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Synthesis of gem 1, 1-Diacetates Using Phosphonitrilic Chloride

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Research Paper - Chemistry

ABSTRACT

Phosphonitrilic Chloride (PNT) was found to be an efficient catalyst for the synthesis of 1, 1 diacetates from various aldehydes with acetic anhydride at room temperature in excellent yields. The advantages of the method are high selectivity and shorter reaction time.

Key words : Phosphonitrilic chloride, 1,1, diacetate, aldehyde.

Introduction :

In the past decades, the synthetic scientific community were interested in the productive concepts of multicomponent processes, domino reactions and sequential transformations.[1-8] In organic synthesis, protection and deprotection of functional group approach is vital/essential to target oriented synthesis [9,10] and has great importance. When a multifunctional compound undergoes a chemical reaction, then the reaction takes place selectively at one reactive site while other site has been blocked temporarily. Therefore, protection of group is essential. For the protection of group, several protective groups were developed.

Among the functional groups, the carbonyl group is one of the most versatile group and a great deal of synthetic work has been performed and masking of the carbonyl compounds. [11] Due to the dominant electrophilic nature of carbonyl group, in several multiuse synthesis, one of the major challenging problem is to protect a carbonyl group from nucleophilic attack until its electrophilic properties can be exploited. Acetals,


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thioacetals, oxathiolanes, 1, 1-diacetates and nitrogenous derivatives are the most important protecting groups for carbonyl compounds. Now a days, several methods were developed for the formation and cleavage of these protecting groups, because of their great utility. [12]

In organic synthesis, acylals (geminal diacetates) or gem-bis(acyloxy)-alkanes are important protecting groups as alternatives to acetals.[9] The protection of aldehydes as acetates is an important transformation because of their stability towards aqueous acids [13] and bases [14] and their easy reconversion into parent aldehydes.[9] Due to the simplicity of the protection procedure, the aldehyde groups can be protected as 1,1-diacetates which is preferred to the corresponding acetals, oxathioacetals and thioacetals. During acetalisation of aldehydes water is formed which can be removed either by physical and chemical means.

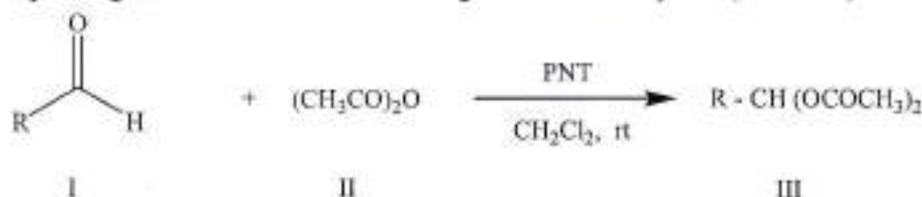
Acylals are important synthons, used in the organic reactions such as Grignard, [15,16] Barbier,[16] Prins,[17-18] Knoevenagel[19] and Benzoin[20] reactions. They were also utilized in the synthesis of chrysanthemic acid,[21] and total synthesis of sphingofungins E and F.[22] In Diel's-Alder cycloaddition reaction,[23] acylals were used as an important starting material for the synthesis of dienes. Due to the great utility of diacetate in industries, they act as a cross-linking reagents for cellulose in cotton[24] and as activators stain bleaching agents for wine-stained fabrics.[19, 20, 25]

Generally the protection of 1,1 diacetate can be carried out by the reaction of aldehyde with acetic anhydride using catalysts. The protection of 1,1 diacetate were carried out using strong protic acids as catalysts like sulfuric acid, phosphoric acid, methanesulfonic acid,[26] Nafion-H.[27] The Lewis acid catalysts such as phosphorus trichloride,[28] FeCl_3 , [29] zinc chloride,[30] iodine,[31] LiBr , [32] $\text{Bi}(\text{OTf})_3$, [33] $\text{InCl}_3/\text{Al}_2\text{O}_3$ [34] were used for the synthesis of 1,1 diacetates.

1,1 diacetate was also prepared using catalysts like $\text{FeCl}_3/\text{SiO}_2$, [35] SbCl_5 , [36] sulphated zirconia,[37] under microwave irradiation. The catalysts such as zinc tetrafluoroborate,[38] copper(II) tetrafluoroborate,[39] InBr_3 , [40] cerium(IV) sulfate tetrahydrate,[41] KHSO_4 , [42] $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, [43] iron(III) fluoride,[44] antimony (III) chloride,[45] boric acid,[46] NbCl_5 , [47] silica chromate,[48] $\text{FePW}_{12}\text{O}_{40}$, [49] were

reported for the protection of 1,1 diacetate under solvent free conditions. The reagents such as β -zeolite, [50] NBS, [51] $\text{TiO}_2 / \text{SO}_4^{2-}$, [52] CAN , [53] $\text{H}_2\text{NSO}_3\text{H}$, [54] $\text{Zn}(\text{OTf})_2 \cdot 6\text{H}_2\text{O}$, [55] GaCl_3 , [56], H- MOR [57], P_2O_5 / Kaolin [58] were used for the preparation of 1,1 diacetate.

Here we report Phosphonitrilic chloride (PNT) as a Lewis acid catalyst for the synthesis of 1,1-diacetates from aldehydes. Various aldehydes were treated with acetic anhydride in the presence of catalytic amount of PNT in dichloromethane, the corresponding 1,1-diacetate were formed in good to excellent yields (Scheme 1)



R = Alkyl, Aryl,
Heterocyclic

Scheme 1

Experimental procedure:

To the mixture of aldehyde (2 mmol) with acetic anhydride (3 mmol) in dichloromethane (10 ml), PNT (5 mol %) was added. The reaction mixture was stirred at room temperature. After completion of reaction (5-20 minutes), monitored by TLC, the organic layer was washed with 10 % NaHCO_3 (2×10 ml) and H_2O (2×10 ml). The combined organic layer was then dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure to get desired product.

Representative spectral data:

1. 4-chlorophenyl methanediyl diacetate (Entry No. 2) IR (KBr) cm^{-1} : 1015, 1210, 1235, 1387, 1524, 1760, 2942. ^1H NMR (300 MHz) δ ppm: 2.1 (s, 6H), 7.8 (s, 1H), 7.3 (d, 2H), 7.5 (d, 2H)
2. 4-methylphenyl methanediyl diacetate (Entry No. 5): IR (KBr) cm^{-1} : 980, 1025, 1240, 1395, 1528, 1756, 2948. ^1H NMR (300 MHz) δ ppm: 2.08 (s, 6H), 2.4 (s, 3H), 7.4 (d, 2H), 7.2 (d, 2H), 7.7 (1, H).

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Results and discussion:

Aldehydes (I) were reacted with acetic anhydride (II) in the presence of PNT (5 mol %) in dichloromethane at room temperature to give corresponding 1,1-diacetates (III) in excellent yield (Table I). The aromatic aldehydes (entries 1-8) were converted to corresponding 1,1 diacetates relatively faster than that of aliphatic aldehydes (entries 11-13). It was also observed that the reactions of aldehydes having electron withdrawing groups (entries 2, 3 and 7, 8) afforded higher yields than electron donating groups (entries 5, 6). The α, β -unsaturated aldehydes (entry 9) and heteroaromatic aldehydes (entry 10) underwent reaction smoothly with acetic anhydride to give corresponding 1,1-diacetates.

Conclusions:

In summary, PNT was found to be an efficient catalyst for the synthesis of 1,1-diacetates from aromatic, aliphatic, heterocyclic aromatic and also unsaturated aldehydes under mild conditions. The advantages of this protocol are excellent yields, easy work up, shorter reaction time, high selectivity, mild conditions, non-toxic and shelf availability of the catalyst.

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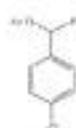

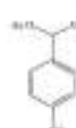

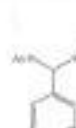

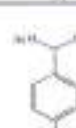



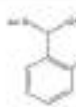


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Table 1 : Synthesis of gem 1,1-diacetates using phosphonitrilic chloride

Entry	Aldehyde	Product	Yield (%)	Time (min.)	M.P.(°C) [Lit]
1			92	7	44 [44-45] ⁴⁰
2			95	5	81 [82-83] ⁵⁴
3			96	6	125 [125-127] ⁵⁴
4			93	9	88 [89-90] ⁴⁹
5			91	11	80 [81] ⁴⁰
6			90	13	62 [63] ⁴⁰
7			92	9	89 [90-91] ⁵⁴
8			93	10	66 [66-67] ⁴⁰




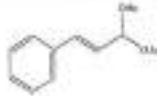








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Entry	Aldehyde	Product	Yield (%)	Time (min.)	M.P (°C) [Lit.]
9			92	12	85 [86] ¹³
10			87	13	50 [50-51] ³¹
11			86	16	Oil [Oil] ³¹
12			88	17	Oil [Oil] ³¹
13			89	20	Oil [Oil] ³¹

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