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$Zn(BH_4)_2/Ac_2O$/DOWEX(R)50WX4: A Novel System for Acylalation of Aldehydes

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Abstract: The acylalation of structurally different aldehydes has been performed by $Zn(BH_4)_2/Ac_2O$/DOWEX(R)50WX4 as new system within 1-5 min at room temperature with excellent yields of the products (92-97%).

Key Words: $Zn(BH_4)_2$, Ac_2O, DOWEX(R)50WX4, acylal, *gem*-diacetate, aldehyde.

Resumen: La acilalación de aldehídos estructuralmente diferentes ha sido realizada empleando $Zn(BH_4)_2/Ac_2O$/DOWEX(R)50WX4 como un sistema novedoso, en 1-5 min a temperatura ambiente, con excelentes rendimientos de los productos (92-97%).

Palabras clave: $Zn(BH_4)_2$, Ac_2O, DOWEX(R)50WX4, acilal, *gem*-diacetato, aldehído.

Introduction

Acylals have been used as starting materials for Diels-Alder [1], Grignard [2a], Barbier [2b], Prins [3], Knoevenagel [4a] and benzoin condensation reactions [4b]. Also, acylals were used in the synthesis of chrysanthemic acid [5a], sphingofungins E and F [5b] and utilized as cross linking reagents [6] in cellulose and cotton industry. However, the protection of carbonyl functional group of aldehydes is the main goal for the synthesis of acylals, because *gem*-diacetates are stable under critically controlled acidic, neutral and basic conditions [7].

Several reagents or catalysts such as amberlyst-15 [8], envirocat EPZ10 [9], montmorillonite [10], zeolites [11], nafion-H [12], $FeSO_4$ [13], $FeCl_3$ [14], $AlCl_3$ [15], TMSCl-NaI [16], $Sc(OTf)_3$ [17], I_2 [18], NBS [19], PCl_3 [20], H_2SO_4 [21], $Cu(OTf)_2$ [22], $LiBF_4$ [23], H_2NSO_3H [24], $InCl_3$ [25], $(NH_4)_2Ce(NO_3)_6$ [26], LiOTf [27], $Zn(BF_4)_2$ [28], $AlPW_{12}O_{40}$ [29], $ZrCl_4$ [30], $Bi(NO_3)_3 \cdot 5H_2O$ [31], $Bi(CF_3SO_3) \cdot 4H_2O$ [32], zirconium sulfohenyl phosphonat [33], $GaCl_3$ [34], GaI_3 [35], sulphated zirconia [36], poly(*N,N'*-dibromo-*N*-ethyl-benzene-1,3-disulfonamide) [PBBS] and *N,N,N',N'*-tetrabromobenzene-1,3-disulfon-amide [TBBDA] [37], saccharin sulfonic acid [38], zirconium hydrogen sulfate [39], $Fe_2(SO_4)_3 \cdot xH_2O$ [40], erbium triflate [41], alum[$KAl(SO_4)_2 \cdot 12H_2O$] [42], sulfated zirconia [43], $KHCO_3$ [44], H_2SO_4-silica [45], indium tribromide [46], $HClO_4$-SiO_2 [47], solid lithium perchlorate [48], zinc(II) perchlorate [49] and [Hmim] HSO_4 [50] have been used for synthesis of *gem*-diacetates.

These methods are convenient but have some disadvantages such as long reaction times, harsh reaction conditions, use of strong acids, strictly reaction conditions and moisture sensitivity. Also, several of these catalysts are toxic, unavailable and costly. Thus, the research is still so much interest and we have investigated the acylalation of aldehydes in the presence of a reducing agent. So, in this context, we wish to introduce a fast and efficient method for the acylalation of a variety of aldehydes to their corresponding *gem*-diacetates using Ac_2O and DOWEX(R)50WX4 in the presence of $Zn(BH_4)_2$.

Results and discussion

Recently, we have reported that DOWEX(R)50WX4 ion-exchange resin has been used for regioselective synthesis of oximes by $NH_2OH \cdot HCl$/DOWEX(R)50WX4 system [51], reduction of a variety of carbonyl compounds such as aldehydes, ketones, α-diketones, acyloins and α,β-unsaturated carbonyl compounds to their corresponding alcohols by $NaBH_4$/DOWEX(R)50WX4 system [52], synthesis of cyanohydrins by NaCN/DOWEX(R)50WX4 [53] and reductive-amination of a variety of aldehydes and anilines by $NaBH_4$/DOWEX(R)50WX4 [54].

On the other hand, $Zn(BH_4)_2$ is the modified borohydride agent which has better solubility in aprotic solvents such as THF, Et_2O and DME. It is unique because of the better coordination ability of Zn^{2+} which is imparting selectivity in hydride-transferring reactions. We have developed the use of $Zn(BH_4)_2$ under new reducing system such as $Zn(BH_4)_2/H_2O$ [55], $Zn(BH_4)_2/C$ [56], $Zn(BH_4)_2/ZrCl_4$ [57], $Zn(BH_4)_2/Al_2O_3$ [58] and $Zn(BH_4)_2/2NaCl$ [59]. In continuing our efforts for the development of using $Zn(BH_4)_2$ and DOWEX(R)50WX4, herein, we now wish to introduce $Zn(BH_4)_2/Ac_2O$/DOWEX(R)50WX4 as new convenient system for efficient acylalation of aldehydes at room temperature.

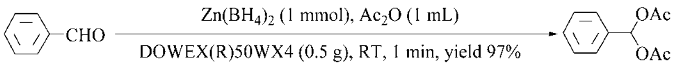
For the selection of appropriate conditions, acylalation of benzaldehyde has been selected as model reaction. This reaction was performed with different amounts of $Zn(BH_4)_2$, Ac_2O and DOWEX(R)50WX4 in different solvents (THF/Ac_2O, Et_2O/Ac_2O, CH_3CN/Ac_2O, EtOAc/Ac_2O, Ac_2O) at room temperature as shown in Table 1.

Experiments show that the reaction was proceeded to give the highest yield in Ac_2O. The optimization reaction conditions showed that the use of 1 molar equivalent of $Zn(BH_4)_2$ and 0.5 g of DOWEX(R)50WX4 in 1 mL Ac_2O are the best conditions to complete the acylalation of benzaldehye (1 mmol) to *gem*-benzyldiacetate (Table 1, entry 4). Our observation revealed that the acylalation was completed within 1 min with 97% yield of product as shown in Scheme 1.

Table 1. The optimization of acylalation of benzaldehyde (1 mmol) to 1,1-diacetoxy-1-phenylmethane with $Zn(BH_4)_2$ and DOWEX(R)50WX4 at RT.

Entry	$Zn(BH_4)_2$/mmol	DOWEX(R)50WX4/g	Solvent/1 mL	Time/min	Conversion/%[a]
1	0	0.5	$EtOAc/Ac_2O$ (0.5:0.5)	30	0
2	0	0.5	Ac_2O (1)	30	0
3	1	0.5	$EtOAc/Ac_2O$ (1:0)	30	0
4	1	0.5	Ac_2O (1)	1	100
5	1	0.5	$EtOAc/Ac_2O$ (0.5:0.5)	30	100
6	0.5	0.5	Ac_2O (1)	30	100
7	1	0.25	Ac_2O (1)	30	100
8	1	0.5	THF/Ac_2O (0.5:0.5)	30	100
9	1	0.5	Et_2O/Ac_2O (0.5:0.5)	30	100
10	1	0.5	CH_3CN/Ac_2O (0.5:0.5)	30	100

[a] Conversions refer to 1,1-diacetoxy-1-phenylmethane and were monitored by TLC (eluent *n*-hexane/EtOAc 9/1).



Scheme 1. The acylalation of benzaldehyde to *gem*-benzyldiacetate based on optimized reaction conditions.

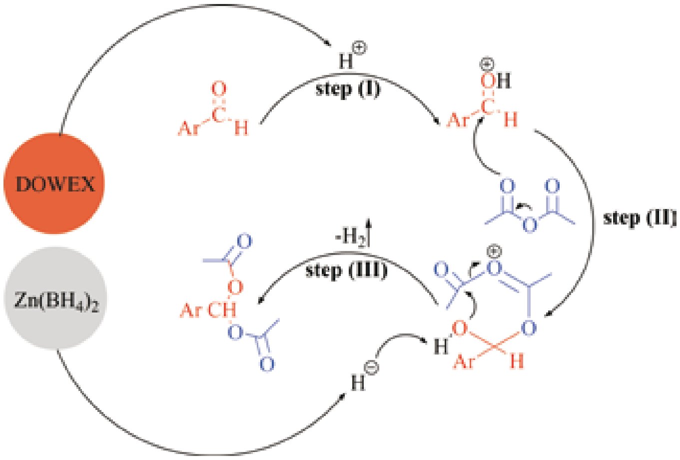
The efficiency of this protocol was examined by using structurally different aldehydes as shown in Table 2. In this Table, the entries 1-12 are simple aromatic aldehydes and entry 14 is a simple aliphatic aldehyde. Also, the entries 2-8 are aromatic aldehydes with electron-withdrawing groups while the entries 9-11 have electron-donating groups. The entry 13, corresponds to a α,β-unsaturated aldehyde. In this approach, the corresponding acylals were obtained in excellent yields (92-97%) and the reactions have been completed within 1-5 min as shown in Table 2. The products were characterized by the ^{1}H-chemical shift of the CHs (Table 2, column 6) which appear around 6.8-8.0 ppm as a singlete (1H). Also the C=O stretching frequency in FT-IR spectrum of the products appears around 1748-1764 cm^{-1} (Table 2, column 7). For more characterization and verification of the products as shown in Table 2 (column 8), the melting points of the products have been measured and were compared with the literature.[46-50]

The ion-exchange resin DOWEX(R)50WX4 is insoluble in Ac_2O. Therefore, the reactions take place under heterogeneous conditions. The influences of DOWEX(R)50WX4 and $Zn(BH_4)_2$ have been shown in Scheme 2. It seems that SO_3H groups on DOWEX(R)50WX4 (as cation-exchange resin, strong acid) protonate the carbonyl group of aldehyde (Scheme 2, step I). Consequently, it is more susceptible for Ac_2O attack (Scheme 2, step II). Also, the hydride attack from the $Zn(BH_4)_2$ promotes the formation of hydrogen gas which is slowly liberated *in situ* (Scheme 2, step III).

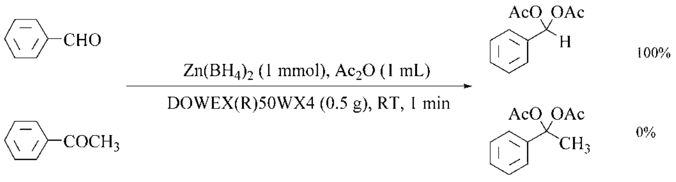
Also, the acylalation of cinnamaldehyde with 1 molar equivalent of $Zn(BH_4)_2$ and Ac_2O (1 mL) in the presence of 0.5 g of DOWEX(R)50WX4 was carried out and the corresponding cinnamyl acylal was obtained within 1 min with 95% yield at room temperature (Table 2, entry 13).

Our attempt for the preparation of *gem*-diacetates from ketones was not successful using this system. Therefore, this system can act as chemoselective system for the acylalation of aldehydes over ketones. Thus, we have performed the acylalation of 1 molar equivalent of benzaldehyde in the presence of 1 molar equivalent of acetophenone under optimized reaction conditions (Table 3, entry 4) as shown in Scheme 3.

The chemoselectivity ratio for the acylalation of benzaldehyde with respect to acetophenone was 100%. The usefulness of chemoselectivity was further examined by the acylalation

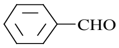
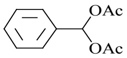
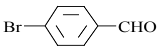
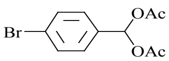
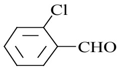
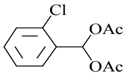
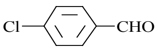
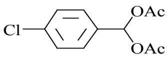
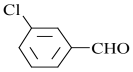
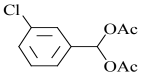
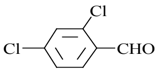
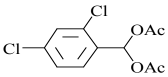
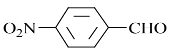
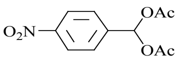
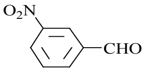
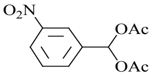
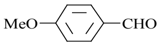
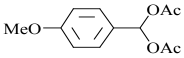
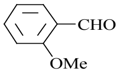
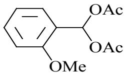
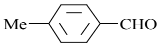
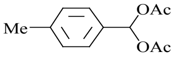
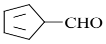
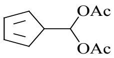
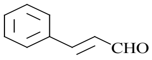
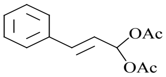
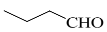
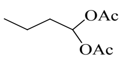


Scheme 2. The mechanism for the acylalation of aldehydes with $Zn(BH_4)_2/Ac_2O$/DOWEX(R)50WX4 system.



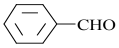
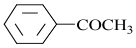
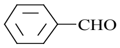
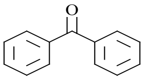
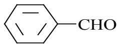
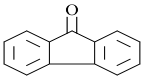
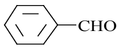
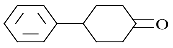
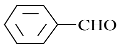
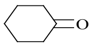
Scheme 3. Comparison of the acylalation of benzaldehyde and acetophenone based on optimized reaction conditions.

Table 2. The acylalation of aldehydes (1 mmol) with Ac_2O (1 mL) and $Zn(BH_4)_2$ (1 mmol) in the presence of DOWEX(R)50WX4 (0.5 g) at RT.

Entry	Aldehydes	Products	Time/min	Yields/% [a]	δ CH/ppm [b]	$\bar{\upsilon}$ C=O/cm^{-1} [b]	m.p./ °C [b]
1			1	97	7.69	1761	44-45
2			1	94	7.62	1764	94-95
3			1	93	7.54	1760	52-53
4			1	96	7.62	1760	83-84
5			1	96	7.78	1761	64-65
6			1	97	7.67	1763	99-101
7			1	92	7.73	1759	124-125
8			1	95	7.74	1760	66-67
9			5	95	7.61	1748	65-66
10			5	92	8.03	1761	69-70
11			2	93	7.66	1759	80-81
12			1	95	7.70	1763	52-53
13			1	95	7.38	1762	83-85
14			1	93	6.81	1755	oil

[a] Yields refer to isolated pure products.[b] The obtained data were compared with the literature.[46-50]

Table 3. Competitive acylalation of aldehydes (1 mmol) and ketones (1 mmol) with $Zn(BH_4)_2$ (1 mmol)/Ac_2O (1 mL)/DOWEX(R)50WX4 (0.5 g) system at RT.

Entry	Substrate 1	Substrate 2	Molar Ratio[a]	Time/min	Conversion 1/Converstion 2/%[b]
1			1:1	1	100:0
2			1:1	1	100:0
3			1:1	1	100:0
4			1:1	1	100:0
5			1:1	1	100:0

[a] Molar Ratio as: Substrate 1/Substrate 2. [b] Conversions refer to TLC monitoring (eluent; *n*-hexane/EtOAc: 9/1).

of benzaldehyde in the presence of other ketones as shown in Table 3.

The reusability of the catalyst has been checked by using recovered DOWEX(R)50WX4 for the acylalation of benzaldehyde under optimized reaction conditions (Table 1, entry 4). We have observed that the recovered DOWEX(R)50WX4 is not convenient for a second run without regeneration. However, after regeneration of DOWEX(R)50WX4 (stirred with HCl 5-10% for 30-60 min and then washed with distillated water), the acylalation reaction has been carried out as well as the first run as shown in Table 4.

Experimental

General. All substrates and reagents were purchased from commercially sources with the best quality and used without further purification. IR spectra were recorded on Perkin-Elmer FT-IR RXI and ^1H NMR spectra were determined in a 300 MHz Bruker spectrometer. The products were characterized by their ^1H NMR, ^{13}C NMR or IR spectra and by comparison with authentic samples (melting points). All yields referred to isolated pure products. ^1H NMR was applied for the purity determination of products and TLC for reaction monitoring over silica gel 60 F_{254} aluminum sheets.

The acylalation of benzaldehyde with $Zn(BH_4)_2$/DOWEX(R)50WX4/Ac_2O system. A typical procedure

In a round-bottom flask (5 mL) equipped with a magnetic stirrer, a mixture of benzaldehyde (0.106 g, 1 mmol), Ac_2O (1 mL) and DOWEX(R)50WX4 (0.5 g) was treated with $Zn(BH_4)_2$ (0.095 g, 1 mmol). The resulting reaction mixture was stirred at room temperature. After completion of the reaction within 1 min, the catalyst was filtered and washed with ethyl acetate (15 mL). The combined organic layers were washed with saturated $NaHCO_3$ solution (3 × 10 mL), water (10 mL) and then dried over anhydrous Na_2SO_4. The solvent was removed on a rotary evaporator under reduced pressure to give 1,1-diacetoxy-1-phenylmethane (0.201 g, 97% yield). The product was characterized by ^1H-NMR, ^{13}C-NMR and FT-IR spectroscopy.

Spectral data for selected compounds

1,1-Diacetoxy-1-phenylmethane (Table 1, entry 1): ^1H NMR ($CDCl_3$): δ 2.14 (s, 6H), 7.41-7.43 (Ar, 3H), 7.52-7.55 (Ar, 2H), 7.69 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 20.85, 89.67, 126.65, 128.58, 129.74, 135.40, 169.79; IR (KBr) v = 3021, 1761, 1373, 1243, 1216, 1009, 767 cm^{-1}.

1,1-Diacetoxy-1-(4-bromoyphenyl)methane (Table 1, entry 2): ^1H NMR ($CDCl_3$): δ 2.11 (s, 6H), 7.37-7.40 (Ar, 2H), 7.51-7.54 (Ar, 2H), 7.62 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 20.78, 89.05, 123.90, 128.40, 131.76, 134.46, 168.64; IR (KBr) v = 3025, 1764, 1373, 1236, 1208, 1070, 1012, 758 cm^{-1}.

1,1-Diacetoxy-1-(4-nitrophenyl)methane (Table 1, entry 7): ^1H NMR ($CDCl_3$): δ 2.11 (s, 6H), 7.70 (Ar, 2H), 7.73 (s, 1H), 8.27 (Ar, 2H; ^{13}C NMR ($CDCl_3$): δ 20.74, 88.30, 123.84, 127.86, 141.87, 148.61, 158.55; IR (KBr) v = 3033, 1759, 1367, 1239, 1208, 1067, 1007, 812 cm^{-1}.

1,1-Diacetoxy-1-(4-methoxyphenyl)methane (Table 1, entry 9): ^1H NMR ($CDCl_3$): δ 2.06 (s, 6H), 3.75 (s, 3H), 6.70 (Ar, 2H), 7.43 (Ar, 2H), 7.61 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 20.47, 55.08, 89.63, 113.79, 128.01, 131.86, 160.49, 168.72; IR (KBr) v = 3018, 1748, 1600, 1367, 1259, 1160, 1027, 833 cm^{-1}.

1,1-Diacetoxy-1-(2-metoxyphenyl)methane (Table 1, entry 10): ^1H NMR ($CDCl_3$): δ 2.10 (s, 6H), 3.82 (s, 3H), 6.90 (Ar, 1H), 6.98 (Ar, 1H), 7.34 (Ar, 1H), 7.49 (Ar, 1H), 8.03 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 20.69, 55.52, 85.54, 110.88, 120.37, 123.72, 126.78, 130.84, 156.89, 168.44; IR (KBr) v = 3016, 1761, 1602, 1372, 1220, 1005, 764 cm^{-1}.

1,1-Diacetoxy-1-(4-methylphenyl)methane (Table 1, entry 11): ^1H NMR ($CDCl_3$): δ 2.12 (s, 6H), 2.38 (s, 3H), 7.23 (Ar, 2H), 7.43 (Ar, 2H), 7.66 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 20.86, 21.28, 89.77, 126.60, 129.25, 132.59, 139.78, 168.80; IR (KBr) v = 3033, 1759, 1367, 1239, 1067, 1039, 812 cm^{-1}.

1,1-Diacetoxy-1-(cinnamyl)methane (Table 1, entry 13): ^1H NMR ($CDCl_3$): 2.13 (s, 6H), 6.22 (dd, J = 15 Hz, 6 Hz, 1H), 6.82 (d, J = 15 Hz, 1H), 7.27-7.44 (m, 5H), 7.37 (d, J =6 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 20.90, 89.71, 121.65, 127.00, 128.66, 128.83, 135.09, 135.60, 168.70; IR (KBr) v = 3024, 1762, 1373, 1243, 1216, 1001, 756, cm^{-1}.

Conclusions

In this research, we have shown that $Zn(BH_4)_2$/DOWEX(R)50WX4/Ac_2O system is convenient method for the acylalation of a variety of aldehydes to their corresponding *gem*-diacetates in excellent yields. The acylalation reactions were carried out with 1 molar equivalents of $Zn(BH_4)_2$ and Ac_2O (1 mL) in the presence of 0.5 g DOWEX(R)50WX4 at room temperature. High efficiency, shorter reaction times

Table 4. Reusability of DOWEX(R)50WX4 in the preparation of 1,1-diacetoxy-1-phenylmethane from benzaldehyde under optimized conditions (Table 1, Entry 4).

Yields^c/%	Conversion^b/100%	Time/min^a	Run Number	Entry
97	100	1	1	1
30	100<	30	2	2
95	100	1	—	3^d

^{a} It is the highest time when the reaction ends or not further progress.

^{b} Conversion refer to TLC monitoring (eluent; *n*-hexane/EtOAc: 9/1); ^{c} Yields refer to isolated pure products . ^{d} Regeneration by HCl (5-10%).

and easy work-up make to this new protocol attractive for the acylalation of aldehydes. Therefore, this new system could be a useful addition to the present methodologies.

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