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Zinc(II) perchlorate as a new and highly efficient catalyst for formation of aldehyde 1,1-diacetate at room temperature and under solvent-free conditions

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Abstract

Zinc(II) perchlorate efficiently catalysed the conversion of aromatic, heteroaromatic, and aliphatic aldehydes to 1,1-diacetates under solvent-free conditions at room temperature. It was compatible with other functional groups (e.g., ether, ester, nitro, and cyano) likely to interfere by complex formation with the catalyst. Other anhydrides such as isobutyric, pivalic, and benzoic anhydrides afforded the corresponding 1,1-dicarboxylates and established the generality. The reaction rate was influenced by the steric and electronic nature of the anhydride. The rate of 1,1-dicarboxylate formation was found to follow the order $Ac_2O > (i\text{-}PrCO)_2O > (t\text{-}BuCO)_2O > (PhCO)_2O$ and no 1,1-dicarboxylate formation took place with $(ClCH_2CO)_2O$, and $(F_3CO)_2O$. During inter- and intra-molecular competition between a ketone and an aldehyde group with Ac_2O, 1,1-diacetate formation took place exclusively with the aldehyde group. An 88:12 selectivity was observed for 1,1-diacetate formation in favour of 1-naphthaldehyde during competition with 2-methoxy-1-naphthaldehyde.

Keywords: Zinc perchlorate hexahydrate; Catalyst; 1,1-Diacetate; Aldehyde; Anhydride; Selectivity; Solvent-free

1. Introduction

The stability of 1,1-diacetates (acylals) under neutral, acidic, and basic media adopted for routine work-up makes the 1,1-diacetate formation an important strategy for protection of aldehydes [1–3]. Further, 1,1-diacetates are ambident substrates [4] and are precursors of 1-acetoxydienes [5] and 2,2-dichlorovinyl acetate [6] for Diels-Alder reactions. Compounds bearing the 1,1-diacetate functionality find industrial applications as cross linking agents for cellulose in cotton [7] and activators in the composition of bleaching mixtures for wine-stained fabrics [8]. The synthesis of acylals involves the reaction of aldehydes with Ac_2O in the presence of protic [9] and Lewis [10] acid catalysts. The existing methodologies suffer from one or more of disadvantages such as prolonged reaction times, high temperatures, use of solvents, use of moisture sensitive and costly catalysts, special efforts required to prepare the catalyst, need to use excess Ac_2O, and requirement of special apparatus. Thus, there is necessity to develop a better catalyst for 1,1-diacetate formation.

While designing a suitable catalyst we reasoned that the role of a metal derived catalyst was to activate the anhydride, through coordination with the carbonyl oxygen atoms of the anhydride, to make it susceptible to nucleophilic attack by the carbonyl oxygen atom of the aldehyde to form the transition state **I** that subsequently undergoes rearrangement to form the 1,1-diacetate and liberates the catalyst (Scheme 1).

In search for a more effective catalyst we thought that a Lewis acid that can form a strong coordinate bond with the anhydride should induce better 'electrophilic activation' and enable 1,1-diacetate formation under mild conditions and at short times. Recently, we developed various 'electrophilic activation' catalysts derived from metal halides, perchlorates, tetrafluoroborates, and protic acid adsorbed on solid support [11]. Our experience in the development of various metal salts for heteroatom acylation reaction [11h,k,l,n–q] suggested that a metal salt derived from a stronger protic acid should be a better activator of electrophiles. Thus, the strong acidic property of $HClO_4$ encouraged us to develop $HClO_4$-SiO_2 [11p] and metal

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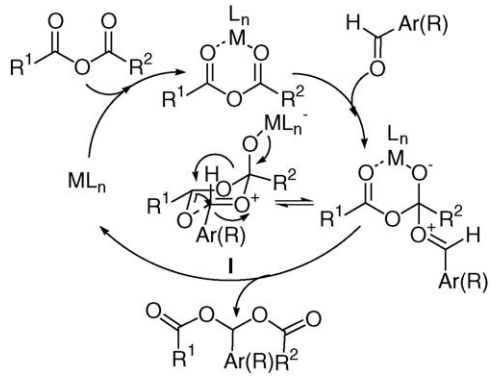


Scheme 1. Electrophilic activation during Lewis acid catalysed 1,1-diacetate formation.

perchlorates [11c,l,n] as highly efficient 'electrophilic activation' agents for heteroatom acylation and thia-Michael addition reactions. We disclose herein our findings on the catalytic efficiency of $Zn(ClO_4)_2{\cdot}6H_2O$ for 1,1-diacetate formation.

2. Results and discussion

To find the standard experimental procedure, we took 4-nitrobenzaldehyde (**1**) as model substrate and treated with Ac_2O in the presence of various metal perchlorates at room temperature under different conditions (Table 1). The reaction was best carried out using 1.5 equiv of Ac_2O under solvent-free conditions for 2 min at room temperature in presence of $Zn(ClO_4)_2{\cdot}6H_2O$ (1 mol%). Although the use of 1 equiv of Ac_2O afforded 80% yield, we preferred to use 1.5 equiv of Ac_2O as otherwise in some cases the reaction remained incomplete due to precipitation of the diacetate. No significant result was obtained in using $LiClO_4$, $Mg(ClO_4)_2$, $Mg(ClO_4)_2{\cdot}6H_2O$, and $Ba(ClO_4)_2$ under similar conditions (entries 2, 6, 9, and 10). Use of a 10 mol% of $Mg(ClO_4)_2{\cdot}6H_2O$ afforded comparable yields after 10 min (entry 5). However, $Mg(ClO_4)_2$ was less effective than $Mg(ClO_4)_2{\cdot}6H_2O$ (compare entries 2–5 with 6–8).

Table 1
Reaction of **1** with Ac_2O in the presence of various catalysts[a]

Entry	Catalyst	Amount (mol%)[b]	Time (min)	Yield (%)[c,d]
1	$Zn(ClO_4)_2$[e]	1	2	92[f]
2	$Mg(ClO_4)_2$[e]	1	5	10
3	$Mg(ClO_4)_2$[e]	1	15	60
4	$Mg(ClO_4)_2$[e]	5	10	90
5	$Mg(ClO_4)_2$[e]	10	5	92
6	$Mg(ClO_4)_2$	1	15	10
7	$Mg(ClO_4)_2$	5	15	50
8	$Mg(ClO_4)_2$	10	15	80
9	$Ba(ClO_4)_2$	1	15	Nil
10	$LiClO_4$	1	15	Nil

[a] **1** (2.5 mmol) was treated with Ac_2O (1.5 equiv) in the presence of the catalyst at room temperature.
[b] Amount of the catalyst used with respect to the aldehyde.
[c] Isolated yield of 1,1-diacetoxy-(4-nitrophenyl)methane.
[d] The unreacted aldehydes, wherever applicable, remained intact (GC, NMR).
[e] Used as hexahydrate.
[f] An 80% yield was obtained in using 1 equiv of Ac_2O.

Table 2
Effect of solvent during reaction of **1**[a]

Entry	Solvent	Time (min)	Yield (%)[b,c]
1	Neat	2	92
2	PhMe	10	65
3	DCM	10	80
4	$MeNO_2$	10	75
5	Et_2O	10	45
6	THF	15	20
7	MeCN	15	25

[a] **1** (2.5 mmol) was treated with Ac_2O (1.5 equiv) in the presence of $Zn(ClO_4)_2{\cdot}6H_2O$ (1 mol%) at room temperature.
[b] Isolated yield of 1,1-diacetoxy-(4-nitrophenyl)methane.
[c] The unreacted aldehydes, wherever applicable, remained intact (GC, NMR).

To find the effect of solvent on the catalytic activity of $Zn(ClO_4)_2{\cdot}6H_2O$, the reaction was carried out in various solvents (Table 2). An 80, 75, and 65% yields were obtained in DCM, $MeNO_2$, and PhMe, respectively, after 10 min (entries 2–4). However, poor results were obtained in Et_2O, THF, and MeCN (entries 5–7). The better catalytic activity of $Zn(ClO_4)_2{\cdot}6H_2O$ under neat conditions compared to that in solvents may be explained due to the better electrostatic effect of the ionic aggregates in the solid state to activate the electrophile. The decrease in polarity of PhMe compared to that of DCM and $MeNO_2$, may be the reason for inferior product yield observed in PhMe. The poor results obtained in Et_2O, THF, and MeCN were due to the competitive interaction of these solvents with the catalyst, through coordination with Zn^{2+} ion.

To find out the effectiveness of $Zn(ClO_4)_2{\cdot}6H_2O$ with other anhydrides, **1** was treated with various anhydrides (Table 3). The formation of 1,1-dicarboxylate was found to be dependent on the steric and electronic nature of the anhydrides. The reaction time increased with the increase in steric factor of the anhydride to afford comparable results (compare entries 1–3). The electron withdrawing nature of the chloromethyl and trifluoromethyl groups in chloroacetic and trifluoroacetic anhydrides, respectively, reduced the elctrophilicity of these anhydrides and no appreciable amount of product formation took place under neat conditions at room temperature for 24 h and in DCM under

Table 3
Reaction of **1** with $(RCO)_2O$ catalyzed[a]

Entry	R	Solvent	Temperature (°C)	Time (h)	Yield (%)[b]
1	Me	Neat	RT	2 min	92
2	*i*-Pr	Neat	RT	10 min	92
3	*t*-Bu	Neat	RT	0.5	91
4	$ClCH_2$	Neat	RT	24	Nil[c]
5	$ClCH_2$	DCM	Reflux	2	Nil[c]
6	F_3C	Neat	RT	24	Nil[c]
7	F_3C	DCM	Reflux	2	Nil[c]
8	Ph	Neat	RT	1	85
9	Ph	DCM	RT	5 min	95

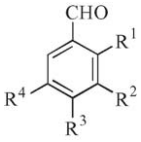
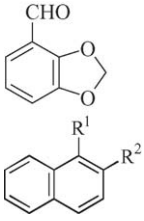
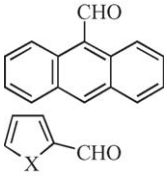
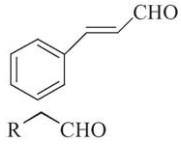
[a] **1** (2.5 mmol) was treated with the anhydride (1.5 equiv) in the presence of $Zn(ClO_4)_2{\cdot}6H_2O$ (1 mol%) at room temperature (except for entries 5 and 7) in the absence of solvent (except for entries 5, 7, and 9).
[b] Isolated yields of 1,1-diacyloxy-(4-nitrophenyl)methanes.
[c] Unreacted substrates remained unchanged (IR, GC, NMR).

reflux for 2 h (entries 4–7). The longer time required for the reaction with benzoic anhydride (entry 8) is the result of steric and electron withdrawing effects of the phenyl group in decreasing its reactivity. However, 95% yield was obtained in carrying out the reaction in DCM for 5 min at room temperature (entry 9). The most significant observation of the present methodology was the 1,1-dibenzoate formation at room temperature in the absence of solvent as both the reactants, e.g., 4-nitrobenzaldehyde and benzoic anhydride were solid. The reaction with benzoic anhydride could be visually monitored. The formation of a melt after stirring the reaction mixture for some time indicated 1,1-dibenzoate formation.

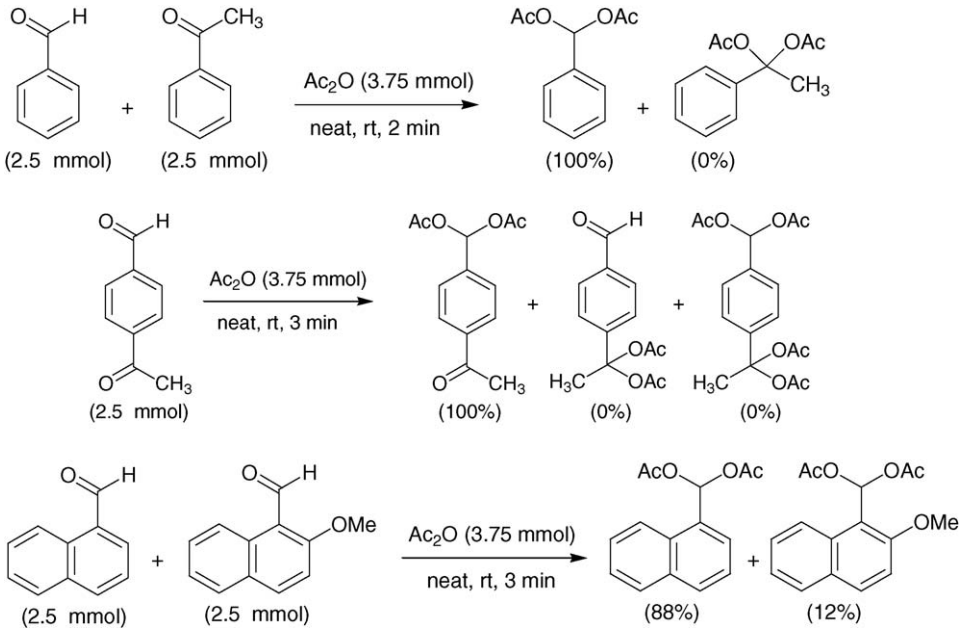
To establish the generality, various aromatic, heteroaromatic, and aliphatic aldehydes were subjected to 1,1-diacetate formation under the catalytic influence of $Zn(ClO_4)_2{\cdot}6H_2O$ (Table 4). Excellent results were obtained in 2–45 min. In general, the products obtained after usual work-up were clean (spectral analyses) and did not require any further purification. The reaction was compatible with other functionality such as nitro, cyano, ether, and ester. In case of hydroxybenzaldehyde, the corresponding triacetates were formed (entry 16). No diacetate formation was observed for acetophenone (at RT for 2 days or at 80 °C for 12 h). In case of aromatic aldehydes, it was possible to monitor the reaction visually: a clear solution was obtained after mixing the aldehyde, Ac_2O and the catalyst and the formation of a solid precipitate (after stirring the reaction mixture for a few min) indicated completion of the reaction. For aliphatic aldehydes, an exothermic reaction took place after addition of Ac_2O to the magnetically stirred mixture of the aldehyde and the catalyst indicating the completion of the reaction. The reaction rate was found to be dependent on the steric crowding surrounding the aldehyde group. Thus, the combined steric effects of the peri hydrogen and the 2-OMe group made the reaction of 2-methoxy-1-naphthaldehyde sluggish. An 88% yield was obtained in carrying out the reaction with 2.5 equiv of Ac_2O for 45 min (entry 20).

The difference in the reactivity of aldehydes and ketones for 1,1-diacetate formation encouraged us to test the efficiency of $Zn(ClO_4)_2{\cdot}6H_2O$ for selective 1,1-diacetate formation during inter- and intra-molecular competitions between an aldehyde and a ketone. Thus, a mixture of benzaldehyde (2.5 mmol) and acetophenone (2.5 mmol) was treated with Ac_2O (3.75 mmol) for 2 min at room temperature in the presence of $Zn(ClO_4)_2{\cdot}6H_2O$ (1 mol%) under solvent-free conditions (Scheme 2). Benzaldehyde 1,1-diacetate was obtained in quantitative yields and no significant formation of the 1,1-diacetate of acetophenone was observed (NMR). The treatment of 4-acetylbenzaldehyde (2.5 mmol) with Ac_2O (3.75 mmol) for 3 min under similar conditions resulted in exclusive formation of the 1,1-diacetate of the aldehyde group (Scheme 2). We next planned to exploit the differences in the rate of 1,1-diacetate formation of 1-naphthaldehyde and 2-methoxy-1-naphthaldehyde (compare entries 18 and 20, Table 4) for selective 1,1-diacetate formation during inter-molecular competion between 1-naphthaldehyde and 2-methoxy-1-naphthaldehyde. An 88:12 selectivity in favour of the formation of the 1,1-diacetate of 1-naphthaldehyde was observed (NMR) when a

Table 4
$Zn(ClO_4)_2{\cdot}6H_2O$-catalysed 1,1-diacetate formation of different aldehydes with Ac_2O[a]

Entry	Substrate	Time (min)	Yield (%)[b]
			
1	$R^1 = R^2 = R^4 = H$; $R^3 = NO_2$	2	92
2	$R^1 = R^3 = R^4 = H$; $R^2 = NO_2$	2	92
3	$R^1 = R^2 = R^4 = H$; $R^3 = CN$	5	98
4	$R^1 = R^2 = R^4 = H$; $R^3 = CF_3$	5	95
5	$R^1 = R^2 = R^4 = H$; $R^3 = OCOPh$	3	96
6	$R^1 = R^2 = R^4 = H$; $R^3 = Cl$	3	91
7	$R^1 = Br$; $R^2 = R^3 = R^4 = H$	5	92
8	$R^1 = R^2 = R^4 = H$; $R^3 = F$	3	93
9	$R^1 = R^2 = R^3 = R^4 = H$	2	93
10	$R^1 = R^2 = R^4 = H$; $R^3 = Me$	2	93
11	$R^1 = R^2 = R^4 = H$; $R^3 = OMe$	5	95
12	$R^1 = R^3 = R^4 = H$; $R^2 = OMe$	2	95
13	$R^1 = R^2 = OMe$; $R^3 = R^4 = H$	3	92
14	$R^1 = R^4 = H$; $R^2 = R^3 = OMe$	3	94
15	$R^1 = H$; $R^2 = R^3 = R^4 = OMe$	3	91
16	$R^1 = R^4 = H$; $R^2 = OMe$; $R^3 = OH$	15	92[c,d]
17		5	91
18	$R^1 = CHO$; $R^2 = H$	3	91
19	$R^1 = H$; $R^2 = CHO$	2	91
20	$R^1 = CHO$; $R^2 = OMe$	45	88[c]
21		5	90
22	X = O	2	86
23	X = S	3	88
24		10	95
25	$R = CH_2Ph$	3	92
26	R = Me	5	90

[a] The aldehyde (2.5 mmol) was treated with Ac_2O (1.5 equiv except for entries 16 and 20) in the presence of $Zn(ClO_4)_2{\cdot}6H_2O$ (1 mol%) under neat conditions at room temperature.
[b] Isolated yield of the corresponding 1,1-diacetate.
[c] The reaction was carried out with 2.5 equiv of Ac_2O.
[d] Yield of the corresponding triacetate.



Scheme 2. Selectivity in acylal formation during inter- and intra-molecular competition studies.

mixture of 1-naphthaldehyde (2.5 mmol) and 2-methoxy-1-naphthaldehyde (2.5 mmol) was treated with Ac_2O (3.75 mmol) for 3 min under similar conditions (Scheme 2).

3. Conclusion

In conclusion, $Zn(ClO_4)_2{\cdot}6H_2O$ is a new and highly efficient catalyst for 1,1-dicarboxylate formation from aldehydes. The advantages include low cost, short reaction time, operation at room temperature, excellent yields, and selectivity. With the increasing tight legislation on the release of waste and use of toxic substances as a measure to control environmental pollution [12], the use of solvent-free reaction conditions employed in the present method makes it "environmentally friendly" and suitable for large scale synthesis.

4. Experimental

The ^1H and ^{13}C NMR spectra were recorded on Bruker Avance DPX 300 (300 MHz) spectrometer in $CDCl_3$ using TMS as internal standard. The IR spectra were recorded on Nicolet Impact 400 spectrometer as KBr pellets for solid and neat for liquid samples. The reactions were monitored by TLC (silica gel-G) and Shimadzu QP 5000 GCMS. Evaporation of solvents was performed at reduced pressure, using a Büchi rotary evaporator.

4.1. Typical procedure for 1,1-diacetate formation

$Zn(ClO_4)_2{\cdot}6H_2O$ (9.3 mg, 0.025 mmol, 1 mol%) was added to a mixture of **1** (0.37 g, 2.5 mmol) and Ac_2O (0.35 mL, 3.75 mmol, 1.5 equiv). The mixture was stirred magnetically under neat conditions at room temperature for 2 min, diluted with EtOAc (15 mL), washed with aq. $NaHCO_3$ (2 × 10 mL), brine (10 mL), dried ($MgSO_4$) and concentrated to afford the product (0.58 g, 92%, Table 1, entry 1), which was in full agreement with the mp and spectral data (IR and NMR) of an authentic sample of 1,1-diacetoxy-1-(4-nitrophenyl)methane. The remaining reactions were carried out following this general procedure. In each occasion, the product obtained after usual work was of sufficient purity (spectral data) and did not require any further purification. The spectral data (IR and NMR) of all known products were identical with those reported in the literature. Following compounds were not reported in the literature.

4.2. 1,1-Di-(3-methylbutoxy)-1-(4-nitrophenyl)methane (entry 2, Table 3)

IR (neat) $\nu = 1763\,cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.19$–1.25 (m, 6H), 2.63–2.70 (m, 2H), 7.72 (d, 2H, $J = 8.5$ Hz), 7.76 (s, 1H), 8.26 (d, 2H, $J = 8.5$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 18.3$, 33.7, 88.0, 123.7, 127.5, 142.2, 148.4, 174.52; Elemental Anal. $(CHNS)_{cal}$: C, 58.25%; H, 6.19%; N, 4.53%; $(CHNS)_{obs}$: C, 58.23%; H, 6.21%; N, 4.51%.

4.3. 1,1-Di-(3,3-dimethylbutoxy)-1-(4-nitrophenyl)methane (entry 3, Table 3)

mp = 76–78 °C; IR (KBr) $\nu = 1761\,cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.24$ (s, 18H), 7.68 (d, 2H, $J = 7.4$ Hz), 7.73 (s, 1H), 8.27 (d, 2H, $J = 7.4$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 26.8$, 38.8, 88.2, 123.8, 127.5, 142.5, 148.4, 176.0; Elemental Anal. $(CHNS)_{cal}$: C, 60.52%; H, 6.87%; N, 4.15%; $(CHNS)_{obs}$: C, 60.49%; H, 6.88%; N, 4.16%.

4.4. 1,1-Dibenzoyloxy-1-(4-nitrophenyl)methane(entry 8, Table 3)

mp = 114–115 °C; IR (KBr) $\nu = 1737\,cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.44$–7.49 (m, 4H), 7.58–7.63 (m, 2H),

7.89 (d, 2H, $J = 8.5$ Hz), 8.09–8.11 (m, 4H), 8.28 (s, 1H), 8.32 (d, 2H, $J = 8.5$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 89.3$, 123.9, 127.9, 128.6, 130.0, 133.9, 142.2, 164.3; Elemental Anal. $(CHNS)_{cal}$: C, 66.84%; H, 4.01%; N, 3.71%; $(CHNS)_{obs}$: C, 66.82%; H, 4.03%; N, 3.70%.

4.5. 1,1-Diacetoxy-1-(2-bromophenyl)methane (entry 9, Table 4)

mp = 74–76 °C; IR (KBr) $\nu = 1764\ cm^{-1}$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.91$ (s, 1H), 7.54–7.59 (m, 2H), 7.34–7.39 (m, 1H), 7.22–7.28 (m, 1H), 2.13 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 20.6$, 88.9, 122.4, 127.6, 127.8, 131.0, 133.1, 134.8, 168.3; Elemental Anal. $(CHNS)_{cal}$: C, 46.02%; H, 3.86%; $(CHNS)_{obs}$: C, 46.07%; H, 3.84%.

4.6. 1,1-Diacetoxy-1-(2,3-dimethoxyphenyl)methane (entry 13, Table 4)

mp = 61–62 °C; IR (KBr) $\nu = 1756\ cm^{-1}$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.10$ (s, 6H), 3.86 (s, 3H), 3.89 (s, 3H), 6.94–6.97 (m, 2H), 7.09 (m, 1H), 7.98 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 20.7$, 55.7, 60.9, 85.8, 113.6, 118.4, 124.1, 129.3, 146.9, 152.6, 168.4; Elemental Anal. $(CHNS)_{cal}$: C, 58.20%; H, 6.01%; $(CHNS)_{obs}$: C, 58.22%; H, 5.99%.

4.7. 1,1-Diacetoxy-1-(3,4-dimethoxyphenyl)methane (entry 14, Table 4)

mp = 63–64 °C, IR (KBr) $\nu = 1750\ cm^{-1}$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.12$ (s, 6H), 3.89 (s, 3H), 3.91 (s, 3H), 6.87 (d, 1H, $J = 8.2$ Hz), 7.00 (s, 1H), 7.10 (d, 1H, $J = 8.2$ Hz), 7.62 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 20.8$, 55.8, 89.7, 109.4, 110.7, 119.5, 127.9, 149.0, 150.0, 168.7; Elemental Anal. $(CHNS)_{cal}$: C, 58.20%; H, 6.01%; $(CHNS)_{obs}$: C, 58.18%; H, 5.99%.

4.8. 1,1-Diacetoxy-1-(2,3-methylenedioxy)methane (entry 17, Table 4)

mp = 65–67 °C, IR (KBr) $\nu = 1760\ cm^{-1}$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.13$ (s, 6H), 6.01 (s, 2H), 6.85–6.95 (m, 3H), 7.79 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 22.5$, 88.0, 103.3, 111.4, 118.9, 121.3, 123.4, 146.9, 149.7, 170.2; Elemental Anal. $(CHNS)_{cal}$: C, 57.14%; H, 4.80%; $(CHNS)_{obs}$: C, 57.19%; H, 4.83%.

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