Aluminium Chloride: A Mild and Efficient Catalyst for Selective Deprotection of 1,1-Diacetates†

J. Chem. Research (S), 1999, 272–273†

Iraj Mohammadpoor-Baltork* and Hamid Aliyan

Department of Chemistry, Esfahan University, Esfahan 81744, Iran

A mild, efficient and excellent yield method for the selective deprotection of 1,1-diacetates to the corresponding aldehydes in the presence of aluminium chloride ($AlCl_3$) is described.

Selective introduction and removal of protecting groups is of great significance in the total synthesis of complex organic molecules. 1,1-Diacetates are synthetically useful and have received considerable attention, since these compounds are moderately stable,[1] easily prepared[1–10] and can be used as protecting groups for the selective protection of aldehydes. They are also important building blocks for the synthesis of dienes for Diels–Alder cycloaddition reactions.[11]

Regeneration of the original aldehydes from their corresponding 1,1-diacetates is a useful transformation in organic chemistry. Several methods for this purpose have been introduced in the chemical literature.[1,12–21] However, some of the reported methods suffer from drawbacks such as the use of strong proton acids,[12,13] long reaction time,[1] low yield of the product[14] and the requirement for microwave radiation.[6,20,21]

We now report a selective deprotection of 1,1-diacetates under the catalysis of aluminium chloride in refluxing acetonitrile. As shown in Table 1, different 1,1-diacetates, including those with electron-withdrawing substituents, are converted into the corresponding aldehydes in excellent yields (Scheme 1).

$$RCH(OAc)_2 \xrightarrow[\text{reflux}]{AlCl_3-CH_3CN} RCHO$$

Scheme 1

It is noteworthy that deprotection of aryl aldehyde diacetates occurs selectively without cleavage of phenolic acetate function (entries 14, 15). We have also tried the reaction of 1,1-diacetoxyheptane as an example of an aliphatic aldehyde diacetate in refluxing acetonitrile for 1 h in the presence of the catalyst. Only a 7% conversion into heptanal was observed under these conditions. To stress the selectivity of this method, we have performed a competitive reaction between 4-methylphenylmethanediol diacetate and 1,1-diacetoxyheptane in the presence of a 0.4 molar ratio of aluminium chloride and observed the following conversions (Scheme 2).

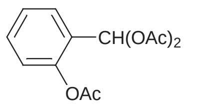
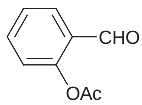
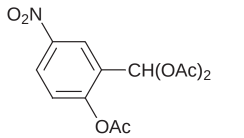
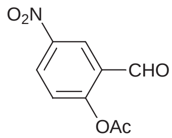
$$4\text{-}MeC_6H_4CH(OAc)_2 + C_6H_{13}CH(OAc)_2 \xrightarrow[\text{reflux, 15 min}]{AlCl_3-CH_3CN}$$

$$\underset{98\%}{4\text{-}MeC_6H_4CHO} + \underset{2\%}{C_6H_{13}CHO}$$

Scheme 2

Therefore, the present procedure offers a selective deprotection of aryl aldehyde diacetates in the presence of aliphatic aldehyde diacetate and phenolic acetate.

Table 1 Deprotection of 1,1-diacetates in the presence of $AlCl_3$ in refluxing MeCN

Entry	Substrate	Time (t/min)	Product[a]	Yield (%)[b]
1	$PhCH(OAc)_2$	15	PhCHO	98
2	$2\text{-}MeOC_6H_4CH(OAc)_2$	7	$2\text{-}MeOC_6H_4CHO$	97
3	$4\text{-}MeOC_6H_4CH(OAc)_2$	5	$4\text{-}MeOC_6H_4CHO$	99
4	$4\text{-}ClC_6H_4CH(OAc)_2$	5	$4\text{-}ClC_6H_4CHO$	93
5	$4\text{-}BrC_6H_4CH(OAc)_2$	5	$4\text{-}BrC_6H_4CHO$	97
6	$4\text{-}MeC_6H_4CH(OAc)_2$	5	$4\text{-}MeC_6H_4CHO$	99
7	$2,5\text{-}(MeO)_2\text{-}C_6H_3CH(OAc)_2$	3	$2,5\text{-}(MeO)_2\text{-}C_6H_3CHO$	99
8	$2\text{-}O_2NC_6H_4CH(OAc)_2$	15	$2\text{-}O_2NC_6H_4CHO$	98
9	$3\text{-}O_2NC_6H_4CH(OAc)_2$	20	$3\text{-}O_2NC_6H_4CHO$	98
10	$4\text{-}O_2NC_6H_4CH(OAc)_2$	20	$4\text{-}O_2NC_6H_4CHO$	95
11	$PhCH{=}CHCH(OAc)_2$	10	PhCH=CHCHO	98
12	$5\text{-}Me\text{-}2\text{-}furyl\text{-}CH(OAc)_2$	5	5-Methylfurfural	99
13	$1\text{-}Naphthyl\text{-}CH(OAc)_2$	5	1-Naphthaldehyde	97
14		15		97
15		10		88

[a]All products were identified by comparison of their physical and spectral data with those of authentic samples. [b]Isolated yield.

Table 2 Reaction of phenylmethanediol diacetate to benzaldehyde with 0.4 molar equivalent of various Lewis acids in refluxing MeCN

Entry	Metal halide	Yield(%)
1	$ZnCl_2$	69
2	$NiCl_2$	60
3	$CeCl_3$	10
4	$ZrCl_4$	9
5	$CuCl_2 \cdot 2H_2O$	79
6	$MnCl_2 \cdot 4H_2O$	48
7	$CoCl_2 \cdot 6H_2O$	65

The catalytic effects of several other Lewis acids for this transformation were also studied. To this end, various metal halides, such as $ZnCl_2$, $NiCl_2$, $CeCl_3$, $ZrCl_4$, $CuCl_2 \cdot 2H_2O$, $MnCl_2 \cdot 4H_2O$ and $CoCl_2 \cdot 6H_2O$, were reacted with phenylmethanediol diacetate in refluxing acetonitrile for 30 min. The experimental results show that these Lewis acids are much less efficient for this purpose (Table 2).

In conclusion, we have introduced an efficient methodology for the selective deprotection of aryl aldehyde diacetates to the corresponding aldehydes.

* To receive any correspondence.
† This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

Experimental

Deprotection of 1,1-*Diacetates.—General Procedure.* A solution of 1,1-diacetate (1 mmol) in MeCN (5 ml) was treated with $AlCl_3$ (0.4 mmol) and the mixture was stirred under reflux conditions for the time indicated in Table 1. The reaction was followed by GLC. The solvent was evaporated and the resulting crude material was purified on a silica-gel plate (eluent: CCl_4-Et_2O, 4 : 1). Evaporation of the solvent afforded the pure product; yield 88–99% (Table 1). The reactions of nitro derivatives were performed in the presence of a 0.5 molar equivalent of $AlCl_3$.

We are thankful to the Esfahan University Research Council for partial support of this work.

Received, 15th September 1998; Accepted, 4th January 1999
Paper E/8/07187J

References

1 K. S. Kochhar, B. S. Bal, R. P. Deshpande, S. N. Rajadhyaksha and H. W. Pinnick, *J. Org. Chem.*, 1983, **48**, 1765.
2 F. Freeman and E. M. Karchefski, *J. Chem. Eng. Data*, 1977, **25**, 355.
3 J. K. Michie and J. A. Miller, *Synthesis*, 1981, 824.
4 G. A. Olah and A. K. Mehrotra, *Synthesis*, 1982, 962.
5 C. Pereira, B. Gigante, M. J. Marcelo-Curto, H. Carreyre, G. Perot and M. Guisnet, *Synthesis*, 1995, 1077.
6 P. Kumar, V. R. Hegde and T. P. Kumar, *Tetrahedron Lett.*, 1995, **36**, 601.
7 Z.-H. Zhang, T.-S. Li and C.-G. Fu, *J. Chem. Res. (S)*, 1997, 174.
8 T.-S. Jin, G.-Y. Du, Z.-H. Zhang and T.-S. Li, *Synth. Commun.*, 1997, **27**, 2261.
9 B. P. Bandgar, N. P. Mahajan, D. P. Mulay, J. L. Thote and P. P. Wadgaonkar, *J. Chem. Res. (S)*, 1995, 470.
10 N. Deka, D. J. Kalita, R. Borah and J. C. Sarma, *J. Org. Chem.*, 1997, **62**, 1563.
11 B. B. Sinder and S. G. Amin, *Synth. Commun.*, 1978, **8**, 117.
12 S. V. Lieberman and R. Connor, *Org. Synth.*, 1951, Coll. Vol. II, 441.
13 S. M. Tsang, E. H. Wood and J. R. Johnson, *Org. Synth.*, 1955, Coll. Vol. III, 641.
14 C. Narayana, S. Padmanabhan and G. W. Kabalka, *Tetrahedron Lett.*, 1990, **31**, 6977.
15 P. Cotelle and J.-P. Catteau, *Tetrahedron Lett.*, 1992, **33**, 3855.
16 R. S. Varma, A. K. Chatterjee and M. Varma, *Tetrahedron Lett.*, 1993, **34**, 3207.
17 Y.-Y. Ku, R. Patel and D. Sawick, *Tetrahedron Lett.*, 1993, **34**, 8037.
18 T.-S. Li, Z.-H. Zhang and C.-G. Fu, *Tetrahedron Lett.*, 1997, **38**, 3285.
19 T.-S. Jin, Y.-R. Ma, Z.-H. Zhang and T.-S. Li, *Synth. Commun.*, 1997, **27**, 3379.
20 D. Villemin and B. Martin, *J. Chem. Res. (S)*, 1994, 146.
21 E. R. Perez, A. L. Marrero, R. Perez and M. A. Autie, *Tetrahedron Lett.*, 1995, **36**, 1779.