SHORT PAPER

J. Chem. Research (S),
2002, 144–146

A facile method for the preparation and cleavage of 1,1-diacetates of aldehydes

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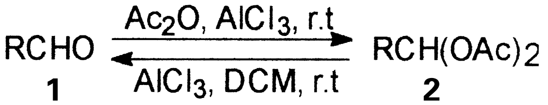
A convenient method for the preparation and cleavage of 1,1-diacetates of aldehydes is reported using $AlCl_3$ as catalyst.

Keywords: 1,1-diacetates, aluminium chloride, aldehydes

1,1-Diacetates are stable, easily prepared and are gaining importance in synthetic organic chemistry as an alternative to acetals for aldehyde protection[1] and as starting materials for the Diels–Alder cycloaddition reaction.[2,3] The preparation of 1,1-diacetates has been carried out with strong acids as sulfuric acid,[4] phosphoric acid or methanesulfonic acid[5] and Lewis acids such as $FeCl_3$[6] and PCl_3[7]. The use of PCl3 gave good yields but the reaction times ranged from 1 to 120 hours and yields were poor for aromatic aldehydes containing electron-withdrawing groups. Zeolites[8,9] of different types have also been used as catalysts for this reaction but require heating.[8] More recently, montmorillonite clay,[10] iodine,[11] expansive graphite[12] and ferrous sulfate[13] have also been employed to obtain better results. However, development of efficient reagents which provide better yields is still of interest.

Even though numerous methods have been developed for the protection of aldehydes as their diacetates, a limited number of methods are available for the deprotection of 1,1-diacetates to aldehydes. Strong acids such as: (1) sulfuric acid[14] or HCl;[15] (2) sodium hydroxide or potassium carbonate in aqueous THF overnight;[6] (3) boron tri-iodide-*N*,*N*-diethylaniline complex;[16] (4) ceric ammonium nitrate coated on silica gel;[17] (5) neutral alumina under microwave irradiation;[18] and (6) montmorillonite clay,[19] in refluxing dichloromethane or benzene have been employed for the deprotection of 1,1-diacetates. Each of the above methods has its disadvantages, method (1) may affect other functional groups, method (2) requires long reaction times, method (3) proceeds in low yields, (4) involves high cost, (5) requires the use of an additional microwave oven and (6) requires heating. Hence, there is a need to develop a facile alternate procedure for the deprotection of 1,1-diacetates to aldehydes at room temperature. Here, we report an efficient method for the conversion of aldehydes into their 1,1-diacetates and regeneration of aldehydes from the respective 1,1-diacetates at room temperature employing aluminium chloride.



$$\underset{\mathbf{1}}{\mathrm{RCHO}} \underset{\mathrm{AlCl_3,\ DCM,\ r.t}}{\overset{\mathrm{Ac_2O,\ AlCl_3,\ r.t}}{\rightleftarrows}} \underset{\mathbf{2}}{\mathrm{RCH(OAc)_2}}$$

Thus aromatic, heterocyclic and aliphatic aldehydes of different types were subjected to protection with acetic anhydride in the presence of catalytic amount of anhydrous $AlCl_3$ at room temperature for different lengths of time. The corresponding diacetates were obtained in good to excellent yields. The results are summarised in Table 1. It is noteworthy that the phenolic group in *m*-hydroxybenzaldehyde (entry 8) was also protected as acetate. All the products were purified either by crystallisation or distillation.

Deprotection of 1,1-diacetates of above aldehydes in presence of $AlCl_3$ in dichloromethane at room temperature afforded the respective aldehydes in good to excellent yields. The results are also summarised in Table 1. Further, deprotection of *m*-acetoxybenzaldehyde diacetate is achieved selectively without affecting the acetoxy group. In the case of aliphatic aldehyde diacetates (entries 13 and 14), decomposition was observed at 0°C due to their polymerisation in the presence of Lewis acid.[20] The present reaction conditions were utilised for the protection of various heterocylic aldehydes and for their regeneration which have not been reported previously. In conclusion, our protocol provides a new addition to the existing methodologies for protection of aldehydes and deprotection of aldehyde 1,1-diacetates in terms of easy availability of catalyst and a simple procedure at room temperatures.

Experimental

General procedure for the protection of aldehydes to diacetates (**2**): To a mixture of the aldehyde (**1**, 10 mmol) and Ac_2O (20 mmol), anhydrous $AlCl_3$ (2.5 mmol) was added portionwise over 10min. and the mixture was stirred at room temperature, under N_2 atmosphere for the time given in Table 1. The progress of the reaction was followed by TLC and upon completion of the reaction, it was worked up by adding water (15 ml) and chloroform (30 ml) to the reaction mixture. The organic layer was washed with 15% $NaHCO_3$ solution followed by water (3×15ml) and dried over Na_2SO_4. Removal of the solvent under vacuum furnished the desired 1,1-dicetates (**2**). Further purification was achieved by distillation or recrystallisation.

3-formylchromone diacetate (entry 10): m.p. 121°C ($CHCl_3$–hexane). IR (KBr) : 1760, 1650, 1570, 1400, 1190, 1010 cm^{-1}; ^1H NMR ($CDCl_3$); δ 2.14 (s, 6H, $COCH_3$), 7.40–7.50 (m, 2H, ArH), 7.65–7.80 (m, 2H, ArH), 8.10 (s, 1H), 8.25 (d, *J* = 8.0Hz 1H, ArH); MS: *m*/*z*: 276, 191, 175(100), 146, 121, 104, 92, 76, 63, 43(100).

Anal. calcd for $C_{14}H_{12}O_6$: C, 60.86; H, 4.34. Found C, 60.55, H, 4.11.

5-Phenylpyran-4-one-3-carboxaldehyde diacetate (entry 11): m.p. 147°C ($CHCl_3$– hexane). IR (KBr) : 1755, 1650, 1365, 1320, 1190, 1000 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.12 (s, 6H, $COCH_3$), 7.30–7.60 (m, 5H, ArH), 7.70 (s, 1H, vinylic), 7.95 (s, 1H, vinylic), 8.00 (s, 1H); MS: *m*/*z*: 302, 217, 201, 199, 172, 115, 102, 89, 53, 43(100).

Anal: calcd for $C_{16}H_{14}O_6$: C, 63.57; H, 4.63. Found: C, 63.86; H, 4.30.

5-Chloro-3-methyl-1-phenylpyrazol-4-carboxaldehyde diacetate (entry 12): m.p. 87°C ($CHCl_3$–hexane). IR (KBr): 1750, 1560, 1365, 1235, 1055, 1000cm^{-1}; ^1H NMR ($CDCl_3$). d 2.15 (s, 6H, COCH3), 2.45 (s, 3H), 7.40–7.60 (m, 5H, ArH), 8.68 (s, 1H); MS: *m*/*z*: 322, 223, 222, 221(100), 155, 104, 77, 51, 43.

Anal. calcd for $C_{15}H_{15}ClN_2O_4$: C, 55.81; H, 4.65; N, 8.68. Found: C, 55.65; H, 4.91; N, 8.42.

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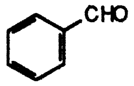
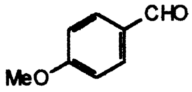
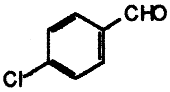
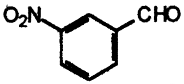
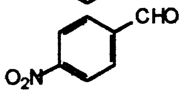
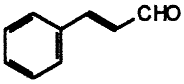
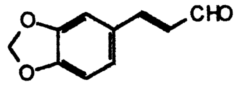
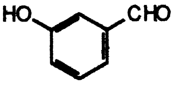
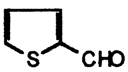
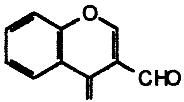
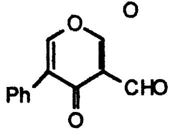
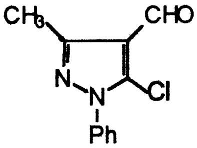
† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.

Table 1 Protection and deprotection of aldehydes by formation and cleavage of 1,1-diacetates catalysed by $AlCl_3$

Entry	Aldehydes	Formation		b.p./torr or m.p./°C		Cleavage	
		Time /h	Yield /%[a]	Found	Reported	Time /min	Yield /%
1		3	96	43–44	44–45[6]	60	94
2		1.5	78	67	67–68[7]	30	86
3		2	88	80	79.5[7]	30	90
4		9	73	62–64	63–64[5]	30	90
5		8	71	124	125[9]	20	92
6		7	84	85	84–86[7]	15	79
7		1.5	81	77–78	75–76[5]	15	94
8		3	85	75–76	74–75[5]	15	92
9		1	93	66–67	67–68[5]	60	95
10		2.5	92	121	(-)[b]	60	98
11		5	98	147	(-)[b]	60	87
12		3	77	87	(-)[b]	60	89
13		1	65	136–137/2mm	(-)[b]	Decomposition	
14		2	68	90–91/15	90–91/15	Decomposition	

[a] All products gave satisfactory spectral analysis for IR,^{1} H NMR, and MS. Yields are all of isolated pure products.

[b] New compound.

Heptanal diacetate (entry 13): IR (KBr): 1760, 1055, 1000cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.9 (t, J = 6.8 Hz, 3H), 1.2–1.5 (m, 8H), 1.9–2.0 (m, 2H), 2.1 (s, 6H, $COCH_3$), 6.4 (t, J = 6.0 Hz, 1H). MS: *m/z*: 216, 173, 157(100), 131, 115, 103, 97, 89.

Anal. calcd for $C_{11}H_{20}O_4$: C, 61.11; H, 9.20. Found: C, 61.35, H, 9.44.

General procedure for the cleavage of diacetates to aldehydes (**1**): A mixture of 1,1-diacetates (**2**, 2mmol) and anhydrous $AlCl_3$ (1mmol) in dichloromethane (5 ml) was stirred at room temperature under N_2 atmosphere for the time indicated in Table 1. The reaction was monitored by TLC. After completion, the reaction mixture was washed with water dried over Na_2SO_4 and concentrated to give the corresponding aldehyde (**1**).

One of the authors (SA) thank CSIR for the award of fellowship. This is IICT Communication No. 4045.

Received 27 June 2001; accepted 9 September 2001
Paper 01/957

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