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A Rapid and Convenient Synthesis of 1,1-Diacetates from Aldehydes and Acetic Anhydride Catalyzed by PVC-$FeCl_3$ Catalyst

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A RAPID AND CONVENIENT SYNTHESIS OF 1,1-DIACETATES FROM ALDEHYDES AND ACETIC ANHYDRIDE CATALYZED BY PVC-$FeCl_3$ CATALYST

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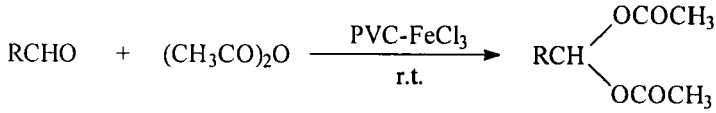
Abstract: A variety of aldehydes can be converted into 1,1-diacetates rapidly and conveniently in the presence of catalytic amounts of poly(vinyl chloride) supported ferric chloride reagent at room temperature in excellent yields.

1,1-diacetaes are synthetically useful for protecting aldehyde groups owing to their moderate stability in neutral or basic media and easy formation as well as deprotection.[1] The 1,1-diacetaes of α,β -unsaturated aldehydes are also an important building blocks for the synthesis of dienes in Diels-Alder cycloaddition reactions.[2]

The preparation of 1,1-diacetates from aldehydes and acetic anhydride using Brønsted acids and Lewis acids as catalysts has been known for a long time. However these methods are not entirely satisfactory, due to such drawbacks as low yields, long reaction time, the environmental problems and tedious work-up, etc. In recent years, several catalysts have been employed for this reaction to

improve the yields, to decrease reaction time and eliminate the unfavorable effects mentioned. Iodine,[3] expansive graphite,[4] Y-zeolite,[5] β-zeolite,[6] Nafion-H,[7] Sulfate zirconia,[8] HZSM-5,[9] montmorilllonite clay[10] and Fe^{3+}-montmorillonite,[11] etc. have been relatively successfully used as catalyst for the synthesis of 1,1-diacetates. However, problems of a long reaction time, high reaction temperature and/or low yields occasionally present. Consequently, there is a need for developing an efficient and convenient catalytic method for the reaction using inexpensive and non-polluting reagent.

Polymer supported reagents used as catalysts have gained wide interest in recent years. This is primarily because polymeric reagents can expand the range of applicable solvents, provide convenience of work-up and product purification, lower the environmental hazards, and in most case provide for recovery and reuse of polymer supported reagent. Herein we first report a poly(vinyl chloride) supported ferric chloride (PVC-$FeCl_3$) catalyzed rapid, convenient and general synthesis of 1,1-diacetates from aldehydes and acetic anhydride (scheme 1).



1 **2**

Scheme 1

The synthesis of 1,1-diacetate is performed at room temperature in the presence of catalytic amount of PVC-$FeCl_3$ and produces the desired products in excellent yields. After 5 times of repeated use, no decrease in the activity of the catalyst is observed. The results are summarized in table 1.

Table 1 Conversition of aldehydes into 1,1-diacetates catalyzed by PVC-$FeCl_3$

Aldehydes (1) R	1,1-Diacetates[a] (2) R	Time (min)	Yield[b] (%)	Acetal CH chemical shift (ppm)
CH_3**(1a)**	CH_3**(2a)**	5	80	6.78
$CH_3(CH_2)_2$**(1b)**	$CH_3(CH_2)_2$**(2b)**	15	85	6.50
CH_2=CH**(1c)**	CH_2=CH**(2c)**	10	75	7.03
(E)-CH_3CH=CH**(1d)**	(E)-CH_3CH=CH**(2d)**	10	84	6.70
(E)-PhCH=CH**(1e)**	(E)-PhCH=CH**(2e)**	10	88	7.33
4-MeC_6H_5**(1f)**	4-MeC_6H_5**(2f)**	10	95	7.64
C_6H_5**(1g)**	C_6H_5**(2g)**	10	93(91)[c]	7.69
4-ClC_6H_5**(1h)**	4-ClC_6H_5**(2h)**	15	91	7.64
4-BrC_6H_5**(1i)**	4-BrC_6H_5**(2i)**	15	92	7.64
2-$NO_2C_6H_5$**(1j)**	2-$NO_2C_6H_5$**(2j)**	20	87	8.21
4-$NO_2C_6H_5$**(1k)**	4-$NO_2C_6H_5$**(2k)**	20	90	7.74
2-Furyl**(1l)**	2-Furyl**(2l)**	10	82	7.71

[a]All the products give satisfactory spectral analysis for IR, ^{1}H NMR and MS.

[b]Isolated yields.

[c]yield in parenthesis obtained from the catalyst after five experiments

In conclusion, our result confirm that the PVC-$FeCl_3$ reagent can offer definite advantages over the traditional catalysts in terms of activity, ease of separation, mild reaction condition and higher yields. Moreover, it can be reused.

Experimental

Boiling points and melting points are uncorrected. Infrared spectra were recorded using KBr pellet on a Perkin-Elmer 16PC spectrometer. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker ARX 300 (300MHz) instrument with TMS

as an internal standard. Mass spectra were obtained on a Finnigan Mat TSQ7000 spectrometer.

Preparation of PVC-$FeCl_3$

Commercially available poly(vinyl chloride) (20g) was dissolved in dichloromethane (1000ml). Anhydrate ferric chloride (100g) was added in one portion to the refluxing mixture. The result mixture was refluxed for additional 2h until there were black precipitate appeared. The precipitate was filtered off and washed with water, acetone and diethyl ether. Then 25g of dry PVC-$FeCl_3$ was obtained after dried in vacuum. The capacity of ferric chloride was found to be 1.54mmol/g of dry resin by titration.

General procedure for the preparation of 1,1-diacetates

A mixture of the aldehyde (10mmol), acetic anhydride (50mmol) and PVC-$FeCl_3$ (200mg, 0.30mmol Fe^{3+}) was stirred at room temperature for the length of the time indicated in Table 1. The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was filtered off and washed with ether (10ml×3). The filtrate was washed with brine and then dried over anhydride sodium sulfate. Evaporation of the solvent under reduce pressure afford the corresponding product which was subsequently chromatographied over silica or crystallized from petroleum ether (40~60°C) to give pure products.

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