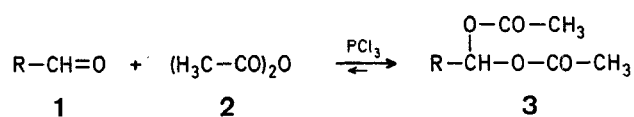


## Phosphorus Trichloride as Catalyst in the Preparation of 1,1-Diacetates from Aldehydes

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It has long been known<sup>1</sup> that aldehydes **1** react with simple anhydrides, notably acetic anhydride (**2**), to form diesters of 1,1-diols **3**. Usually, the formation of 1,1-diacetates **3** is catalysed by strong proton acids, such as sulphuric<sup>2</sup>, phosphoric<sup>3</sup>, or methanesulphonic<sup>3</sup> acids, or by Lewis acids, such as zinc chloride<sup>4</sup>. We now report that good yields can readily be obtained when this reaction is catalysed by phosphorus trichloride.



### 1,1-Diacetates **3**; General Procedure:

Acetic anhydride (**2**; 10.2 g, 0.1 mol) and the aldehyde **1** (0.1 mol) are mixed under nitrogen at room temperature. Phosphorus trichloride (1 drop) is then added, the mixture swirled gently, and then set aside until reaction has either gone to completion, or has come to equilibrium. This is most conveniently assessed by <sup>1</sup>H-N.M.R. spectroscopy. For most aromatic aldehydes, the reaction mixture solidifies, and the 1,1-diacetates **3** are purified by recrystallization (cyclohexane). For aliphatic aldehydes, volatile material is removed by rotary evaporation and pure 1,1-diacetates **3** obtained by distillation in vacuo (Table).

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- <sup>1</sup> (a) E. Knoevenagel, *Justus Liebigs Ann. Chem.* **402**, 111 (1905).  
(b) P. Clausner, *Ber. Dtsch. Chem. Ges.* **38**, 2861 (1905).  
(c) J. Thiele, E. Winter, *Justus Liebigs Ann. Chem.* **311**, 355 (1960).  
(d) R. Wedscheider, E. Späth, *Monatsh. Chem.* **30**, 825, 840 (1909).  
(e) M. F. Semmler, *Ber. Dtsch. Chem. Ges.* **42**, 584 (1909).

**Table.** 1,1-Diacetates **3** from Aldehydes **1** using Phosphorus Trichloride as Catalyst

R	Reaction conditions (solvent/temperature/time)	Yield [%]		m.p. [°C] or b.p. [°C]/torr		Purity <sup>a</sup> by G.L.C.
		by <sup>1</sup> H-N.M.R.	isolated	observed	reported	
C <sub>6</sub> H <sub>5</sub>	none/20°C/12 h	100	98	44-46°	44-45° <sup>5c</sup>	—
4-H <sub>3</sub> CO-C <sub>6</sub> H <sub>4</sub>	CHCl <sub>3</sub> /20°C/1 h	100	—	—	—	—
	none/20°C/12 h	98	92	67-68°	64-65° <sup>5c</sup>	—
4-Cl-C <sub>6</sub> H <sub>4</sub>	CCl <sub>4</sub> /20°C/48 h	95	88	81-81.5°	80-81° <sup>5c</sup>	—
4-O <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub>	CCl <sub>4</sub> /20°C/24 h	10	4	123-125°	125° <sup>1c</sup>	—
4-H <sub>3</sub> C-C <sub>6</sub> H <sub>4</sub>	CCl <sub>4</sub> /20°C/6 h	85	80	68-69°	67-68° <sup>5c</sup>	—
2-furyl	none/30°C/120 h	88	70	132-136°/18	143-144°/20° <sup>9</sup>	—
H <sub>3</sub> C	none/120°C/7 h	96	82	73-75°/15	63-64°/10 <sup>1a</sup>	97
H <sub>3</sub> C-CH=CH-	none/20°C/4 h	100	97	89-90°/15	92-93°/10 <sup>4a</sup>	>99
(H <sub>3</sub> C) <sub>2</sub> C=CH-	none/20°C/3 h	98	— <sup>b</sup>	—	—	—
H <sub>2</sub> C=C(CH <sub>3</sub> )-	none/20°C/10 h	95	88	82-84°/15	74-76°/10 <sup>4a</sup>	>99
C <sub>6</sub> H <sub>5</sub> -CH=CH-	none/20°C/24 h	70	30	84-87°	84-85° <sup>8</sup>	—

<sup>a</sup> G.L.C. conditions: 10% Silicone oil on Chromosorb A (60-80 mesh), 2 m column at 130°C.

<sup>b</sup> Partially decomposes on distillation.

Our results are presented in the Table. They reveal that use of phosphorus trichloride catalysis generally results in good yields with aromatic aldehydes (except those with electron-withdrawing substituents), and with  $\alpha,\beta$ -unsaturated aldehydes. Our method is noteworthy in that it uses an aprotic catalyst under very mild conditions, and that the amount of catalyst used is minute. This allows ready purification of the resultant 1,1-diacetates **3** and indeed they can be used directly, without purification, for many reactions.

Although these aldehyde derivatives are not common functional groups they can have value in preparative organic chemistry. Thus, they are converted readily into the parent aldehyde<sup>5</sup> and are potential aldehyde protecting groups<sup>4a,6</sup>. Furthermore, they can be induced to lose acetic acid, especially when the product is an 1-acetoxy-1,3-diene, often a valued component of Diels-Alder cycloaddition reactions<sup>7</sup>.

<sup>2</sup> This was the original catalyst and is still the most generally used reagent.

<sup>3</sup> F. Freeman, E. M. Karchevski, *J. Chem. Eng. Data* **22**, 355 (1977).

<sup>4</sup> (a) I. Scriabine, *Bull. Soc. Chim. Fr.* **1961**, 1194.

(b) F. O. Cockerille, *U. S. Patent* 2264789 (1941); *C. A.* **36**, 1620 (1942).

<sup>5</sup> This reaction has been the subject of a number of mechanistic studies, e.g.:

(a) R. P. Bell, B. Lukianenko, *J. Chem. Soc.* **1957**, 1686.

(b) P. Salomaa, *Acta Chem. Scand.* **11**, 247 (1957).

(c) M. J. Gregory, *J. Chem. Soc. [B]* **1970**, 1201.

<sup>6</sup> This is the basis of the preparation of aromatic aldehydes from the corresponding toluenes, e.g. S. V. Liebermann, R. Connor, *Org. Syn. Coll. Vol.* **III**, 441 (1955).

<sup>7</sup> (a) G. Saucy, R. Marbet, H. Lindlar, O. Isler, *Helv. Chim. Acta* **42**, 1945 (1959).

(b) B. B. Snider, S. G. Amin, *Synth. Commun.* **8**, 117 (1978).

(c) R. Banks et al., *J. Chem. Soc. Perkin Trans. 1* **1981**, 1096.

<sup>8</sup> N. S. Vul'fson, *Zh. Obshch. Khim.* **20**, 425 (1950); *C. A.* **45**, 557 (1951).

<sup>9</sup> *Dictionary of Organic Compounds*, 4th Edn., Vol. 3, Eyre and Spottiswoode, London, 1965, p. 1478.