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A rapid and efficient procedure for deprotection of 1,1-diacetates catalysed by silica sulfate

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An efficient procedure for converting a number of 1,1-diacetates into the corresponding aldehydes was developed with silica sulfate as catalyst. The advantages of this procedure is its brevity, and high yield. It is environmentally friendly and the catalyst is also inexpensive and reusable.

Keywords: deprotection, 1,1-diacetates, silica sulfate

1,1-Diacetates play an important role in protecting aldehydes in synthesis, 1,1-Diacetates have received attention because of their stability to oxidants,[1,2] rapid and easy preparation prepared[3-12] and direct conversion to the corresponding aldehydes.[13,14] They have been used to prepare intermediates for DielsAlder reactions and as substrates for nucleophilic substains.[15]

In recent years, many reagents have been found to convert 1,1-diacetates into parent aldehydes. These include sodium hydroxide or potassium carbonate in aqueous THF,[3] ceric ammonium nitrate coated on silica gel in dichloromethane,[16] potassium phenoxide,[17] and montmorrillonite K10[18] under microwave irradiation. Each of these reactions has its own merits. There are some drawbacks such as long reaction time,[3] low yield[16] and expensive or rare catalysts.[19] More recently, aluminum chloride,[20] anhydrous ferrous sulfate[21] and β-cyclodextin[22] have been applied as catalysts to obtain better results. Although a series of catalyst have been reported for the deprotection of 1,1-diacetates, it was still necessary for us to find a cheap, easily prepared and nonpollutive catalyst. Herein, we report a facile and efficient method for the deprotection of 1,1-diacetates catalysed by silica sulfate in good yields (Scheme 1).

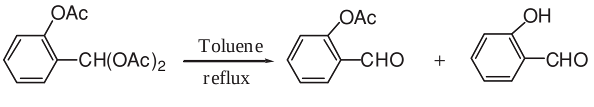
When 1,1-diacetates **1** are heated in refluxing dichloromethane, benzene or toluene in the presence of silica sulfate, the corresponding aldehydes **2** are obtained in excellent yield (Table 1).

As shown in Table 1, a number of 1,1-diacetates were heated in refluxing temperature for 1–3 min in the presence of silica sulfate, to obtain the corresponding aldehydes in excellent yields.

The phenolic acetate function (**1m**) can be converted almost completely to the other two compounds (**2m**) and (**3m**) in one minute as revealed by the disappearance of the substrate which was monitored by TLC (Scheme 2). At that time, the quantity of (**2m**) occupied the total's 95%. More (**3m**) was obtained with a longer reaction time. If the reaction proceeded for about 1 h, (**1m**) can be converted into (**3m**) completely. We obtained the similar results with **1n** (Scheme 3). In 1 min, almost all the 1,1-diacetate has disappeared. The yield of (**2n**) in the product is 88%. After 20 min, (**1n**) was also converted into (**3n**) completely. Above all of this, we can conclude that the deprotection of aldehyde group is superior to hydroxyl group. Moreover, with the longer time, we can get the more aldehydes.

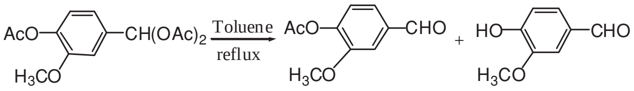
$$\underset{\mathbf{1}}{\mathrm{ArCH(OAc)_2}} \xrightarrow[\text{solvent, reflux}]{\text{Silica sulfate, } H_2O} \underset{\mathbf{2}}{\mathrm{ArCHO}} + \mathrm{CH_3COOH}$$

Scheme 1



1m **2m** **3m**

Scheme 2



1n **2n** **3n**

Scheme 3

Table 1 Deprotection of 1,1-diacetates in presence of silica sulfate

Entry	Substrate	Solvent	Time	Yield	B.p./torr or M.p./°C	
			/min	/%	Found	Reported
1	$C_6H_5CH(OAc)_2$ **1a**	CH_2Cl_2	1	95	65–67/15	60–62/10[21]
2	4-$ClC_6H_4CH(OAc)_2$ **1b**	Benzene	1	98	45–46	46–47[21]
3	3-$ClC_6H_4CH(OAc)_2$ **1c**	Benzene	1	98	102–104/15	95–97/10[21]
4	2-$ClC_6H_4CH(OAc)_2$ **1d**	Benzene	2	99	100–102/15	213–214/760[23]
5	2,4-$Cl_2C_6H_3CH(OAc)_2$ **1e**	Toluene	1	97	73–74	74.5[23]
6	4-$BrC_6H_4CH(OAc)_2$ **1f**	Toluene	3	95	58–59	59–60[23]
7	2-$NO_2C_6H_4CH(OAc)_2$ **1g**	Toluene	2	99	44–45	43–44[23]
8	3-$NO_2C_6H_4CH(OAc)_2$ **1h**	Toluene	2	92	56–57	57–58[21]
9	4-$NO_2C_6H_4CH(OAc)_2$ **1i**	Toluene	2	97	106–107	105–107[21]
10	4-$MeC_6H_4CH(OAc)_2$ **1j**	CH_2Cl_2	2	99	110–112/15	104–106/10[21]
11	4-$MeOC_6H_4CH(OAc)_2$ **1k**	Toluene	1	94	130–132/10	130–133/10[21]
12	$C_6H_5CH{=}CH(OAc)_2$ **1l**	Toluene	3	96	116–118/10	128–130/20[21]
13	2-$AcOC_6H_4CH(OAc)_2$ **1m**	Toluene	1	95	36–37	38–39[23]
14	3-MeO-4-$AcOC_6H_3CH(OAc)_2$ **1n**	Toluene	1	88	100–101	102–103[24]

[a] Yields refer to isolated products.

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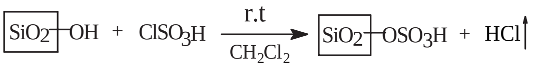

Scheme 4

Silica sulfate is easily regenerated and was reused five times for the deprotection of (**1d**) without significant loss of activity. This method is better than many other existing ones.

In conclusion, we have found a facile and efficient method for deprotection of 1,1-diacetates. These reactions have the advantage of short time, good yields, convenient-workup procedure and are environmentally friendly.

Experimental

1,1-Diacetates were synthesised as described previously.[11] The products were characterised by comparison of their melting or boiling points with authentic samples.[21]

Preparation of catalyst: A 500 ml suction flask was used. It was equipped with a constant pressure dropping funnel containing of chlorosulfonic acid (58.3g, 0.5mol) and a gas inlet tube for conducting of HCl gas over an absorbing solution. It was charged with silica gel (100g) and CH_2Cl_2 (50ml). Chlorosulfonic acid was added drop wise over a period of 30 min with stirring at room temperature. HCl gas was evolved from reaction vessel immediately. After the addition was completed, the mixture was shaken for 60 min. Evaporation of the CH_2Cl_2 and HCl under reduced pressure gave a white solid (silica sulfate) 120.0g(~100%) which was stored in a desiccator until use.

General procedure for the deprotection of 1,1-diacetates: A mixture of the 1,1-diacetate (**1**) (1.00 mmol), dichloromethane, benzene or toluene (5 ml) and silica sulfate (50 mg), and two drops of water was stirred under reflux for the length of time indicated in Table 1. The reaction procedure was monitored by TLC. After completion of the reaction, the reaction mixture was cooled and silica sulfate was filtered off. The catalyst was washed with ether and then the organic layer was washed with brine two times and dried with anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure and the crude product was chromatographed on silica gel with petroleum-ether as eluent to give the pure product (**2**).

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References

1 S.V. Lieberman and R. Connor, *Org. Syn.*, 1951, **2**, 441.
2 S.M. Tsang, E.H. Wood and J.R. Johnson, *Org. Syn.*, 1995, **3**, 641.
3 K.S. Kochhar, B.S.Bal, R.P. Deshpande, S.N. Rajadhyaksha and H.W. Pinnick, *J. Org. Chem.*, 1983, **48**, 1765.
4 F. Freeman and E.M. Karchefski, *J. Chem. Eng. Data.*, 1997, **22**, 355.
5 J.K. Michie and J.A. Miller, *Synthesi*, 1981, 824.
6 G.A. Olah and A.K. Karcherski, *Synthesis*, 1982, 962.
7 C. Pereira, B. Cigante, M.J. Marcelo-Curto, H. Carreyre, G. Perot and M.Guisnet, *Synthesis*, 1995, 1077.
8 P. Kumar, V.R. Hegda and T.P. Kumar, *Tetrahedron Lett.*, 1995, **36**, 601.
9 T.S. Jin, Y.R. Ma, G.Y. Du, Z.H. Zhang and T.S. Li, *Synth. Commun.*, 1997, **27**, 2261.
10 J.S. Yadav, B.V.S. Reddy, C. Venugopal and T. Ramalingam, *Synlett*, 2002, 604.
11 T.S. Jin, Y.R. Ma, X. Sun, D. Liang and T.S. Li, *J. Chem. Res.(S)*, 2000, 96.
12 T.S. Jin, Y.R. Ma, G. Sun, Y.W. Li and T.S. Li, *Green Chem.*, 2002, **4**, 255.
13 R.E. Banks, J.A. Miller, M.J. Nunn, P. Stanley, T.J.R. Weakley and Z. Ullah, *J. Chem. Soc., Perkin Trans., 1*. 1981, 1096.
14 B.B. Snider and S.G. Amin, *Synth. Commun.*, 1978, **8**, 117.
15 J.S. Yadav, B.V.S. Reddy and G.S. Kiran Kumar Reddy, *Tetrahedron Lett.*, 2000, **41**, 2695.
16 P. Ctelle and J.P. Catteau, *Tetrahedron Lett.*, 1992, **33**, 3855.
17 Y.Y. Ku, R. Patel and D. Sawick, *Tetrahedron Lett.*, 1993, **34**, 8037.
18 E.R. Perez, A.L. Marrero, R. Perez and M.A. Autie, *Tetrahedron Lett.*,1995, **36**, 1779.
19 C. Narayana, S. Padmanabhan and G.W. Kabalka, *Tetrahedron Lett.*, 1990, **31**, 6977.
20 I. Mohammadpoor-Baltork, *J. Chem. Res.*, 1999, 272.
21 T.S. Jin, Y.R. Ma, Z.H. Zhang and T.S. Li, *Org. Prep. Procep. Int.*,1998, **30**, 463.
22 M.A. Reddy, L.R. Reddy, N. Bhanumathi and R.K. Rao, *Synth. Commun*., 2002, **32**, 273.
23 J. Buckingham and S.M. Donaghly, *Dictionary of Organic Compounds*, 5th edn. Chapman and Hall, New York, 1982.
24 J. Buckingham and F. Macdonald, *Dictionary of Organic Compounds*, 6th edn. Chapman and Hall, New York, 1996.