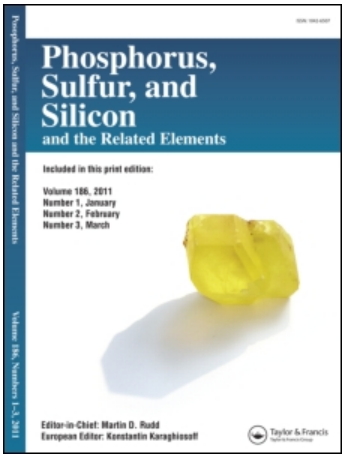

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AN EFFICIENT CONVERSION OF ALDEHYDES TO THEIR CORRESPONDING ACYLALS WITH P_2O_5/SiO_2 UNDER MILD CONDITION

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A combination of P_2O_5 and SiO_2 was used for an efficient conversion of aldehydes to their corresponding acylals with excellent yields at room temperature under mild conditions.

Keywords: Acylals; 1,1-diacetate; diphosphorous pentoxide

Acylals are important protective group for carbonyl compounds because they are stable to neutral and basic condition.[1–5] 1,1-Diacetates are synthetically useful precursors for the synthesis of dienes for Diels- Alder cycloaddition reactions.[6] In 1905, Knovenagel and Claussner reported that aldehydes could be transformed in to acylals with acetic anhydride in the presence of a catalytic amount of sulfuric acid, then several modification of this transformation were reported. A number of these methods include the use of protic acids, e.g., methane sulfonic acid, phosphoric acid, triflicacid.[7] NH_2SO_3H,[8] Lewis acids such as WCl_6,[9] $ZnCl_2$,[10] $FeCl_3/SiO_2$,[11] PCl_3,[12] I_2,[13] $Sc(OTf)_3$,[14] $Cu(OTf)_2$,[15] $Bi(OTf)_3 \cdot x H_2O$,[16] $LiBF_4$,[17] and neutral condition such as NBS.[18] Recently, solid acidic materials like Nafion-H,[19] zeolites,[20] graphite,[21] clay,[22] EPZG,[23] zirconium sulfophenyl phosphonate,[24] and zinc-montmorillonite[25] in the heterogeneous media have received attention as catalysts for

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Dedicated to our teacher, professor Abdolhossein Rustaiyan, on the occasion of his seventy-fifth birthday.

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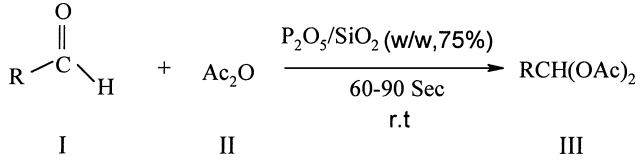
the preparation of acylals due to enhanced reaction rates and easier work-up.

Although some of these methods present a convenient procedure with good to excellent yields, two exceptions are noteworthy for example,[13,18] most of the currently available methods suffer from strong acidic condition or require high temperature. Therefore, any effort for finding a novel, mild, and facile protocol for the efficient conversion of aldehydes in to acylals is of general interest.

A literature survey shows that phosphorus pentoxide (phosphoric anhydride) as a dehydrating agent was used for formation of anhydride from two molecules of an ordinary acid, ketenimine from amide, vinyl ether from acetal, nitrile from amide,[26] amide from oxime,[27] phenolic ester from carboxylic acid,[28] and so on. On the basis of the above mentioned ability of P_2O_5, we decided to use it for the preparation of gem diactates from aldehydes. Therefore, we have used the silica supported form of P_2O_5 due to advantages which was reported by Eshghi and et al.[28]

RESULTS AND DISCUSSION

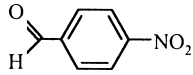
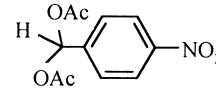
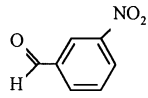
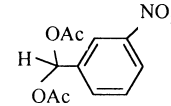
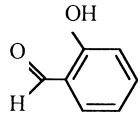
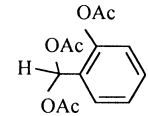
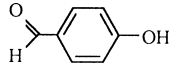
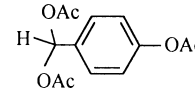
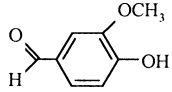
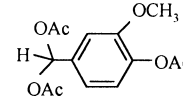
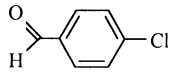
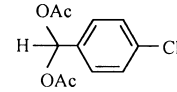
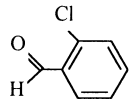
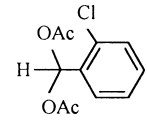
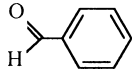
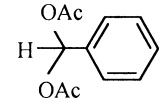
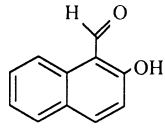
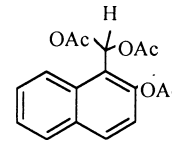
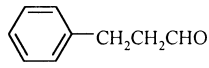
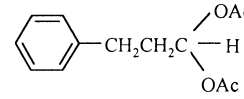
We report herein that acylals can be prepared very fast and in excellent yields by the direct condensation of aldehydes with acetic anhydride under heterogeneous and mild condition by employing of P_2O_5/SiO_2 (w/w 75%) at room temperature (Scheme 1).



SCHEME 1

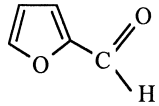
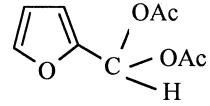
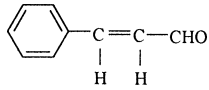
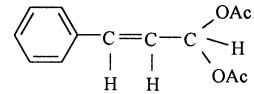
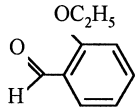
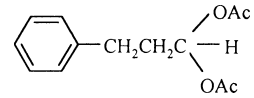
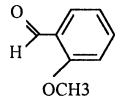
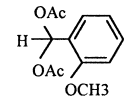
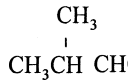
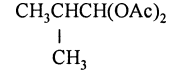
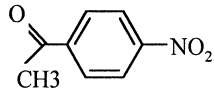
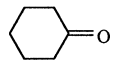
Different kinds of aldehydes were subjected to formation of acylals in the presence of P_2O_5/SiO_2 (w/w 75%). Reaction is exothermic and work-up procedures are very easy and convenient. This procedure is very fast and is comparable with acylal formation under microwave irradiation.[11] As shown in the Table I various types of aromatic aldehydes bearing either electron-withdrawing or electron releasing group including cinnamaldehyde and furfural can be converted to their corresponding 1,1-diacetates in the presence of Ac_2O and P_2O_5 in good to excellent yields (Table I, entries 1–15). Mild reaction condition and

TABLE I Conversion of Aldehydes (1 mmol) into 1,1-Diacetates in the Presence of P_2O_5/SiO_2 (W/W 75%, 0.15 g) at Room Temperature Under Mild Conditions

Entry	Substrate (I)	Ac_2O[a] (II)	Product (III)	Yield[b]
1		0.2		92
2		0.2		87
3		0.12		80
4		0.2		85
5		0.2		84
6		0.2		92
7		0.12		85
8		0.12		81
9		0.2		70
10		0.12		82

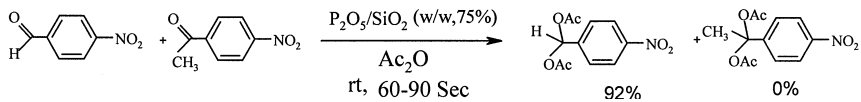
(Continued on next page)

TABLE I Conversion of Aldehydes (1 mmol) into 1,1-Diacetates in the Presence of P_2O_5/SIO_2 (W/W 75%, 0.15 g) at Room Temperature Under Mild Conditions (Continued)

Entry	Substrate (I)	Ac_2O^a (II)	Product (III)	Yield[b]
11		0.12		58
12		0.12		85
13		0.12		79
14		0.12		83
15		0.12		81
16		0.12	—	0
17		0.12	—	0

[a] ml of Ac_2O per mmol of substrate.
[b] Yields refer to isolated products.

minimal environmental impact are major advantages of the described method. Phenolic groups were also protected as acetates in hydroxyl containing aromatic aldehydes (Table I, entries 3, 4, 5, and 9) under these conditions. Ketones such as *p*-nitroacetophenone or cyclohexanone did not produce any acylal under the same condition (Table I, entries 16 and 17), This suggested that chemoselective protection of aldehydes in the prescence of ketones could be achieved with this process (Scheme 2)



SCHEME 2

In conclusion, the low cost and the availability of the reagents, easy and clean work-up, and good yields make this method attractive for organic chemists.

EXPERIMENTAL

General

Chemicals such as carbonyl compounds, diphosphorus pentoxide, acetic anhydride, and silica gel were purchased from Fluka and Merck chemical companies. The diacetylation products were characterized by comparison of their spectral (IR, ^{1}H-NMR), TLC and physical data with that of authentic samples.

Preparation of Acylal(III-1) from 4-Nitro Benzaldehyde-(I-1). A Typical Procedure

To a stirred mixture of 4-nitrobenzaldehyde (0.15 g, 1 mmol) and acetic anhydride (0.2 mL, 2 mmol), P_2O_5/SiO_2 [(w/w 75%), 0.15 g] was added. Reaction is exothermic and completed after 90 s. The reaction vessel was cooled and the heterogeneous mixture washed with dichloromethane and then decanted. After removal of solvent, by addition of ethanol and water, the acylal as pure crystal was obtained. Yield: 0.24 g (92%), m.p: 124–125 [Lit,[8] m.p: 125–126°C].

REFERENCES

[1] M. A. Zolfigol, M. H. Zebarjadian, I. Mohammadpoor-Baltork, and M. Shamsipur, *Synth. Commun.*, **32**, 2803 (2002).
[2] T. S. Jin, G. Sun, Y. W. Li, and T. S. Li, *J. Chem. Res. (Synop)*, 30 (2003).
[3] I. Mohammadpoor-Baltork and H. Aliyan, *Synth. Commun*., **29**, 2741 (1999).
[4] I. Mohammadpoor-Baltork and H. Aliyan, *J. Chem. Res. (Synop)*, 272 (1999).
[5] H. W. Pinnick, K. S. Kochhar, B. S. Bal, R. P. Deshpandy, and S. N. Rajadhyaksha, *J. Org. Chem.*, **48**, 1765 (1983).
[6] a) B. B. Sinder and S. G. Amin, *Synth. Commun.*, **8**, 117 (1978); b) G. Saucy, R. Marbet, H. Lindlar and O. Isler, *Helv. Chim. Acta.*, **42**, 1945 (1959).
[7] I. Freeman and E. M. Karchefski, *J. Chem. Eng. Data.*, **22**, 355 (1977).
[8] T. S. Jin, G. Sun, Y. W. Li, and T. S. Li, *Green Chemistry*, **4**, 255 (2002).
[9] B. Karimi, G. R. Ebrahimian, and H. Seradj, *Synth. Commun*. **32**, 669 (2002).
[10] I. Scribine, *Bull. Soc. Chem. Fr.*, 1194 (1961).
[11] a) K. S. Kochhar, B. S. Bal, R. P. Deshpande, S. N. Rajadhyaksha, and H. W. Pinnick, *J. Org. Chem.*, **48**, 1765 (1983); b) C. Wang and M. Li, *Synth. Commun.*, **32**, 3469 (2002).
[12] J. K. Michie and J. A. Miller, *Synthesis*, 824 (1981).
[13] N. Deka, D. J. Kalita, R. Borah, and J. C. Sarma, *J. Org. Chem.*, **62**, 1563 (1997).

[14] V. K. Aggarwal, S. Fonquerna, and G. P. Vennall, *Synlett*, 849 (1998).
[15] K. L. Chandra, P. Saravanan, and V. K. Singh, *Synlett*, **3**, 359 (2000).
[16] M. D. Carrigan, K. J. Eash, M. C. Oswald, and R. S. Mohan, *Tetrahedron Lett.*, **42**, 8133 (2001).
[17] J. S. Yadav, B. V. S. Reddy, C. Venugopal, and T. Ramalingam, *Synlett*, **4**, 604 (2002).
[18] B. Karimi, H. Seradj, and G. R. Ebrahimian, *Synlett*, **5**, 623 (2000).
[19] G. A. Olah and A. K. Mehrotra, *Synthesis*, 962 (1982).
[20] B. Gigante, C. Pereira, M. J. Marcelo-Curto, H. Carreyre, G. Perot, and M. Guisnet, *Synthesis*, **1077** (1995).
[21] T. S. Jin, G. Y. Du, Z. H. Zhang, and T. S. Li, *Synth. Commun.*, **27**, 2261 (1997).
[22] Z. H. Zhang, T. S. Li, and C. G. Fu, *J. Chem. Res. (Synop)*, **174** (1997).
[23] B. P. Bandgar, N. P. Mahajan, D. P. Mulay, J. L. Thote, and P. P. Wadgaonkar, *J. Chem. Res. (Synop)*, 470 (1995).
[24] M. Curini, F. Epifano, M. C. Marcotullio, O. Rosati, and M. Nocchetti, *Tetrahedron Lett.*, **43**, 2709 (2002).
[25] N. M. Nagy, M. A. Jakab, J. Konya, and S. Antus, *Applied Clay Science*, **21**, 213 (2002).
[26] J. March, *Advanced Organic Chemistry* (Wiely, New York, 1985), 3rd ed., p. 904.
[27] C. L. Eaton, *J. Org. Chem.*, **38**, 4071 (1973).
[28] H. Eshghi, M. Rafei, and M. H. Karimi, *Synth. Commun.*, **31**, 771 (2001).