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Montmorillonite Clay Catalysis. Part 4.[1] An Efficient and Convenient Procedure for Preparation of 1,1-Diacetates from Aldehydes†

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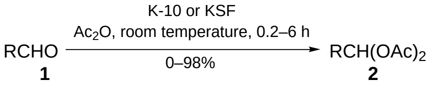
An easy preparation of 1,1-diacetates from aldehydes with montmorillonite clays as catalysts has been carried out in excellent yield.

1,1-Diacetates have attracted considerable attention owing to their moderate stability and easy conversion into parent aldehydes.[2–7] They are an alternative protecting group to acetals for protecting aldehydes and can be used as starting materials for the synthesis of valuable intermediates for Diels–Alder cycloaddition reactions.[8] Usually, the syntheses of 1,1-diacetates are carried out under the catalysis of strong proton acids, such as sulfuric acid,[9,10] phosphoric or methanesulfonic acid,[10] and Lewis acids, such as zinc chloride.[11] These methods have not been entirely satisfactory, owing to such drawbacks as low yields, long reaction times, corrosivity, difficult work-up and effluent pollution. In recent years, several catalysts have been employed for this reaction to improve yields, to decrease reaction time and to eliminate the mentioned unfavourable effects. Phosphorus trichloride was used as a catalyst resulting in good yields with most aldehydes, but the yields were poor for aromatic aldehydes containing electron-withdrawing groups.[12] Kochlar *et al.*[2] developed a fast reaction (less than 30 min), catalysed by iron(III) chloride, even for α,β-unsaturated aldehydes and aromatic aldehydes having electron-withdrawing groups. Nafion-H,[13] Y-zeolite,[14] β-zeolite,[15] sulfated zirconia[16] and HZSM-5[17] have been relatively successfully used as catalysts for the conversion of aldehydes into 1,1-diacetates.



$$\underset{\mathbf{1}}{\mathrm{RCHO}} \xrightarrow[\text{0–98\%}]{\text{K-10 or KSF}\atop \mathrm{Ac_2O}\text{, room temperature, 0.2–6 h}} \underset{\mathbf{2}}{\mathrm{RCH(OAc)_2}}$$

Scheme 1

Montmorillonite clays have been used as efficient catalysts for a number of organic reactions and offer several advantages over classic acids: strong acidity, non-corrosivity, cheapness, mild reaction conditions, high yield and selectivity, and ease of set-up and work-up.[18] Here we report an easy and efficient procedure for the synthesis of 1,1-diacetates from aldehydes catalysed by montmorillonite clays (Scheme 1).

As shown in Table 1, a series of 1,1-diacetates **2** were synthesized using montmorillonite K-10 or KSF as a catalyst at room temperature. K-10 and KSF gave similar results in terms of reaction time and yield. Both aromatic and aliphatic aldehydes gave high, although unmaximized, yields of the corresponding 1,1-diacetates. For example, furfural gave 2-furylmethanediyl diacetate (**2j**) in 74% yield and chloral diacetate (**2b**) was obtained in 53% yield after distillation. 4-Nitrobenzaldehyde (**1h**) required a relatively longer reaction time (6 h), possibly owing to the strong electron-withdrawing nitro substituent. Interestingly, the α,β-unsaturated aldehyde **1k** gave a better yield in a shorter reaction time than the previously mentioned methods.[2,12,16]

Table 1 Conversion of aldehydes into 1,1-diacetates in the presence of montmorillonite clays

Aldehyde **1** R	Diacetate **2** R	Catalyst/Solvent Time (t/h)	Yield (%)	Mp (T/°C) [bp (T/°C)/Torr] Found	Reported
Et (**1a**)	Et (**2a**)	K-10/none/0.8	87	[105–109/35]	115–118/8[2]
$Cl_3CCH(OH)_2$ (**1b**)	Cl_3C (**2b**)	K-10/none/4	53	[145–148/32]	98–99/6[19]
Ph (**1c**)	Ph (**2c**)	K-10/none/0.2	98	44–45	44–45[4]
		KSF/none/0.2	98		
4-MeC_6H_4 (**1d**)	4-MeC_6H_4 (**2d**)	K-10/none/0.5	98	80.5–81.5	81–82[4]
4-$MeOC_6H_4$ (**1e**)	4-$MeOCH_6H_4$ (**2e**)	K-10/none/0.5	98[b]	64–65	64–65[4]
4-ClC_6H_4 (**1f**)	4-ClC_6H_4 (**2f**)	K-10/CCl_4/1	96	81–82	80–81[4]
		KSF/CCl_4/0.6	95		
3-ClC_6H_4 (**1g**)	3-ClC_6H_4 (**2g**)	K-10/none/1	94[b]	65–66	65–66[10]
		KSF/none 0.6	96		
4-$O_2NC_6H_4$ (**1h**)	4-$O_2NC_6H_4$ (**2h**)	K-10/CCl_4/6	90	125.5–126.5	123–125[12]
		KSF/CCl_4/6	96		
3-$O_2NC_6H_4$ (**1i**)	3-$O_2NC_6H_4$ (**2i**)	K-10/none/4	94	64–66	64–66[2]
		KSF/none/4	94		
2-furyl (**1j**)	2-furyl (**2j**)	K-10/none/2	74	50.5–51.5	50–51[10]
PhCH=CH (**1k**)	PhCH=CH (**2k**)	K-10/none/0.5	97[b]	83.5–84.5	84–87[12]
2-HOC_6H_4 (**1l**)	2-$AcOC_6H_4$ (**2l**)	K-10/none/1	93[b]	103–104	104–105[20]
3-MeO-4-HOC_6H_3 (**1m**)	3-MeO-4-$AcOC_6H_3$ (**2m**)	K-10/none/1	92[b]	90–91	79–80[10]
3,4-$(OCH_2O)C_6H_3$ (**1n**)	3,4-$(OCH_2O)C_6H_3$ (**2n**)	K-10/none/0.5	98[b]	78–79	75–76[10]
		KSF/none/0.5	96		
4-HOC_6H_4 (**1o**)	no reaction	K-10/none/48	—[c]		
		KSF/none/48	—[c]		
4-$Me_2NC_6H_4$ (**1p**)	no reaction	K-10/none/48	—[c]		
		KSF/none/48	—[c]		
Me_2N (**1q**)	no reaction	K-10/none/48	—[c]		
		KSF/none/48	—[c]		

[a]Isolated yield. [b]Satisfactory elemental analysis obtained: C ±0.20, H ±0.19%. [c]100% aldehyde was recovered.

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†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1997, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

It is worth noting that the hydroxy groups in 2-hydroxy- and 3-methoxy-4-hydroxy-benzaldehyde (**1l** and **1m**) were also acetylised to afford the corresponding triacetates **2l** and **2m** under these conditions.

The scope and limitation of this method were investigated. *N*,*N*-Dimethylformamide (**1q**) was not acetylised with acetic anhydride even under reflux for 3 h in the presence of K-10 or KSF. Ketones, such as cyclohexanone and acetophenone, were not converted into the corresponding 1,1-diacetates at room temperature. Therefore the present procedure is a selective preparation of the 1,1-diacetates **2** of aldehydes in the presence of ketones. We also attempted the reaction of maleic anhydride, phthalic anhydride and succinic anhydride with benzaldehyde (**1c**) with K-10 or KSF as catalyst. However, none of these reagents gave the expected cyclic diesters even when the reaction mixtures were stirred either at room temperature for 2 d or under reflux for 2 h. The starting materials were quantitatively recovered. It is worth noting that when 4-hydroxybenzaldehyde (**1o**) and 4-(dimethylamino)benzaldehyde (**1p**) were treated with acetic anhydride with K-10 or KSF as catalyst, to our surprise, none of the reactions gave the corresponding products even when the reaction mixtures were stirred at room temperature for 2 d. The starting materials were quantitatively recovered. We propose, as an explanation for this result, that selective adsorption of the phenolic and amino compounds (**1o** and **1p**) at the hydroxy and dimethylamino groups of the catalyst occurs. This might keep the aldehyde away from the active site thus stopping the reaction and blocking the sites. Compound **1l** would adsorb favourably for the reaction. The hydrogen bond and the bulk of the methoxy group in **1m** might be enough to discourage adsorption in the 'wrong' manner.

In conclusion, we have provided an alternative preparation of 1,1-diacetates from aldehydes, with the advantages of selectivity, operational simplicity, high yields, short reaction times and minimal environmental impact.

Experimental

Boiling points and melting points are uncorrected. K-10 and KSF were purchased from Fluka and employed directly for the reactions. The products were characterized by their melting or boiling points and/or IR, ^{1}H NMR and mass spectra.

General Procedure for the Preparation of 1,1-*Diacetates* **2**.—A mixture of the aldehyde **1** (10 mmol), acetic anhydride (30 mmol) and K-10 (or KSF) montmorillonite (200 mg) was stirred at room temperature for the time indicated in Table 1. For the reactions with solvent, CCl_4 (5 mL) was also added. The reaction was monitored by TLC. Upon completion, Et_2O (10 mL) was added to the reaction mixture and the catalyst was filtered off. The catalyst was washed with Et_2O (2 × 10 mL) and then the filtrate was washed with 10% HCl (20 mL) and brine (2 × 20 mL) and then dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue was purified by distillation or crystallization from cyclohexane to give 1,1-diacetates **2** in 0–98% yields.

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