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VCl_3: A Mild and Efficient Catalyst for Chemo Selective Synthesis of 1,1-Diacetates From Aldehydes Under Solvent Free Conditions

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A facile and efficient synthesis of 1,1-diacetates in excellent yields from aldehydes and acetic anhydride under solvent free conditions in short time in the presence of a catalytic amount of vanadium(III) chloride is described.

Key Words: 1,1-Diacetates, Aldehydes, VCl_3, Solvent free conditions.

INTRODUCTION

Protection and deprotection is the heart and soul of multistep organic synthesis. Moreover protection of aldehydes are generally stable under neutral, acidic and basic media adopted in routine multistep synthesis[1-3]. Proceeding group is also useful in separation and purification of products particularly in multistep liquid phase methodologies.

Various methods are reported including acetylization and thioacetylization for protection of carbonyl group[4,5]. In recent years, 1,1-diacetates are gaining more attention in the protection of aldehydes because they serve as a marked aldehyde function. The 1,1-diacetates find numerous applications, the ambient nature of 1,1-diacetates[6], make them synthetically important precursors of 1-acetoxydienes[7] and 2,2-dichlorovinyl acetate[8] for Diels-Alder reaction. Compound bearing the 1,1-diacetate functionalities are used as cross-linking agents for cellulose in cotton[9] and activators in the composition of bleaching mixture of wine stained fabrics[10]. In addition 1,1-diacetates are useful starting materials and intermediates in organic synthesis[11]. Smonou and Angelis[12] have reported the synthesis of optical aldehydes by lipase-catalyzed resolution of the corresponding acylals. In presence of acid catalysts, aldehydes react with acetic anhydride to form 1,1-diacetates. Many reagents are reported in the literature for the synthesis of 1,1-diacetates from aldehyde which include strong protonic acids, such as sulfuric, phosphoric, methane sulfonic or perchloric acids[13] and lewis acids such as $ZnCl_2$, $FeCl_3$, $FeSO_4$, LiBr, PCl_3[14], NH_2SO_3H[15] heteropolyacid Well-Dawson ($H_6P_2W_{18}O_{62}.24H_2O$), aluminium dodecatunguston phosphate ($AlPW_{12}O_{40}$)[16] and heterogeneous catalyst like nafion-H, expansive graphite, zeolites, clay and supported reagents[17]. But these procedures

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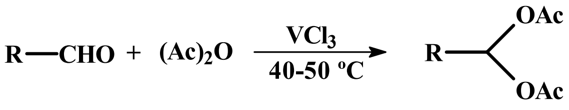
are often accompanied by longer reaction times, low yields, stringent conditions, high catalyst loading, corrosive reagents and require the use of toxic metal ions in solvents. In continuation of our recent studies on the use of VCl_3[18] we herein report for the first time the preparation of 1,1-diacetates from aldehyde and acetic anhydride using VCl_3 as a catalyst.

EXPERIMENTAL

Melting points were determined with an X-4 digital melting-point apparatus and are uncorrected. IR spectra were recorded in KBr on a Digilab FTS-3000 FT-IR spectrophotometer and ^1H NMR spectra on a Varian Mercury plus-400 MHz spectrometer using TMS as a internal reference. Elemental analyses were determined on a PE-2400 CHN instrument.

General procedure: A mixture of aldehyde (1 mmol), Ac_2O (1.5 mmol) and VCl_3 (0.01mmol) was stirred at 40-50 ºC for the appropriate time indicated in Table-1. The progress of the reaction was monitored by TLC. After completion of the reaction, reaction mass was cooled to room temperature. Added dichloromethane (50 mL) and water (50 mL) the mixture was washed successively with 2 % NaOH (aq) and brine. Separated organic layer was dried over Na_2SO_4 the solvent was removed under reduced pressure or recrystallized from ethyl acetate-hexane (2:8) to give pure product in good yield (**Scheme-I**).



Scheme-I

TABLE-1
SYNTHESIS OF 1,1-DIACETATES USING VANADIUM(III) CHLORIDE AS CATALYST*

Substrate	Time (min)	Yields (%)	m.p. (ºC)	Reported[Ref.]
Benzaldehyde	30	97	43-45	44-45[17e]
Anisaldehyde	45	95	64-66	64-65[17e]
4-Chloro benzaldehyde	30	94	80-82	82-83[17e]
2,4-Dichloro benzaldehyde	90	92	100-102	101-102[15]
3-Chloro benzaldehyde	60	96	66-68	65-66[17e]
2-Nitro benzaldehyde	15	97	89-90	85-86[17e]
3-Nitro benzaldehyde	20	95	66-68	67-68[17e]
4-Nitro benzaldehyde	20	95	126-128	125-126[17e]
Cinnamaldehyde	15	90	84-86	84-86[17e]
Piperonal	25	92	81-83	79-80[15]
2-Naphthaldehyde	25	95	97-99	97-99[13c]
4- Fluoro benzaldehyde	30	92	51-53	50-51[13c]
4- Methyl benzaldehyde	30	88	80-82	79-80[17e]

*All products are known and were characterized by ^1H NMR, IR and Mass spectral data.

RESULTS AND DISCUSSION

The use of vanadium(III) chloride as catalyst in organic transformation[19] is not much explored. As a first example the preparation of 1,1-diacetates from aldehydes and Ac_2O in the presence of a catalytic amount of VCl_3 under solvent free conditions at 40-50 ºC as carried and complete conversion was observed in 15-90 min to afford the corresponding diacetates in excellent yield (Table-1). Ketones such as cyclohexanone and acetophenone did not yield any acylates under the present reaction conditions. Both aromatic and aliphatic aldehydes gave the corresponding acetates in high yields (85-97 %) in a short reaction time (15-90 min). However, aromatic aldehydes with electron withdrawing groups like 2-nitro benzaldahyde, 3-nitro benzaldahyde and 4-nitro benzaldehyde required comparatively shorter reaction time to achieve complete conversion.

In summary, this paper describes that the aromatic aldehydes are conveniently react with Ac_2O using vanadium(III) chloride as a catalyst to give 1,1-diacetates. The notable features of this procedure are mild and efficient reaction conditions, high levels of chemoselectivity, simple operation, acid and base-labile protecting group intact, cleaner reaction products, improved yields, enhanced rate and solvent free condition that makes it a useful and attractive process for the synthesis of 1,1-diacetates.

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