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Microwave-Assisted Solvent-Free Synthesis of 1,1-Diacetates Catalyzed by $SbCl_3$ from Aldehydes and Acetic Anhydride

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Microwave-assisted synthesis of a variety of 1,1-diacetates catalyzed by $SbCl_3$ from corresponding aldehydes and acetic anhydride was reported. Only 10 mol% of catalyst was sufficient to push the reaction forward and high amounts of the catalyst did not improve the yields to a great extent. The present protocol offered several advantages including low cost of the catalyst, high yields, short reaction time and simple work-up procedure.

Keywords: Microwave irradiation, 1,1-Diacetates, Solvent-free, $SbCl_3$

INTRODUCTION

The carbonyl group is one of the most versatile functional groups in organic chemistry and a great deal of synthetic work has been performed and masking of the carbonyl compounds [1]. In these methods, formation of 1,1-diacetates from aldehydes and acetic anhydride is one of the most useful aspect. As synthetic intermediates or protecting groups for aldehydes, 1,1-diacetates are stable in neutral and basic media, and easy to convert to parent aldehydes [2-6]. Usually, 1,1-diacetates have been synthesized by the reaction of carbonyl compounds with acetic anhydrides in the presence of an appropriate acid catalyst. Strong protic acids such as sulfuric acid, phosphoric acid, methanesulfonic acid [7] and Nafion-H [8] are usually used as acid catalysts, and Lewis acids such as zinc chloride [9], ferric chloride [6], phosphorus trichloride [10], or LiBr [11], are also applied as mild catalysts for this transformation. However, these methods have not been entirely satisfactory owing to such drawbacks as low yields, long reaction times, problems of corrosion, effluent pollution and so on. Consequently, it is very necessary to develop alternative methods for the synthesis of 1,1-diacetates from aldehydes under mild conditions in short reaction times.

In recent years, β-zeolite [12], sulfated zirconia [13], montmorillonite clays [14], iodine [15], trimethylchlorosilane/ sodium iodide [16], scandium triflate [17], TiO_2/SO_4^{2-} solid superacid [18], H_2NSO_3H [19], Wells-Dawson acid [20], zirconium sulfate tetrahydrate-silica gel [21], $KHSO_4$ [22], zirconium hydrogen sulfate [23], 2,4,4,6-tetrabromo-2,5-cyclohexadienone (TABCO) [24], neutral lithium triflate(LiOTf) [25], aluminum dodecatungstophosphate ($AlPW_{12}O_{40}$) [26], antimony(III) chloride [27] and lanthanum(III) nitrate hexahydrate [28] have been used for the purpose to obtain relatively better results.

Recently, microwave irradiation (MI) has become an established tool in organic synthesis [29-32], because of the rate enhancements, higher yields and, often, improved selectivity, with respect to conventional reaction conditions. In addition, solvent-free MI processes are also clean and efficient, and moreover, using either organic or inorganic solid supports has received increased attention [33]. There are several advantages of performing syntheses in solvent-free media,

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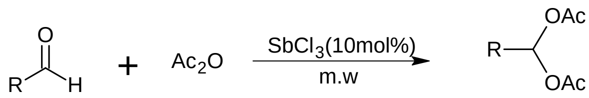


1 **2** **3**

R = aromatic or aliphatic group

Scheme 1

such as, short reaction time, increased safety, economic advantages in absence of solvent.

Herein we wish to report a fast and efficient solvent-free procedure for the synthesis of 1,1-diacetates from aldehydes catalyzed by $SbCl_3$ under microwave irradiation (as shown in Scheme 1). The results are summarized in Table 1.

EXPERIMENTAL

General

All products were characterized by the comparison of their spectral data ([1]H NMR and IR spectroscopy) and physical properties with those of authentic samples.

Table 1. Microwave-assisted Solvent-free Synthesis of 1,1-Diacetates Using $SbCl_3$ as a Catalyst

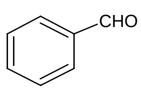
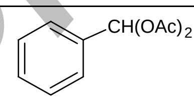
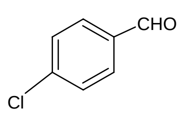
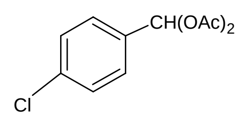
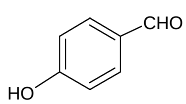
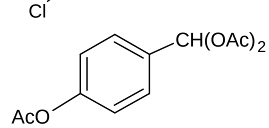
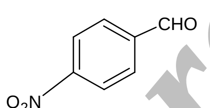
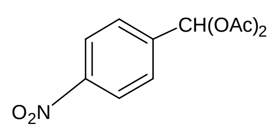
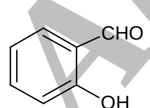
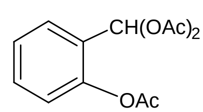
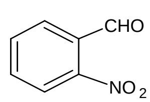
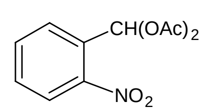
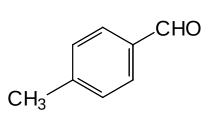
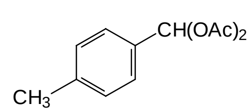
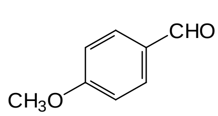
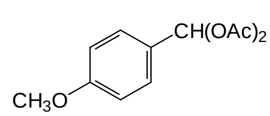
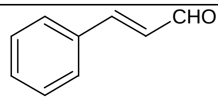
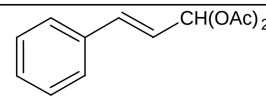
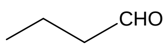
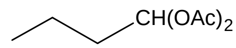
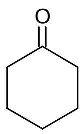
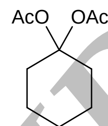
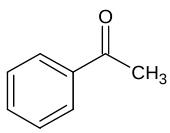
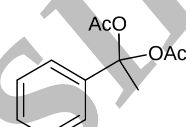
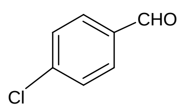
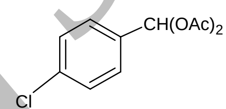
Entry	Aldehyde	Time (s)	Yield (%)	Product[b]	M.p. (ºC) Found	M.p. (ºC) Reported
1		60	90		42-43	44-45 [4]
2		60	92[d],95,95[e]		81-82	82-83 [19]
3		60	91		90-92	89-90 [7]
4		60	89		124-125	125-127 [19]
5		60	93		101-103	103-104 [21]
6		60	91		89-90	90-91 [19]
7		60	93		80-81	81 [22]
8		60	95		61-62	63 [22]

Table 1. Continued

9		60	89		83-85	86 [15]
10		60	91		oil	oil [15]
11		180	0		-	
12		180	0		-	
13[c]		1 h	86		81-82	82-83 [19]

[a]All products were characterized by ^{1}H NMR, IR. [b]The yields refer to the isolated pure products. [c]Heating at 70 ºC instead of microwave irradiation. [d]5mol%. [e]20mol% $SbCl_3$ was used.

General Procedure for the Preparation of 1,1-Diacetates

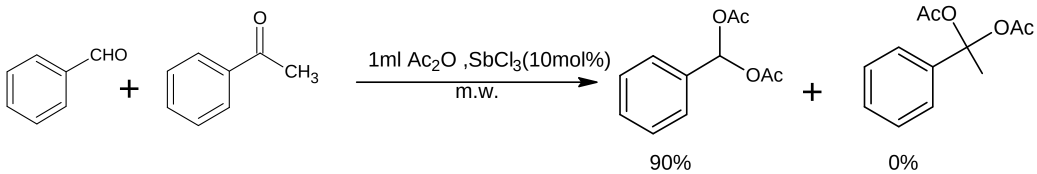
To a mixture of aldehyde (2 mmol) and acetic anhydride (1 ml) was added $SbCl_3$(10 mol%), the reaction mixture was mixed well and placed in a microwave oven (700 W) for an appropriate time (as shown in Table 1). After completion of the reaction, as indicated by TLC, the reaction mixture was extracted with EtOAc, washed with 10% $NaHCO_3$ solution, then with saturated brine. The organic layer was separated and dried over anhydrous Na_2SO_4 and evaporated. The isolated crude product was purified by preparative TLC to give the corresponding 1,1-diacetates.

RESULTS AND DISCUSSION

When a mixture of aldehyde **1**, acetic anhydride **2** and a catalytic amount of $SbCl_3$ (10 mol%) was irradiated by microwave, the corresponding 1,1-diacetates **3** were obtained in good to excellent yields (Table 1). By this method, aromatic and aliphatic aldehydes gave satisfactory results (Table 1, Entries 1-10). 4-Hydroxybenzaldehyde and 2-hydroxybenzaldehyde were subjected to the similar reaction conditions; the hydroxyl group was also acetylated to afford the corresponding triacetates in excellent yields (Table 1, Entries 3 and 5). In the absence of microwave irradiation, the reactions proceeded in longer reaction times at 70 ºC (Table 1, Entry 13). Comparing with the literature results [27], acetylation of 4-hydroxybenzaldehyde proceeded in 25 min to get the product with 92% yield, while with the presented method, the reaction completed within a minute with 91% isolated yield. So microwave irradiation can shorten the reaction time and also assist the reaction process effectively.

Unfortunately, when cyclohexanone and acetophenone were used in this reaction, no corresponding product was isolated (Entry 11, 12). In the case of substrates bearing aldehyde and ketone functionalities, the keto group remains unaffected and aldehyde is converted into 1,1-diacetate. This result indicates that the chemoselective protection of an aldehyde in the presence of ketone could be achieved by this procedure (Scheme 2).

Optimization of the reaction condition was studied with different molar ratios of the catalyst and under different microwave powers. The best ratio was found to be 10 mol% of $SbCl_3$ under 700 W power. Increasing the power of microwave



Scheme 2

decreases the yields of the products.

In summary, under solvent-free conditions, microwave-assisted synthesis of 1,1-diacetates catalyzed by $SbCl_3$ can achieved from aldehydes and acetic anhydride efficiently. The advantages of this protocol are mild reaction conditions, short reaction times, simple work-up and good yields.

Selected Spectral Data

1,1-Diacetoxy-1-(4-chlorophenyl)methane. ^1H NMR ($CDCl_3$, 400 MHz): δ 2.18 (s, 6H), 7.38 (d, *J* = 6.4 Hz, 2H) , 7.46 (d, *J* = 6.4 Hz, 2H), 7.63 (s, 1H); IR (KBr): 1758 cm^{-1}.

1,1-Diacetoxy-1-(4-hydroxyphenyl)methane. ^1H NMR ($CDCl_3$, 400 MHz): δ 2.13 (s, 6H), 2.31 (s, 3H), 7.14 (d, *J* = 6.4 Hz, 2H), 7.45 (d, *J* = 6.4 Hz, 2H), 7.62 (s, 1H); IR (KBr): 1760 cm^{-1}.

1,1-Diacetoxy-1-(2-nitrophenyl)methane. ^1H NMR ($CDCl_3$, 400 MHz): δ 2.15 (s, 6H), 7.54-7.66 (m, 1H), 7.70-7.73 (m, 2H), 8.05-8.08 (m, 1H), 8.21 (s, 1H); IR (KBr): 1755 cm^{-1}.

1,1-Diacetoxy-3-phenylprop-2-ene. ^1H NMR ($CDCl_3$, 400 MHz): δ 2.13 (s, 6H), 6.22 (dd, *J* = 16, 6.4 Hz, 1H), 6.87 (d, *J* = 16 Hz, 1H), 7.31-7.62 (m, 6H); IR (KBr): 1760 cm^{-1}.

1,1-Diacetoxybutane. ^1H NMR ($CDCl_3$, 400 MHz): δ 0.94 (t, *J* = 3.5 Hz, 3H), 1.42-1.45 (m, 2 H), 1.77-1.79 (m, 2H), 2.06 (s, 6H), 6.80 (t, *J* = 5.5 Hz, 1H); IR (KBr): 1755 cm^{-1}.

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