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P_2O_5 / SiO_2 AS CATALYST FOR THE PREPARATION OF 1, 1-DIACETATES UNDER SOLVENT-FREE CONDITIONS[*]

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Abstract – A facile and efficient method for the preparation of 1, 1-diacetates of aldehydes is improved. P_2O_5/SiO_2 catalyzed 1, 1-diacetates formation from aldehydes in dry media. Advantages of this method are the use of an inexpensive and selective catalyst with high yields in simple operation and short reaction time under solvent-free conditions.

Keywords – 1, 1-Diacetates, phosphorous pentoxide, protection, aldehydes, silica gel

1. INTRODUCTION

1, 1-Diacetates are useful protective groups for aldehyde [1]. Relative acid stability of 1, 1-diacetates compared to the corresponding acetal [2], is an interesting feature of such 1, 1-diacetates as carbonyl protecting groups. These are also important building blocks for the synthesis of dienes for Diels-Alder cycloaddition reaction [3]. Usually they are synthesized [4] from aldehydes and acetic anhydride using strong proton acids and Lewis acids as catalysts, typically such as sulfuric acid [5], phosphoric acid [6], methanesulfonic acid [6], Nafion-H [7], zinc chloride [8], ferric chloride [2], iodine [9] or phosphorous trichloride [10]. These methods have not been entirely satisfactory owing to drawbacks such as low yields (4% in the case of 4-nitrobenzaldehyde [10]), long reaction time (up to 120 h in the case of 2-furaldehyde [10]) and tedious work-up. In recent years, β-zeolite [11], sulfated zirconia [12], montmorillonite clays [13], expansive graphite [14], trimethylchlorosilane and sodium iodide [15], scandium triflate [16], N-bromo succinimide [17], and PVC-$FeCl_3$ [18] or TiO_2 / SO_4^{-2} solid super acid [19] were employed as catalysts for this purpose to obtain relatively better results. Although some of these methods present a convenient procedure with good to high product yields, most of the currently available methods suffer from strong acidic conditions, or required high temperature and expensive catalyst loading. Therefore the discovery of a novel mild and catalytic protocol for the efficient conversion of aldehydes into 1, 1-diacetates is of general interest.

Since the early work of Toda [20], application of solid state organic chemistry has been under intensive investigation and has recently been reviewed [21]. The observations obtained were: a) decreasing reaction time and b) cleaner reaction with easier work-up [20-22]. Here, we report a procedure using P_2O_5 / SiO_2 (Silicaphos for short) as a catalyst for the preparation of 1, 1-diacetates from aldehydes in the absence of a solvent.

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2. RESULTS AND DISCUSSION

As shown in the Table 1, a series of 1, 1-diacetates were synthesized using Silicaphos as a catalyst at room temperature in solvent free media. Both aromatic and aliphatic aldehydes gave high yields of the corresponding acylals except 4-(dimethylamino) benzaldehyde, which remained intact in the reactions mixture after prolonged reaction time (20 h). We were pleased to find that aromatic aldehydes containing electron withdrawing or donor groups gave the corresponding 1, 1-diacetates in good to excellent yields in a shorter time using P_2O_5 / SiO_2 than some of the reported methods. The nature of the substituents on the aromatic ring seems to have no effect on the reaction systems. Moreover, sensitive rings (furfural) or the functional group (cinnamaldehyde) were successfully converted to corresponding 1, 1-diacetates. It must be mentioned here that phenol groups were also protected as acetates in hydroxyl containing aromatic aldehydes under these conditions.

$$\text{R-CHO} + Ac_2O \xrightarrow[\text{RT, 20-120 min}\quad 73\text{-}95\%]{P_2O_5\ /\ SiO_2} \text{R-CH(OAc)}_2$$

Scheme

Table 1. Conversion of Aldehydes into 1, 1-Diacetates Catalyzed by Silicaphos

Aldehydes	Acylals	Time	Yield [a,b]	Bp/ Torr or mp (^{0}C)	
R	R	(min)	(%)	Found	Reported [ref]
Ph	Ph	30	95	45-46	44-46 [10]
4-Me-C_6H_4	4-Me-C_6H_4	60	85	67-68	68-69 [10]
3-NO_2-C_6H_4	3-NO_2-C_6H_4	90	81	66-67	64-66 [2]
4-NO_2-C_6H_4	4-NO_2-C_6H_4	100	78	125-126	123-125 [10]
PhCH=CH	PhCH=CH	20	88	85-86	84-87 [10]
4-HO-C_6H_4	4-AcO-C_6H_4	120	95	89-90	89-90 [13]
4-HO-3-MeO-C_6H_4	4-AcO-3-MeO-C_6H_4	75	92	90-91	90-91 [13]
2-furyl	2-furyl	60	75	53-55	52-54 [11]
4-Me_2N-C_6H_4	no reaction	1200	-	-	-
CH_2=CH-	CH_2=CH-	45	73	110-113/ 25	98-105/ 2 [2]
$CH_3(CH_2)_4$-	$CH_3(CH_2)_4$-	60	78	135-137/25	128-129/ 2 [2]
Et	Et	60	78	70-73/18	72-74/20 [11]

a) Isolated yield. b) All the compounds give satisfactory spectral analysis (IR and ^{1}H-NMR)

Aliphatic as well as αβ-unsaturated aldehydes also produced their corresponding 1, 1-diacetates in good yields under the same reaction conditions. It is also worth nothing that ketones, such as acetophenone and benzophenone, did not give any 1, 1-diacetates under the same reaction conditions and this suggested that chemoselective protection of an aldehyde in the presence of a ketone could be achieved. Therefore we have provided an alternative preparation of 1, 1-diacetates from aldehydes with the advantages of the use of an inexpensive and selective catalyst with high yields in simple operation, and short reaction times in dry media.

It must be noted here that the procedure of preparation of Silicaphos (P_2O_5 / SiO_2) and synthesis of 1, 1-diacetates were done in septum vessels. Thus the probability of absorption of water with P_2O_5 to form H_3PO_4 was ruled out. The identity of the P_2O_5 / SiO_2 for this transformation is not clear. To this end, P_2O_5 / SiO_2 and H_3PO_4 / SiO_2 were compared in ability by reaction with benzaldehyde for 30 minutes. The experimental results show that the above reaction could be promoted by both reagents in more than stoichiometric amounts, but the reaction can be catalyzed only by P_2O_5 / SiO_2 , whereas H_3PO_4 / SiO_2 failed.

3. EXPERIMENTAL SECTION

All melting points recorded are uncorrected open capillary measurements. IR spectra were recorded on a Shimadzu -IR 470 spectrophotometer. ^{1}H-NMR spectra were recorded on a Bruker-80 MHz instrument using tetramethylsilane (TMS) as an internal standard. Silica gel 60(230-400 mesh) was obtained from Fluka and was dried in an oven at 120 °C for 2 hrs.

Preparation of Silicaphos

A mixture of phosphorous pentoxide (3 g) and chromatography grade silica gel (230-400 mesh, 7g) was placed in a flask and stirred for 4 hrs. This homogeneous, free flowing, white powder reagent is sensitive towards moisture and should be stored in a disicator.

Preparation of 1, 1-Diacetates

Typical procedure: In a typical reaction, a mixture of benzaldehyde (1.06 g, 10 mmol), acetic anhydride (2.04 g, 20 mmol) and Silicaphos (1 g, 20 mol % of P_2O_5 / benzaldehyde) was ground throughly in a mortar. The resulting mixture was placed in a flask and was mechanically stirred at room temperature for 30 minutes (Table). The progress of the reaction was monitored by TLC and/or IR spectroscopy (ν_{CO} acylal; 1740-1760 cm^{-1}). After completion of the reaction, dichloromethane (50 ml) was added to the mixture and filtered. The solid material was washed with dichloromethane (2 x 10 ml). The filtrates were combined together and washed with a saturated solution of $NaHCO_3$ and brine and then dried over $MgSO_4$. Removal of the solvent gave the crude product, which was subsequently purified by column chromatography (silica gel; eluted with n-hexane / dichloromethane) to afford pure benzaldehyde 1, 1-diacetate in 95 % yield. Mp 45-46 ˚C (lit. [10], 44-46 ˚C); IR (KBr); 3070, 2900, 1750, 1380, 1250, 1200, 1010, 960, 760, 695, 600, 570 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 7.65(s, 1H), 7.4(m, 5H), 2.1(s, 6H).

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