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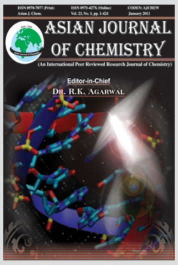

$SnCl_2 \cdot 2H_2O$ and $Ni(OAc)_2 \cdot 4H_2O$: Efficient Heterogeneous Inorganic Catalysts for the Chemoselective Synthesis of *Geminal* Diacetates (Acylal) Under Solvent-Free Conditions

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$SnCl_2 \cdot 2H_2O$ and $Ni(OAc)_2 \cdot 4H_2O$ were found to be efficient catalysts for preparation of 1,1-diacetates under solvent-free conditions at room temperature. Easy work-up and low cost are important features from the environmental and economical points of view, are distinct aspects of this research. Very good to exellent yields, short reaction times, non-toxicity and stability of the catalysts are noteworthy advantages of this method.

Key Words: 1,1-Diacetates, Chemoselective, Efficient, Inorganic catalysts, Solvent-free.

INTRODUCTION

Protection of aldehydes and heteroatoms such as alcohols and thiols are primary important functional group transformations in organic synthesis usually achieved by using acetic anhydride[1,2]. Several methods are available to protect aldehydes[3-15] by using various metal salts *e.g.* chlorides, triflates, perchlorates, *etc.* and supported catalysts. Acylation of hetero atoms under solvent and catalyst free conditions is conducted under reflux at 85 °C. However, the search of suitable catalysts for acylation can be used under milder conditions remains as a continued field of research. The limitations of certain acylation protocols are recognized as follows: expensive catalysts (*e.g.* triflates)[3,5,16,17], environmentally harmful organic solvents (*e.g.* CH_2Cl_2[4,16,18], CH_3CN[6], CH_3NO_2[3]), longer reaction time and incomplete reaction[19,20]. In addition the metal triflates may involve competitive side reaction (*e.g.* dehydration and rearrangement) with acid-sensitive substrates due to large negative Ho value of TfOH[21]. Since perchloric acid is weaker than triflic acid[21] the use of metal perchlorates should reduce the side reactions[22]. Usually, the preparation of 1,1-diacetates from aldehydes includes the use of protic acids such as sulfuric, phosphoric or methane sulfonic acids[23,24], solid acidic materials[25], Lewis acids such as iodine[12], trimethylchlorosiane and sodium iodide[13], zinc chloride[26], $FeCl_3$[27], $FeSO_4$[28], phosphorus trichloride[10], indium trichloride[8], $Sc(OTf)$[33], $Cu(OTf)$[24], $Bi(OTf)$[36], LiOTf[5] and $In(OTf)_3$[29]. The use of montmorillonite clay[30], expensive graphite[25], zeolites[31], N-bromosuccinimide[11], ceric ammonium nitrate[7], NH_2SO_3H[9], WCl_6[32], $AlPW_{12}O_{40}$[33], $H_6P_2W_{18}O_{62} \cdot 24H_2O$[34], zirconium sulfophenyl phosphonate[15], $ZrCl_4$[35], $LiBF_4$[36], LiBr[37], $Zn(BF_4)_2$[38], as catalysts have also been reported. Many of these methods have certain disadvantages such as low yields, expensive and hazardous reagents, long reaction times, corrosivity, tedious work-up and pollution problems. Furthermore, very few methods are known for the chemoselective protection of aldehydes in the presence of ketones. Consequently, the development of novel and mild catalytic methods for the preparation of 1,1-diacetates is still desirable. In continuation of our research on the transformation of functional groups in organic synthesis[39], we wish to report a simple, efficient and chemoselective method for the preparation of acylals with acetic anhydride using $SnCl_2 \cdot 2H_2O$ (**Scheme-I**) and $Ni(OAc)_2 \cdot 4H_2O$ (**Scheme-II**) as heterogeneous and stable catalysts at room temperature under solvent-free conditions.

$$\text{RCHO} \xrightarrow[\text{Ac}_2\text{O (2 mL), RT}]{\text{SnCl}_2\text{.2H}_2\text{O (0.1 mmol)}} \text{RCH(OAc)}_2$$

Scheme-I

$$\text{RCHO} \xrightarrow[\text{Ac}_2\text{O (2 mL), RT}]{\text{Ni(OAc)}_2\text{.4H}_2\text{O (0.15 mmol)}} \text{RCH(OAc)}_2$$

R = aryl

Scheme-II

EXPERIMENTAL

All reagents were purchased from Merck and Aldrich and used without further purification. All yields refer to isolated products after purification. Products were characterized by comparison with authentic samples and by spectroscopic data (IR, ^{1}H NMR spectra). The spectra were measured in $CDCl_3$ unless otherwise stated, relative to TMS (ppm).

General procedure

$SnCl_2·2H_2O$ catalyzed conversion of aldehydes to acylals: A mixture of aldehyde (1 mmol), Ac_2O (2 mL) and $SnCl_2·2H_2O$ (0.1 mmol) was stirred at ambient temperature and the progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was washed with a 10 % aqueous solution of NaOH, then washed with Et_2O and dried (Na_2SO_4) and solvent was removed under reduced pressure. The resultant product was filtered through a column of silica gel to afford pure acylals.

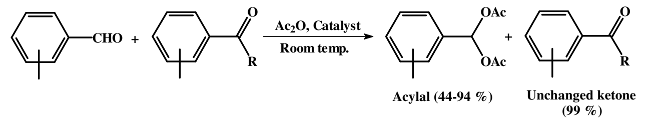
$Ni(OAc)_2·4H_2O$ catalyzed conversion of aldehydes to acylals: A mixture of aldehyde (1 mmol), Ac_2O (2 mL) and $Ni(OAc)_2·4H_2O$ (0.15 mmol) was stirred at ambient temperature and the progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was washed with a 10 % aqueous solution of NaOH, then washed with Et_2O and dried (Na_2SO_4) and solvent was removed under reduced pressure. The resultant product was filtered through a column of silica gel to afford pure acylals.

RESULTS AND DISCUSSION

The results of the conversions of various aldehydes to their corresponding 1,1-diacetates (acylals) are presented in Tables 1 and 2.

The reaction of the aldehydes with acetic anhydride and a catalytic amount of $SnCl_2·2H_2O$ (**Scheme-I**) or $Ni(OAc)_2·4H_2O$ (**Scheme-II**) under solvent-free conditions at room temperature gave the corresponding acylals in good to excellent yields. According to the results, it was observed that $SnCl_2·2H_2O$ is better catalysts than $Ni(OAc)_2·4H_2O$.

This procedure is also useful for the selective conversion of aldehydes to 1,1-diacetates in presence of ketones. Thus when equimolar mixture of aldehyde and ketone were allowed to react with acetic anhydride and a catalytic amount of catalysts, the aldehyde underwent conversion to the acylals, whereas the ketone was recovered unchanged (**Scheme-III**).

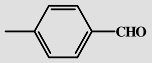
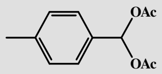
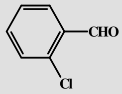
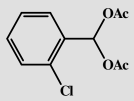
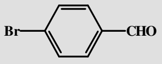
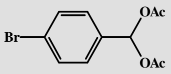
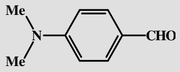
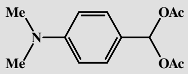
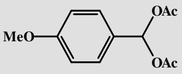
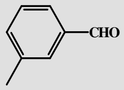
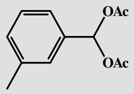
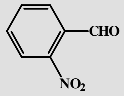
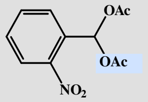
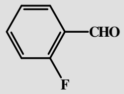
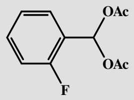
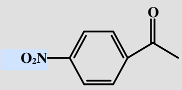
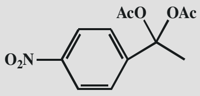
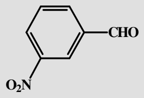
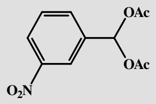
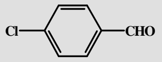
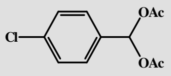
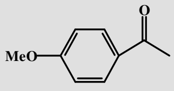
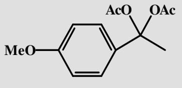
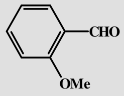
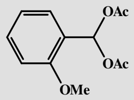
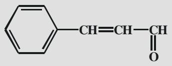
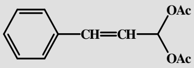
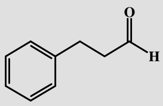
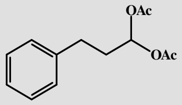


Scheme-III

Spectroscopic data of the products: ^{1}H NMR, IR spectral data and m.p. for some products are as follow, (the number refers to the No. of the products in the Tables 1 and 2):

Compound 1: ^{1}H NMR (90 MHz, $CDCl_3$/TMS): δ 7.32 (s, 1H), 6.98-7.08 (dd, 4H), 2.05 (s, 3H), 1.79 (s, 6H). IR (KBr, ν_{max}, cm^{-1}): 3033, 2926, 1770, 1367, 1244, 1207, 1068, 1006, 959, 815, m.p. 80-82 °C, reported m.p. 81-82 °C (Ref. 9).

TABLE-1
PREPARATION OF ACYLALS IN THE PRESENCE OF $SnCl_2·2H_2O$ (0.1 mmol) AND ACETIC ANHYDRIDE (2 mL) UNDER SOLVENT-FREE CONDITIONS AT ROOM TEMPERATURE

No.	Substrate	Time (min)	Yield (%)^{a,b}	Product
1		20	76	
2		20	100	
3		10	78	
4		2880	–	
5		60	55	
6		25	90	
7		60	67	
8		15	94	
9		2880	–	
10		2880	–	
11		15	87	
12		1440	–	
13		180	90	
14		240	82	
15		5	73	

^{a}Products were characterized by their physical constants, comparison with authentic samples and by their IR and NMR spectra.
^{b}Isolated yields.

TABLE-2
PREPARATION OF ACYLALS IN THE PRESENCE OF $Ni(OAc)_2 \cdot 4H_2O$ (0.15 mmol) AND ACETIC ANHYDRIDE (2 mL) UNDER SOLVENT-FREE CONDITIONS AT ROOM TEMPERATURE

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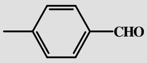
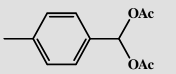
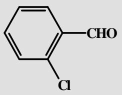
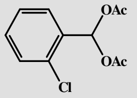
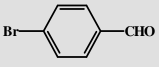
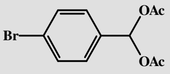
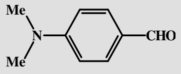
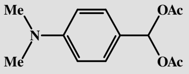
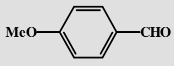
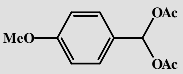
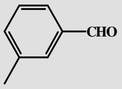
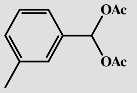
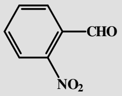
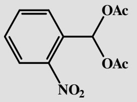
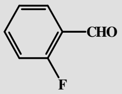
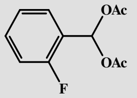
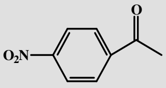
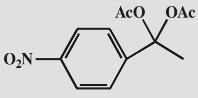
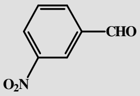
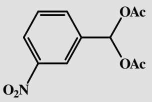
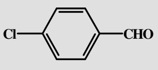
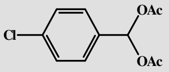
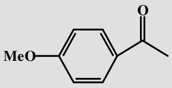
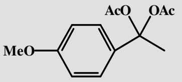
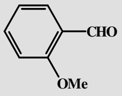
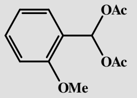
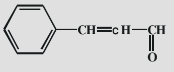
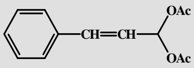
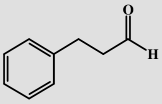
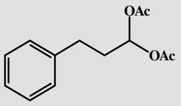
1		60	50	
2		480	76	
3		1200	86	
4		180	31	
5		1440	–	
6		300	32	
7		1440	–	
8		180	79	
9		2880	–	
10		360	-44	
11		300	63	
12		1440	–	
13		150	77	
14		240	54	
15		10	72	

[a]Products were characterized by their physical constants, comparison with authentic samples and by their IR and NMR spectra.
[b]Isolated yields.

Compound 2: ^{1}H NMR (90 MHz, $CDCl_3$/TMS): δ 7.54-7.85 (m, 5H), 2.11 (s, 6H). IR (KBr, ν_{max}, cm^{-1}): 3055, 3025, 1767, 1621, 1495, 1201, 1012, 804, 762, 604, m.p. 51-52 ºC, reported m.p. 52-53 ºC (Ref. 40).

Compound 3: ^{1}H NMR (90 MHz, acetone-d_6/TMS): δ 7.61 (m, 5H), 2.10 (s, 6H). IR (KBr, ν_{max}, cm^{-1}): 3094, 1758, 1592, 1488, 1373, 1234, 1206, 942, 828, m.p. 94-96 ºC, reported m.p. 93-95 ºC (Ref. 41).

Compound 8: ^{1}H NMR (90 MHz, acetone-d_6/TMS): δ 7.91 (s, 1H) 7.19-7.54 (m, 4H), 2.11 (s, 6H). IR (KBr, ν_{max}, cm^{-1}): 2987, 2781, 1769, 1620, 1594, 1495, 1371, 1245, 1200, 1011, 805, 765.

Compound 11: ^{1}H NMR (90 MHz, $CDCl_3$/TMS): δ 7.33-7.55 (m, 5H), 2.03 (s, 6H). IR (KBr, ν_{max}, cm^{-1}): 3055, 2934, 1761, 1600, 1492, 1373, 1207, 1013, 943, 832, m.p. 81-83 ºC, reported m.p. 82-83 ºC (Ref. 9).

Compound 13: ^{1}H NMR (90 MHz, $CDCl_3$/TMS): δ 7.86 (s, 1H), 7.41 (d, 1H), 7.26 (t 1H), 6.91 (t 1H), 6.82 (d 1H), 3.74 (s, 3H), 2.05 (s, 6H). IR (KBr, ν_{max}, cm^{-1}): 3010, 2967, 1761, 1602, 1495, 1372, 1238, 1200, 1021, 950, 758, m.p. 66-73 ºC, reported m.p. 73-74 ºC (Ref. 42).

Compound 14: ^{1}H NMR (90 MHz, $CDCl_3$/TMS): δ 7.20-7.80 (m, 6H), 6.92 (d 1H), 6.33 (dd, 1H), 2.18 (s, 6H). IR (KBr, ν_{max}, cm^{-1}): 3083, 2972, 1750, 1678, 1380, 1248, 1198, 1058, 940, 747, 692, m.p. 84-85 ºC, reported m.p. 84-86 ºC (Ref. 36).

Compound 15: ^{1}H NMR (90 MHz, acetone-d_6/TMS): δ 7.23 (m, 5H), 6.78 (t 1H), 2.73 (m 2H), 2.01 (q, 8H). IR (KBr, ν_{max}, cm^{-1}): 3029, 2932, 2865, 1763, 1549, 1455, 1497, 1375, 1245, 1208, 1111, 1011, 946, 879, 756, 701.

Conclusion

The striking features of present method are short reaction times, easy work-up procedure, high yields, stability and non-toxicity of catalysts, selective conversion of aldehydes to the acylals in the presence of ketones.

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