Green chemistry and mild condition: Synthesis of 1,1- diacetates from Aromatic aldehyde without solvent, reagents and catalyst

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Abstract

An efficient and new procedure for the preparation of 1,1-diacatates(acylals) from various aromatic aldehydes with acetic anhydride; solvent, reagent and catalyst free condition were described. Without volatile, hazard and toxic solvent-free and mild condition, desire products were prepared with excellent yields and a convenient green chemistry protocols.

Keywords: Green Chemistry; 1,1-diacetate (acylal); aldehyde; solvent free; simple and mild condition.

Introduction

The concept of green chemistry has been playing an important role in recent years for meeting the fundamental scientific challenges of protecting the living environment. One of the thrust areas for achieving this target is to explore alternative reaction conditions and reaction media to accomplish the desired chemical transformation with almost negligible by products and waste generation as well as elimination of the use of volatile and toxic organic solvents. It is therefore of utmost importance to evolve a simple and effective methodology for the different organic transformations that cover the concept of green chemistry.

Organic synthesis is one of the important strategies in inventing for the protection and deprotection of functional groups. In organic chemistry, selective protection of carbonyl group as acylals is an important transformation in because of their stability under neutral and basic conditions even as well as under critically controlled acidic conditions. So that, acylals have been also used as substrates for nucleophilic substitution reactions.

Due to the stability of 1,1-diacetates (acylals) in neutral and basic media, which are useful protecting groups for aldehyde [1-8]. The 1,1-diacetates are important building blocks for the synthesis of dienes for Diels Alder cycloaddition reaction and played important roles in organic synthesis [9-11].The preparation of 1,1-diacetates, generally, has been achieved by the reaction of aldehyde under the catalysis of strong protic acid, such as H_2SO_4 [1, 12], H_3PO_4 and CH_3SO_3H [13],NH_2SO_3H [14], Lewis acid, such as $FeCl_3$ [4]/ SiO_2 [2, 15],$ZnCl_2$ [16], PCl_3 [17], TMSCl-NaI [18], I_2 [19],$FeSO_4$

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[20],$Se(OTf)_3$ [21],$Cu(OTf)_2$ [22], $Bi(OTf)_3H_2O$ [23], $LiBF_4$ [24], WCl_6 [25], $InCl_3$ [26], P_2O_5/SiO_2 [27], LiOTf [28],$Zn(BF_4)_2$ [29], $Bi(NO_3)_3.5H_2O$ [30], Mo / $TiO_2 - ZrO_2$ [31], $Zr(SO_4)_2.4H_2O/ SiO_2$ [32], $InBr_3$ [33], BF_3 [34], $ZnSO_4$, Cu(II)SO_4,Fe(II)SO_4 [35], $SnCl_2$ [35, 36], P_2O_5 [37] and neutral condition NBS [38]recently solid acidic materials like-Nafion-H [39], and lot of catalyst such as tugstosilic acid and HZSM-5 [40], Y-zeolite [41], -Zeolite [42], Graphite [43], Sulfated Zircoria [44], Clay [45], EPZG [46], Zarconicum Sulfophenyl phosphonate [47], Well-Dawson (WD) heteropolyacid catalyst ($H_6P_2W_{18}O_{62}.24H_2O$) [48], Amberclyst-15 [49-51], $AlPW_{12}O_{40}$ [52], Zn / imidazole or $Yb(OTf)_3$ [53], P_2O_5 / Montmorillonite k-10 [54], Zinc-montmorillonite [55], Fe^{+3} on montmorillonite [56].

Recently Kavala *et all* extensively studied on the reaction mechanism for the formation of *geminal* diacylates by using tetrabutylammonium tribromide (TBATB) [57]. PVC-$FeCl_3$ complex [58]were recently introduced as catalysts, most of which employed solvent-free reaction conditions. Nevertheless, up to this point the development of procedures for the preparation of 1.1- diacylates relied on the use of rather strong acid, toxic and/or expensive reagent, which led continuing interest to develop an efficient procedure and/or catalyst.

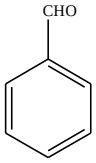
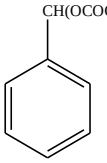
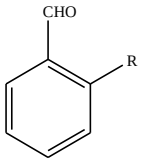
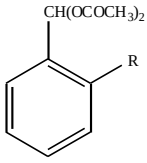
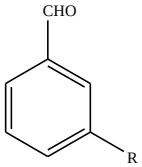
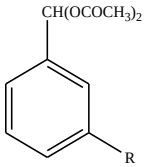
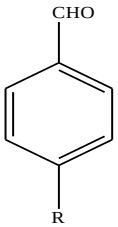
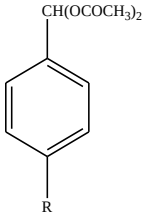
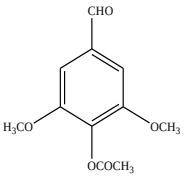
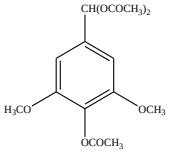
Acylals are important building blocks for the synthesis of dienes for cycloaddition reaction and chiral allyclic esters. One of the most useful protecting groups for carbonyl compounds because of their stability under various reaction conditions and their easy conversion back to the parent compounds are widely utilized [59]. They have several synthetic and industrial applications. Acylals have been also utilized as cross-linking reagents in cellulose and cotton industries, and as stain bleaching agents [60, 61]. Selective protection of carbonyl group plays an important role in the multistep organic synthesis of complex natural products [59]. Therefore, the development of an efficient, general, low cost, selective and simple method for the conversion of aldehydes to acylals is still of interest.

A practical and more efficient alternative using an inexpensive reagent under solvent-free condition is of considerable interest. We herein described a simple and efficient procedure for the preparation of 1.1-diacylates (acylals) of aldehydes with acetic anhydride and avoided volatile, hazard, toxic solvent, expensive chemical. Which will be environmental acceptable.

Materials and Method

The melting points were determined on a Fisher-Jones melting point apparatus and are uncorrected. Infrared spectra were recorded using KBr pellets for solids and neat for liquids on Perkin-Elmer 1330 grating spectrometer. ^1H NMR and ^{13}C NMR spectra were taken on Bruker 250 MHz spectrometer in $CDCl_3$, containing TMS as the internal standard. All *J* values are given in Hz, chemical shifts in units and column chromatography were carried out on 60-120 mesh. E. Merck silica gel. Chemicals and solvents were commercial reagent grate and used without further purification.

Table-1*.Conversion of aldehyde into 1,1- diacetate(acylals)*
General Procedure for the Preparation of 1,1-Diacetates(acylals):

Entry	Aldehydes	Acylals	Reaction Time (h)	Yield (%)	Melting Point (°C)	
					Observed	Reported
1			1.5	85	43-44	44-45[32]
2	 2, R= Br 3, R= NO_2 4, R= F	 2, R= Br 3, R= NO_2 4, R= F	4	73	80	-
3			6	85	92	91-92[32]
4			3.5	82	27	-
5	 5, R= Br 6, R= Cl 7, R= NO_2 8, R= F	 5, R= Br 6, R= Cl 7, R= NO_2 8, R= F	4	79	low	-
6			3	75	65	65-66[32]
7			5.5	93	63	64-66[55]
8			2	78	30-31	-
9	 9, R= SCH_3 10, R= OCH_3 11, R= Br 12, R= Cl 13, R= NO_2 14, R= F	 9, R= SCH_3 10, R= OCH_3 11, R= Br 12, R= Cl 13, R= NO_2 14, R= F	1	70	50	-
10			1.5	71	65	64-65[51]
11			4	82	85	-
12			3	65	84-85	79-80[51]
13			5.5	82	120-121	123-124[51]
14			2	74	39	-
15			3	83	125-127	-

A mixture of the aldehyde (1.00 mmol) and anhydrous acetic anhydride (10 mL) was refluxed for 1-6 h. After completion, as indicated by TLC, evaporated the excess acetic anhydride and poured into 5 % NaOH solution, and then the organic layer was collected by CH_2Cl_2, washed with water successively and dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure to provide crude product and the crude product was chromatographed on silica gel eluting with CH_2Cl_2 : n-Hexane (1:1) to give the pure 1,1-Diacetates(acylals).

Spectral data of the product ^{1}H NMR ($CDCl_3$**):**

Phenyl methylene diacetate(Table 1, Entry **1):**Mp. 43-44 ºC (lit.[32] Mp. 44-45 ºC): δ 7.66 (s, 1H), 7.52-7.48 (m, 2H,), 7.39 (t, *J*=3.3, 3.2 Hz, 3H), 2.10 (s, -$COCH_3$. 2, 6H). ^{13}C NMR ($CDCl_3$): 168.78 (2), 135.41, 129.74, 128.58, 126.65, 89.67, and 20.86 (2).

***o*-Bromo phenyl methylene diacetate (**Table 1, Entry **2):** Mp. 80 ºC:δ 7.88 (s, 1H), 7.55 (dt, *J*=1.2, 7.7 Hz, 2H), 7.34 (dt, *J*=2.0, 7.6 Hz, 1H), 7.24 (dt, *J*=1.6, 7.6 Hz, 1H), 2.12 (s, -$COCH_3$. 2, 6H). ^{13}C NMR ($CDCl_3$): 168.32 (2), 134.77, 133.14, 131.03, 127.80, 127.56, 122.45, 88.96 and 20.64 (2).

***o*-Nitri phenyl methylene diacetate (**Table 1, Entry **3):** Mp. 92 ºC (lit.[32] Mp. 91-92 ºC): δ 8.17 (s, 1H), 8.01 (dd, *J*=1.0, 7.6 Hz, 1H), 7.70 (m, 2H), 7.55 (m, 1H), 2.10 (s, -$COCH_3$. 2, 6H). ^{13}C NMR ($CDCl_3$): 168.26 (2), 147.74, 133.51, 130.56, 130.44, 127.83, 124.96, 85.97 and 20.46 (2).

***o*-Floro phenyl methylene diacetate (**Table 1, Entry **4):** Mp. 27 ºC:δ 7.88 (s, 1H), 7.50 (dt, *J*=1.6, 7.5 Hz, 1H), 7.36 (m, 1H), 7.15 (t, *J*7.5 Hz, 1H), 7.60 (dt, *J*0.8, 9.6 Hz, 1H), 2.10 (s, -$COCH_3$. 2, 6H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): 168.32 (2), 160.10 ($J_{C\text{-}F}$ =249.06 Hz), 131.43 (($J_{C\text{-}F}$ 8.31 Hz), 127.93 (($J_{C\text{-}F}$ =3 Hz), 124.14 ($J_{C\text{-}F}$ =4.31 Hz), 122.90 ($J_{C\text{-}F}$ =12.38 Hz), 115.85 ($J_{C\text{-}F}$ 20.75 Hz), 85.33 ($J_{C\text{-}F}$ =3.87 Hz), and 20.61 (2).

***m*-Bromo phenyl methylene diacetate (**Table 1, Entry **5):** Mp. Low melting solid:δ 7.64 (s, 1H), 7.60 (s, 1H), 7.49 (dt, *J*= 0.65, 0.75, 7.9 Hz, 1H), 7.42 (d, *J*=7.7 Hz, 1H), 7.24 (t, *J*=7.8 Hz, 1H), 2.10 (s, -$COCH_3$. 2, 6H). ^{13}C NMR ($CDCl_3$): 168.55 (2), 137.48, 132.73, 130.11, 129.64, 125.37, 122.48, 88.63, and 20.70 (2).

***m*-Chloro phenyl methylene diacetate (**Table 1, Entry **6):** Mp. 65 ºC (lit.[32] Mp. 64-65 ºC).δ 7.57 (s, 1H), 7.45 (d, *J*=1.7 Hz, 1H), 7.28 (m, 3H), 2.04 (s, -$COCH_3$. 2, 6H). ^{13}C NMR ($CDCl_3$): 168.39 (2), 137.23, 134.26, 129.75, 129.62, 126.60, 124.77, 88.54, and 20.49 (2).

***m*-Nitro phenyl methylene diacetate (**Table 1, Entry **7):** Mp. 63 ºC (lit.[55] Mp. 64-65 ºC). δ 8.36 (t, *J*= 1.65 Hz, 1H), 8.24 (dt, *J*=1.08, 8.2 Hz, 1H), 7.82 (d, *J*=7.7 Hz, 1H), 7.70 (s, 1H), 7.61-7.59 (t, *J*= 8.0 Hz, 1H), 2.13 (s, -$COCH_3$. 2, 6H). ^{13}C NMR ($CDCl_3$): 168.55 (2), 148.32, 137.50, 132.92, 129.72, 124.54, 121.85, 88.32, and 20.72 (2).

***m*-Floro phenyl methylene diacetate (**Table 1, Entry **8):** Mp. 30-31 ºC: δ= 7.64 (s, 1H), 7.36(m, 1H), 7.29 (s, 1H), 7.23 (m, 1H), 7.07 (m, 1H), 2.11 (s, -$COCH_3$. 2, 6H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): 168.55 (2), 162.60 ($J_{C\text{-}F}$ =245.38 Hz), 137.72 (($J_{C\text{-}F}$ =7.31 Hz), 130.20 (($J_{C\text{-}F}$ =8.0 Hz), 122.35 ($J_{C\text{-}F}$ =6.13 Hz), 116.61 ($J_{C\text{-}F}$ =21 Hz), 113.60 ($J_{C\text{-}F}$ =22.75 Hz), 88.67 ($J_{C\text{-}F}$ =1.81 Hz), and 20.65 (2).

***p*-Sulfonyl methyl phenyl methylene diacetate (**Table 1, Entry **9):** Mp. 50 ºC: δ= 7.62 (s, 1H), 7.43 (d, *J*=8.4 Hz, 2H), 7.26 (d, *J*=8.3 Hz, 2H), 2.48 (s, S-CH_3, 3H), 2.11 (s, -$COCH_3$. 2, 6H). ^{13}C NMR ($CDCl_3$): 168.75 (2), 140.84, 131.99, 127.14, 126.09, 89.54, 20.87 (2), and 15.41.

***p*-Methoxy phenyl methylene diacetate (**Table 1, Entry **10):** Mp. 65 ºC (lit.[51] Mp. 64-65 ºC): δ 7.60 (s, 1H), 7.43 (d, *J*=8.7 Hz, 2H,), 6.89 (d, *J*=8.7 Hz, 2H), 3.79 (s, -OCH_3, 3H), 2.09 (s, -$COCH_3$. 2, 6H). ^{13}C NMR ($CDCl_3$): 168.75 (2), 137.99, 131.85, 127.14 (2), 104.10 (2), 89.52, 55.04, and 20.87 (2).

***p*-Bromo phenyl methylene diacetate (**Table 1, Entry **11):** Mp. 85 ºC: δ 7.60 (s, 1H), 7.52 (d, *J*=8.43 Hz, 2H), 7.37 (d, *J*=8.43 Hz, 2H), 2.10 (s, -$COCH_3$. 2, 6H). ^{13}C NMR ($CDCl_3$): 168.65 (2), 134.45, 131.78 (2), 128.39 (2), 123.94, 89.01, and 20.80 (2).

***p*-Chloro phenyl methylene diacetate (**Table 1, Entry **12):** Mp. 84-85 ºC (lit.[51] Mp. 79-80 ºC): δ 7.61 (s, 1H), 7.44 (dd, *J*=1.7, 6.7 Hz, 2H), 7.40 (dd, *J*=1.7, 6.7 Hz, 2H), 2.10 (s, -$COCH_3$. 2, 6H). ^{13}C NMR ($CDCl_3$): 168.69 (2), 135.71, 133.96, 128.84 (2), 128.15 (2), 89.06, and 20.83 (2).

***p*-Nitro phenyl methylene diacetate (** Table 1, Entry **13):** Mp. 120-121 ºC (lit.[51] Mp. 123-124 ºC): δ 8.23 (d, *J*=8.7 Hz, 2H), 7.71 (s, 1H), 7.68 (d, *J*=8.7 Hz, 2H,), 2.13 (s, -$COCH_3$. 2, 6H). ^{13}C NMR ($CDCl_3$): 168.51 (2), 148.66, 141.92, 127.84 (2), 123.83 (2), 88.34, and 20.70 (2).

***p*-Floro phenyl methylene diacetate (**Table 1, Entry **14):** Mp. 39 ºC: δ 7.61 (s, 1H), 7.48 (dd, *J*=1.94, 5.3 Hz, 1H), 7.48 (dd, *J*=2.15, 5.4 Hz, 1H), 7.06 (dd, *J*=1.94, 7.7 Hz, 1H), 7.02 (dd, *J*=2.0, 7.7 Hz, 1H), 2.08 (s, -$COCH_3$. 2, 6H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): 168.60 (2), 163.27 (J_{C-F} =247.30 Hz), 131.43 (J_{C-F} =3.19 Hz), 128.64 (2) (J_{C-F} =34.25 Hz), 115.47 (2) (J_{C-F} =21.81 Hz), 89.04, and 20.66 (2).

3,5-dimethoxy-4-methanoic methane phenyl methylene diacetate (Table 1, Entry **15):** Mp. 125-127 ºC: δ 7.60 (s, 1H), 6.76 (s, 2H,), 3.82 (s, -OCH_3. 2, 6H), 2.31 (s, -$OCOCH_3$, 3H), 2.10 (s, -$COCH_3$. 2, 6H).^{13}C NMR ($CDCl_3$): 168.62 (2), 168.50, 152.21 (2), 133.59, 129.80, 103.47 (2), 89.43, 56.20 (2), 20.86 (2) and 20.40.

Results and Discussions

K. Shelke *etal*.reported a facile and efficient method for the preparation of acylals from a variety of aromatic and heteroaryl aldehydes with acetic anhydride in the presence of a catalytic amount of alum at room temperature under solvent free conditions. They used catalyst. Recently, scientists and researchers have focused on the investigations whose aim has been to find those chemical processes or methodologies that are not dangerous for the environment. The term “green chemistry” includes the fabrication and catalysis of those chemical compounds, which possess a reduced threat to human beings as well as the environment. During the past decade he chemical manufacturers started to use ionic liquids (ILs) as solvents for organic fabrication as catalysis and media for various extraction processes. This considerable interest towards ionic liquids is due to their unique characteristics such as being non-volatile, non-flammable, as well as their ability

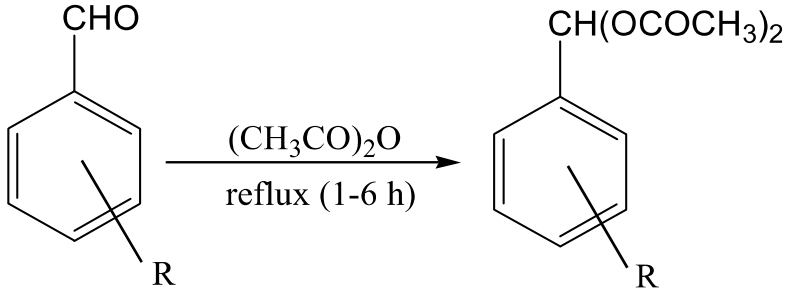
to be used many times, and also their potential for being a very proper media for the environment. Some of the ionic liquids are approved to be used as catalysts because they possess a kind of polarity[62]. Another paper claimed that they used catalyst as Brønsted acidic ionic liquid (BALL) and different solvent system (**Table -2**). This paper repotted, a clean and efficient catalyst for the preparation of 1,1-diacatates from various aldehydes with the use of acetic anhydride in the presence of [Msei]Cl as a new catalyst [63].

Table 2*. The solvent effect for synthesis of 1,1-diacetate*[a3]

Entry	Solvent(10ml)	Time	Yield(%)[b]
1	H_2O	95	74
2	H_2O:EtOH[c]	60	78
3	Ethanol	65	81
4	*n*-Hexane	55	83
5	Acetonitrile	80	65
6	Ethylacetate	45	85
7	Dichloromethane	50	86
8	Solvent-Free	5	99

Solvent-free organic reactions have attracted great interest in recent years as possessing many advantages such as high efficiency and selectivity, separation, purification, and mild reaction conditions; they can be beneficial to industry as well as the environment.

In this communication, we disclose the reaction of aldehyde with acetic anhydride in absence of catalyst, reagents and solvent except acetic anhydride (**Scheme-1**). Our goal, this method is simple, efficient and does not involved either a halogenated solvent or and additive and no other catalyst, which is important from the economical and environmental point of view. One important thing is that, we can use these protected aldehydes for next step without changing reaction flask or reaction bath, because there is no other solvent, reagents or catalysts.



Scheme-1

However, a variety of aldehydes are converted into 1,1-diacetates (**Table-1**), mostly, all aldehyde gave good to excellent isolated yield of 1,1-diacetates, in the case of 2-chlorobenzaldehyde, the yield of 1,1-diacetate is zero percent.

[3] Condition reaction: benzaldehyde (1 mmol) and acetic anhydride (2 mmol) in presence [Msei]Cl (0.03 mol%) at room temperature, [b]Yield of isolated products, [c]1:1 ratio

Conclusion

In conclusion, we provide an efficient and a new method for the preparation of 1,1-diacetates (acylals) from aromatic aldehyde and acetic anhydride, in absence catalysts, and no other solvent except acetic anhydride. The advantages of this method are mild reaction condition, generality, operational simplicity, high yield, non-corrosive, non-polluting, cleaner reaction profile, efficiency and rapid procedure. Therefore, the reaction process is convenient, more economical and environmentally friendly as well as green chemistry protocols.

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