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Synthesis of 1,1-Diacetates from Aldehydes using Trimethylchlorosilane and Sodium Iodide as Catalyst†

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A variety of aldehydes react with acetic anhydride in the presence of trimethylchlorosilane and sodium iodide or trimethylchlorosilane alone to afford 1,1-diacetates in excellent yields.

Aldehydes may be protected as their 1,1-diacetates by a variety of methods. These diacetates are synthetically useful as protecting groups[1] having stability towards aqueous acids as well as mild bases,[2] and are useful as important building blocks for the synthesis of dienes for Diels–Alder cycloaddition reactions.[3] Diacetates of some aldehydes are reported to be good cross-linking reagents for cellulose in cotton.[4] One European patent claims the peroxygen compounds of the type 1,1,5-triacetoxypent-4-ene as activators in the composition of a bleaching mixture for wine stained fabrics.[5] Kula has successfully demonstrated in his patent[6] the utility of this protecting group in the synthesis of an intermediate for chrysenthemic acid.

$$\mathrm{RCHO} + \mathrm{Ac_2O} \xrightarrow{\text{TMCS–NaI}} \mathrm{RCH(OAc)_2}$$

Recently, several reports have appeared on the synthesis of diacetates from aldehydes using different catalysts.[7] Some other methods employed for the preparation of 1,1-diacetates from aldehydes include the use of protic acids,[8] Lewis acids such as BF_3,[9] PCl_3,[10] $FeCl_3$,[2] *etc.* and the super acid Nafion-H.[11] But in most cases, either a long reaction time (up to 120 h in the case of 2-furaldehyde with PCl_3[10]), or a low product yield (4% in the case of 4-nitrobenzaldehyde[10]) is incurred. Herein we wish to report a high yielding method for the preparation of 1,1-diacetates from aldehydes using TMCS–NaI as catalyst.

When an aldehyde was treated with acetic anhydride (1 ml of dry $CHCl_3$ or CH_3CN was added to solubilise, if needed) at room temp. [at 0–5 °C in case of hydroxycitronellal (**1**)] in the presence of a catalytic amount of TMCS (20 mol%) and sodium iodide (20 mol%) it yielded the corresponding diacetate in excellent yield (Table 1). The same reaction took longer to complete in TMCS alone (reaction in refluxing acetonitrile giving a comparable result). A blank reaction of aldehyde, acetic anhydride and sodium iodide failed to react even after 8 h of stirring at room temp. Because of its high yield and short reaction time at ambient temperature this method will better many existing ones.[7,11] The catalyst is also easily available, cheap and easy to handle.

Experimental

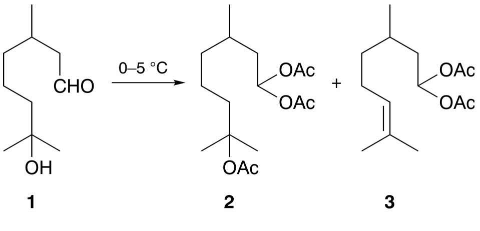
Mps were determined on a Buchi capillary apparatus. IR spectra were recorded on a Perkin Elmer 237B IR spectrophotometer. NMR spectra were recorded on a Varian 360L instrument. Mass spectra were recorded on a INCOS 50 GC-MS instrument.

General Procedure.—In a typical reaction a mixture of 2 mmol of benzaldehyde was treated at room temp. with 4 mmol of acetic anhydride followed by 0.4 mmol of TMCS and 0.4 mmol of NaI.

Table 1[a]

Entry	Substrate	Reaction time (*t*/min)	Yield (%)	Mp (°C) found/reported
1	Benzaldehyde	25	87	45–46 (44–45[2])
2	4-Cl-C_6H_4CHO	40	92	79–80 (79–80[7])
3	4-NO_2-C_6H_4CHO	40	96	125 (125[7])
4	4-MeO-C_6H_4CHO	50	96	67–68 (67–68[10])
5	Furfural	60	70	55 (52–54[7])
6	Butyraldehyde[12]	40	84	
7	Cinnamaldehyde	30	70	85–86 (84–86[2])
8	Crotonaldehyde[12]	50	90	
9	Gluteraldehyde[b]			
10	Acrolein[2]	50	60	
12	Hydroxycitronellal[c]	60	70 (2 + 3)	

[a]All the compounds give satisfactory spectral analysis for IR, NMR (60 MHz) and MS. Yields are of isolated pure products and mps are uncorrected. [b]No reaction in 25% water solution. [c]This reaction was carried out at 0–5 °C in 60 min. The major products isolated were triacetate (**2**) (50% yield) and diacetate (**3**) (20% yield) along with a complex mixture of minor products.



1 **2** **3**

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When the reaction was over (TLC monitoring) excess water was added and the product extracted with CH_2Cl_2. The organic layer was washed with a dilute solution of sodium thiosulfate followed by water, dried over anhydrous sodium sulfate and evaporated under reduced pressure. In most cases pure solid products were obtained.

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