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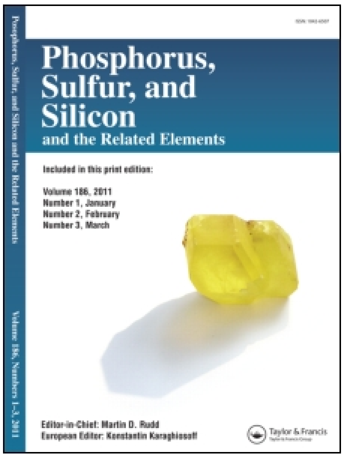

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PHOSPHORUS PENTOXIDE-MONTMORILLONITE K-10 AS CATALYST FOR THE PREPARATION OF 1,1-DIACETATES UNDER SOLVENT-FREE CONDITIONS

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PHOSPHORUS PENTOXIDE-MONTMORILLONITE K-10 AS CATALYST FOR THE PREPARATION OF 1,1-DIACETATES UNDER SOLVENT-FREE CONDITIONS

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A facile and efficient method for the preparation of 1,1-diacetates of aldehydes is improved. P_2O_5/montmorillonite K10 catalyzed 1,1-diacetates formation from aldehydes in dry media. Both aromatic and aliphatic aldehydes gave high yields (70–95%) of the corresponding 1,1-diacetates. 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: Aldehydes; 1,1-diacetates; montmorillonite; phosphorus pentoxide; protection

Many organic reactions have been devised in which the reagents are deposited on various inorganic solid supports such as silica gels, zeolites and layered clay minerals. The variety and the versatility of these heterogeneous methods are evident from recent reviews.[1–3] Since the early work of Toda,[4] application of solid state organic chemistry has been under intensive investigation and recently has been reviewed.[5] The observations obtained were: decreasing reaction time, increasing yield and/or selectivity, cleaner reaction and easier work-up.[4–6]

1,1-Diacetates are a useful protective group for aldehydes.[7] Relative acid stability of 1,1-diacetates compared to the corresponding acetal,[8] 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.[9] Usually, they are synthesized[10] from aldehydes and acetic anhydride using strong proton acids and Lewis acids as catalyst, typically such as sulfuric acid,[11]

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phosphoric acid,[12] methanesulfonic acid,[12] Nafion-H,[13] zinc chloride,[14] ferric chloride,[8] iodine,[15] or phosphorous trichloride.[16] These methods have not been entirely satisfactory, owing to such drawbacks as low yields (4% in the case of 4-nitrobenzaldehyde[16]), long reaction time (up to 120 h in the case of 2-furaldehyde[16]) and tedious work-up. In recent years, β-zeolite,[17] sulfated zirconia,[18] montmorillonite clays,[19] expansive graphite,[20] trimethylchlorosilane and sodium iodide,[21] scandium triflate,[22] N-bromo succinimide,[23] PVC-$FeCl_3$[24] or TiO_2/SO_4^{-2} solid super acid[25] were employed as catalyst 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, require high temperature or long reaction time 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. We report here a procedure using P_2O_5/montmorillonite K10 (Clayphos, for short), as a catalyst for the preparation of 1,1-diacetates from aldehydes in the absent of solvent.

RESULTS AND DISCUSSION

As shown in Table I, a series of 1,1-diacetates were synthesized using Clayphos 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 that remained intact in the reaction mixture after prolonged reaction time (20 h).

$$\text{R—CHO} + \text{Ac}_2\text{O} \xrightarrow[\text{RT, 10 min. Grinding}]{\text{P}_2\text{O}_5\text{/Montmorillonite K-10}} \text{R—CH(OAc)}_2 \qquad (1)$$

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 shorter time using P_2O_5/montmorillonite K10 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, the compounds with sensitive rings (furfural) or functional groups (cinnamaldehyde) successfully were converted to the corresponding 1,1-diacetates. However, phenol groups were also protected as acetates in hydroxyl containing aromatic aldehydes under these conditions.[27] Whereas literature showed that protection of 4-HO-benzaldehyde failed[19a] in the presence of montmorillonite K-10 after 48 h, or take place[19b] in the presence of Fe^{+3}-montmorillonite after 8 h, our catalyst improved this reaction by 95% yield in 10 min.

TABLE I Conversion of Aldehydes into 1,1-Diacetates Catalyzed by Clayphos

Aldehydes R	Acylals R	Catalyst	Time (min)	Yield (%)[a,b]	Bp/Torr or mp (°C)	
					Found	Reported[ref]
Ph	Ph	Clayphos	10	90	45–46	44–46[16]
4-Me-C_6H_4	4-Me-C_6H_4	Clayphos	10	85	67–68	68–69[16]
3-NO_2-C_6H_4	3-NO_2-C_6H_4	Clayphos	10	80	66–67	64–66[8]
4-NO_2-C_6H_4	4-NO_2-C_6H_4	Clayphos	10	75	125–126	123–125[16]
PhCH=CH	PhCH=CH	Clayphos	10	85	85–86	84–87[16]
4-HO-C_6H_4	4-AcO-C_6H_4	Clayphos	10	95	89–90	89–90[19b]
4-HO-C_6H_4	No reaction	Montmorillonite K10	28800	0[c]	—	[19a]
4-HO-C_6H_4	4-AcO-C_6H_4	Fe^{+3} -Montmorillonite	480	90[d]	89–90	89–90[19b]
4-HO-3-MeO-C_6H_4	4-AcO-3-MeO-C_6H_4	Clayphos	10	94	90–91	90–91[19b]
2-furyl	2-furyl	Clayphos	10	92	53–55	52–54[17]
2-furyl	2-furyl	Montmorillonite K10	120	74	53–55	52–54[17]
4-Me_2N-C_6H_4	no reaction	Clayphos	1200	0[c]	—	[19]
CH_2=CH–	CH_2=CH–	Clayphos	10	71	110–113/25	98–105/2[8]
$CH_3(CH_2)_5$–	$CH_3(CH_2)_5$–	Clayphos	10	80	136	135–136[26]
$CH_3(CH_2)_4$–	$CH_3(CH_2)_4$–	Clayphos	10	70	135–137/25	128–129/2[19b]
$CH_3(CH_2)_2$–	$CH_3(CH_2)_2$–	Clayphos	10	85	126	125–128[12]
Et	Et	Clayphos	10	75	70–73/18	72–74/20[17]

[a] Isolated yield.

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

[c] 100% aldehyde recovered.

[d] 6 equiv. of acetic anhydride were used, conversion rate = 39%.

Aliphatic as well as $\alpha\beta$-unsaturated aldehydes also produced their corresponding 1,1-diacetates in good yields under the same reaction conditions. It is also worth noting 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.

Mention must be made here that the procedure of preparation of Clayphos (P_2O_5/montmorrilonite K-10) and synthesis of 1,1-diacetates were done in a 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 Clayphos for this transformation is not clear.

EXPERIMENTAL

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.

Preparation of Clayphos

A mixture of phosphorous pentoxide (3 g) and montmorrilonite K-10 (7 g) was placed in a flask and stirred for 4 h. This homogeneous, free flowing powder reagent is sensitive towards moisture and should be stored in a desiccator.

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 Clayphos (1 g, 20 mol% of P_2O_5/benzaldehyde) was ground throughly in a mortar for 10 min. 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 (2×10 ml). The filtrates were combined together and were 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. m.p.: 45–46°C (lit.,[16] m.p. 44–46°C); IR (KBr); 1750 cm^{-1}. ^{1}H-NMR (80 MHz, CDCl$_3$): 7.65(s, 1H), 7.4–7.8(m, 5H), 2.2(s, 6H).

4-Acetoxybenzaldehyde-1,1-diacetate: m.p.: 89–90°C (lit.,[19b] m.p. 89–90°C); IR (KBr); 1760 cm^{-1}. ^{1}H-NMR (80 MHz, CDCl$_3$): 10.5(s, 1H), 6–6.8(complex AA′BB′, 4H), 2.2(s, 3H), 2.0 (s, 6H).

4-Acetoxy-3-methoxybenzaldehyde-1,1-diacetate: m.p.: 90–91°C (lit.,[19b] m.p. 90–91°C); IR (KBr); 1760 cm^{-1}. ^{1}H-NMR (80 MHz, CDCl$_3$): 8.0(s, 1H), 7.3–7.7(m, 3H), 4.2(s, 3H), 2.5(s, 3H), 2.3(s, 6H).

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