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# HIGHLY EFFICIENT AND CHEMOSELECTIVE CONVERSION OF ALDEHYDES TO ACYLALS CATALYZED WITH TUNGSTEN HEXACHLORIDE (WCI<sub>6</sub>)

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### SYNTHETIC COMMUNICATIONS, 32(5), 669-673 (2002)

# HIGHLY EFFICIENT AND CHEMOSELECTIVE CONVERSION OF ALDEHYDES TO ACYLALS CATALYZED WITH TUNGSTEN HEXACHLORIDE (WCl<sub>6</sub>)

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#### ABSTRACT

Different types of aldehydes react chemoselectively with acetic anhydride in the presence of a catalytic amount of tungsten hexachloride (WCl<sub>6</sub>) to produce the corresponding *gem*-diacetates in good to excellent yields.

The reaction of aldehydes with organic acid anhydrides to give the corresponding acylals has been known for a long time.<sup>1</sup> 1,1-Diacetates are useful protective group for aldehydes,<sup>2</sup> and synthetically important precursors for the preparation of 1-acetoxydienes for Diels-Alder reactions.<sup>3</sup> On the other hand, relative acid stability of 1,1-diacetates is compared with the corresponding O,O-acetals,<sup>4</sup> is an interesting feature of such *gem*-diacetates

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as carbonyl protecting groups. The preparation of 1,1-diacetates, generally, has been achieved by the reaction of aldehydes with acetic anhydride under the catalysis of strong protic acids such as  $H_2SO_4$ ,<sup>1,5</sup>  $H_3PO_4$  and  $CH_3SO_3H$ ,<sup>6</sup> and Nafion-H.<sup>7</sup> Lewis acids such as  $ZnCl_2$ ,<sup>8</sup> FeCl<sub>3</sub>,<sup>4</sup> PCl<sub>3</sub>,<sup>9</sup>  $I_2$ ,<sup>10</sup> Sc(OTf)<sub>3</sub>,<sup>11</sup> and solid acidic catalysts like zeolites,<sup>12</sup> expansive graphite,<sup>13</sup> and clay<sup>14</sup> have also been shown as alternative catalysts for the formation of 1,1-diacetates.<sup>15</sup>

Although, in a number of these methods some improvement has been observed, in practice the yields of the desired acylals and the chemoselectivity and rate of the reactions were not always satisfactory. We have developed new applications of tungsten hexachloride (WCl<sub>6</sub>) as either an oxophilic metal chloride or a powerful Lewis acid in recent years. In this regard, chemoselective dithioacetalization of carbonyl compounds and transdithioacetalization of acetals,<sup>16</sup> deoxygenation of sulfoxides and reductive dimerization of sulfonyl chlorides,<sup>17</sup> chemoselective acetalization of carbonyl compounds,<sup>18</sup> deprotection of acetals,<sup>19</sup> and one-pot ring expansion-chlorination of 1,3-dithiolanes and 1,3-dithianes<sup>20</sup> have been reported.

This communication wish to report that WCl<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub> or in the absence of solvent can act as an efficient catalyst for the chemoselective conversion of aldehydes to the corresponding 1,1-diacetates (table). As shown in the table various types of aromatic aldehydes bearing either electronwithdrawing or electron-releasing group including cinnamaldehyde were converted to their acylals in the presence of Ac<sub>2</sub>O (1ml) and WCl<sub>6</sub> (1-4 mol%) under solvent-free conditions in excellent yields (table, Entries 1–6).<sup>20</sup> Aliphatic aldehydes as well as  $\alpha,\beta$ -unsaturated aldehydes were also furnished the corresponding acylals in good to excellent yields under the same reaction conditions (table, Entries 7 and 8). When benzaldehyde or 4-nitrobenzaldehyde (1 mmol) allowed to react with 1 ml acetic anhydride at room temperature in  $CH_2Cl_2$  as solvent, TLC analysis of the reaction mixture after 15 min indicate almost the complete disappearance of starting aldehydes. After work up, the corresponding 1,1-diacetate were also isolated in excellent yields (table, Entries 9 and 10). As shown in the scheme, when a 1:1 mixture of benzaldehyde and acetophenone allowed to react with acetic anhydride (1 ml) in the presence of WCl<sub>6</sub> (1 mol%), and the reaction mixture



Scheme.



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Entry	Substrate	Product	WCl <sub>6</sub> (mole%)	T (min)	Yield <sup>a</sup> (%)
1	СНО		1	3	98
2 Me	ео-Сно	MeO-CAc	2	10	90
3 N	ЛеСНО	MeOAc	2	3	95
4 C	сно	CI-CI-OAc	1	3	92
5 O <sub>2</sub>	NСНО		1	5	9 <b>8</b>
6	Ph	Ph OAc	4	6	81, 95 <sup>b</sup>
7	/ СНО	OAc	3	6	92
8	<u> </u>	OAc	2	7	95
9 0 <sub>2</sub> 1	NСНО		4	15	96°
0	СНО		3	15	95°

Tungsten Hexachloride Catalyzed Formation of *gem*-Diacetates Tabla

(a) Yields refer to isolated products unless otherwise stated. (b) Yields was determined by NMR spectroscopy. (c) Reactions were performed in CH2Cl2 (3 mL per mmol of substrate) as solvent.

worked up after 3 min, NMR analysis of the crude products consisted of a 1:1 mixture of benzaldehyde diacetyl acetal and acetophenone.

These experiments clearly indicated the ability of the method for chemoselective protection of aldehydes as 1,1-diacetates in keto aldehydes. In light of the simplicity of the procedure, excellent yields of the pro-

duct and high yields of the product, this procedure could be an alternative



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for the available methods of this transformation. Further investigation on the new applications of  $WCl_6$  and its related reagents are ongoing in our laboratories.

## EXPERIMENTAL

### General Procedure for the Preparation of 1,1-Diacetates

To a solution of aldehyde (2 mmol) and freshly distilled acetic anhydride (2 ml) in anhydrous  $CH_2Cl_2$  (25 ml) or under solvent-free conditions, tungsten hexachloride (0.02–0.08 mmol) was added at room temperature and the mixture was stirred for the time indicated in the table. Progress of the reaction was monitored by TLC or GC. After completion of the reaction the reaction was quenched with water (25 ml), and the mixture was extracted with  $CH_2Cl_2$  (2 × 25 ml). The organic layer was separated, and washed with saturated NaHCO<sub>3</sub> (2 × 25 ml) and water (15 ml) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvent under reduced pressure gave the almost pure 1,1-diacetate.

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