$_3$CO), 7.70 (s, 1H, CH), 7.72-8.28 (m, 3H, ArH); IR (KBr) δ: 1760, 1591, 1373, 1238, 1197, 1078, 1017 cm$^{-1}$.

**3j:** $^1$H NMR (CDCl$_3$, 300MHz) δ: 2.14 (s, 6H, 2CH$_3$CO), 7.61 (t, *J* = 8.0 Hz, 1H, ArH), 7.84 (s, 1H, CH), 7.83 (d, *J* = 7.6 Hz, 1H, ArH), 8.27 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H, ArH), 8.41 (s, 1H, Ar-H); IR (KBr) δ: 2954, 1748, 1376, 1248, 1217, 1078 cm$^{-1}$.

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