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.

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

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

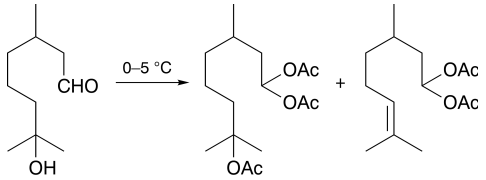
Mps were determined on a Buchi capillary apparatus. IR spectra were recorded on a Perkin Elmer 237B IR spectrophotometer. NMR spectra were recorded on a Varian 360L instrument. Mass spectra were recorded on a INCOS 50 GC-MS instrument.

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.



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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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References

1 S. V. Leibermann and R. Connor, *Org. Synth. Coll. Vol. III*, 1955, 441.
2 K. S. Kochhar, B. S. Bal, R. P. Deshpande, S. N. Rajadhyaksha and H. W. Pinnick, *J. Org. Chem.*, 1983, **48**, 1765.
3 B. B. Snider and S. G. Amin, *Synth. Commun.*, 1978, **8**, 117.
4 J. G. Frick Jr. and R. J. Harper Jr., *J. Appl. Polym. Sci.*, 1984, **29**, 1433.
5 W. R. Sanderson, Eur. Pat. Appl., EP. 125, 781 (1984) (*Chem. Abstr.* **102**, p64010k).
6 J. Kula, Pol. Pat. PL143, 824 (1988) (*Chem. Abstr.* **112**, p216290y).
7 P. Kumar, V. R. Hegde and T. P. Kumar, *Tetrahedron Lett.* 1995, **36**, 601; C. Pereira, B. Gigante, M. J. Marcelo-Curoto, H. Carreyre, G. Perot and M. Guisnet, *Synthesis*, 1995, 1077; B. P. Bandgar, N. P. Mahajan, D. P. Mulay, J. L. Thote and P. P. Wadgaonkar, *J. Chem. Res.* (*S*), 1995, 470.
8 M. J. Gregory, *J. Chem. Soc.* (*B*), 1970, 1201.
9 J. March, *Advanced Organic Chemistry*, Wiley Eastern, New Delhi, 3rd edn., 1986, p. 861.
10 J. K. Michie and J. A. Miller, *Synthesis*, 1981, 824.
11 G. Olah and A. K. Mehrotra, *Synthesis*, 1982, 962.
12 N. Deka, D. J. Kalita, R. Borah and J. C. Sarma, *J. Org. Chem.*, 1997, 1563.