A Facile and Efficient Conversion of Aldehydes into 1,1-Diacetates (Acylals) using Iron(III) Fluoride as a Novel Catalyst

V. T. Kamble,^{A,D} R. A. Tayade,^B B. S. Davane,^C and K. R. Kadam^A

^AOrganic Chemistry Research Laboratory, School of Chemical Sciences, Swami Ramananad

Teerth Marathwada University, Nanded 431 606, M.S., India.

^BDepartment of Chemistry, Institute of Science, Nagpur, M.S., India.

^CDepartment of Chemistry, Yeshwant College, Nanded, M.S., India.

^DCorresponding author. Email: vtkd@rediffmail.com

Aldehydes are smoothly converted into the corresponding 1,1-diacetates (acylals) in high yields in the presence of a catalytic amount (0.1 mol-%) of iron(III) fluoride at room temperature. The noteworthy features of the present system are shorter reaction times, chemoselective protection of aldehydes, and solvent-free conditions. The procedure is especially useful for large-scale syntheses as the catalyst is highly effective from the view of activity, selectivity, reusability, and economy in the preparation of 1,1-diacetates (acylals).

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Introduction

Since protective groups play an important role in the multistep synthesis of complex natural products, there are always demands for selective reagents. Among the various functional groups, protection of the carbonyl group as a 1,1-diacetate (acylal) is important for the following reasons. First, they are stable under neutral and mild conditions^[1] and are easily converted into the parent aldehydes.^[2] Second, they are used as building blocks for the synthesis of dienes^[3] and cross-linking reagents for cellulose in cotton.^[4] Hence, methods for their synthesis have received considerable attention. In the literature, there are many methods reported for the preparation of 1,1diaceates (acylals) from aldehydes and acetic anhydride that employ protic acids, such as sulfuric,^[5a] methanesulfonic,^[5b] phosphoric,^[5c] or perchloric acid^[5d] and Lewis acids, such as PCl₃,^[6a] ZnCl₂,^[6b] TMSCI-Nal,^[6c] I₂,^[6d] FeCl₃,^[6e] NBS,^[6f] anhydrous ferrous sulfate,^[6g] LiBr,^[6h] InCl₃,^[6i] WCl₆,^[6j] CAN,^[6k] LiBF₄,^[6] and CoCl₂.^[6m] Some heterogeneous cat-alysts like clay,^[7a,b] zeolites,^[2a,7c,d] Nafion-H,^[7e] expansive graphite,^[7f] and supported reagents^[7g-i] are also used. But these procedures are often accompanied by low product vields, longer reaction times, stringent conditions, corrosive reagents, high catalyst loading, high temperature, and require the use of toxic solvents. Recently, other methods that employ catalysts like $ZrCl_4$,^[8] $Zn(BF_4)_2$,^[9] $Fe_2(SO_4)_3 \cdot xH_2O$,^[10] $Bi(NO_3)_3 \cdot 5H_2O$,^[11] $Cu(BF_4)_2 \cdot xH_2O$,^[12] $KHSO_4$,^[13] $InBr_3$,^[14] 2,4,4,6-tetrabromo-2,5-cyclohexadienone,^[15] $AlPW_{12}O_{40}$,^[16] $\begin{array}{l} Mg(ClO_{4})_{2}, ^{[17]} Zn(ClO_{4})_{2}, ^{[18]} [Zr(CH_{3}PO_{3})_{1.2}(O_{3}PC_{6}H_{4}SO_{3} \\ H)_{0.8}], ^{[19]} H_{2}NSO_{3}H, ^{[20]} silica sulfuric acid, ^{[21]} and triflates, such as Sc(OTf)_{3}, ^{[2b]} Cu(OTf)_{2}, ^{[22]} LiOTf, ^{[23]} and Er(OTf)_{3}, ^{[24]} \end{array}$ have been reported for the synthesis of acylals. However, the former catalysts^[8–13,15–21] are required in large amounts where



as the later triflates^[2b,22-24] are costly, moisture sensitive, and special efforts are required for their preparation. In some of the reported methods,^[23] a large excess of acetic anhydride (5– 8 equiv.) is essential for the 1,1-diacetate (acylal) formation. Moreover, only a few reports are available for the acylation of aldehydes using low catalyst loading (0.1 mol-%).^[14,24] Therefore, an environmentally benign reagent that can catalyze this transformation with low catalyst loading, is still desirable.

Results and Discussion

Although iron(III) chloride has been used widely as a Lewis acid catalyst in a variety of organic transformations,^[6e,25] the susceptibility to aqueous media impedes its use for large-scale synthesis. On the other hand, iron(III) fluoride has emerged as a mild, non-toxic, inexpensive, and water-tolerant Lewis acid catalyst for various organic transformations.^[26a–c] However, there have been no reports on the use of iron(III) fluoride for the synthesis of 1,1-diacetates (acylals) from aldehydes under solvent-free conditions. In a continuation of our work to apply iron(III) fluoride to organic reactions in the context of green and economical chemistry, herein, we report a facile synthesis of 1,1-diacetates (acylals) using a small amount of iron(III) fluoride (0.1 mol-%) without any solvent (Scheme 1).

To optimize the reaction conditions, initially, we tried to convert benzaldehyde (1 mmol) into its corresponding acylal with iron(III) fluoride (0.1 mol-%) and acetic anhydride (3 mmol) in

Table 1. The results of the reaction of benzaldehyde (1 mmol) with acetic anhydride (3 mmol) under different reaction conditions

Entry	Catalyst ^A	Solvent ^B	Time [min]	Yield ^C [%]
1	None	None	6 ^D	0
2	FeF ₃	MeCN	90	72
3	FeF ₃	THF	90	70
4	FeF ₃	CH_2Cl_2	90	65
5	FeF ₃	Et ₂ O	90	60
6	FeF ₃	None	5	97

^AThe reaction was carried out in the presence of FeF₃ (0.1 mol-%).

^BThe reaction was carried out in 5 mL of solvent at room temperature.

^CYield of pure isolated product.

^DTime in hours.

the presence of various solvents and also under solvent-free conditions. As shown in Table 1, in comparison to conventional methods (Table 1, entries 2–5), the yield of the reaction under solvent-free conditions in the presence of FeF₃ (0.1 mol-%) is higher and the reaction time is shorter (Table 1, entry 6). However, under solvent-free conditions without catalyst, benzaldehyde did not give any product even after 6 h (Table 1, entry 1).

The reaction of benzaldehyde (10 mmol) with acetic anhydride (30 mmol) in the presence of iron(III) fluoride (0.1 mol-%) at room temperature afforded the corresponding 1,1-diacetate (acylal) in excellent yield (97%). The catalyst was recovered and reused five consecutive times to give excellent yields. The reusability of iron(III) fluoride was examined by using benzaldehvde as a model substrate and the results are described in the typical experimental procedure. The results as summarized in Table 2 clearly reveal the scope and generality of the reaction with respect to a variety of aliphatic and aromatic aldehydes. The aliphatic (Table 2, entries 9-11), aromatic (Table 2, entries 1–8), and α , β -unsaturated (Table 2, entries 17–18) aldehydes can be efficiently transformed into their corresponding 1,1diacetates (acylals). The tolerance of various functional groups under the present conditions have been examined by reacting substrates that bear Cl, F, Me, OMe, CN, and NO2 groups, and it was found that reaction conditions are compatible with these functional groups. Acid sensitive substrates like furfural, thiophene-2-aldehyde (Table 2, entries 15-16) are also protected as 1,1-diacetates (acylals) in excellent yields without any side reactions, which are normally encountered under acidic conditions. It is noteworthy that substrates that have acid sensitive protecting groups such as O-TBDMS, O-allyl, OPNB, OBz, -OCH2O-, OPh, OBn, NHBoc, and OTIPS (Table 2, entries 20-27) were converted into their acylals without cleavage, which is normally observed in strong acidic medium. The present reaction conditions work equally well for naphthaldehydes (Table 2, entries 12-13) and anthraldehyde (Table 2, entry 14) to afford excellent yields of the corresponding 1,1-diacetates (acylals) although the time required for conversion is slightly longer. In almost all cases, the reactions are quicker than those of the recently reported methods and the yields are quite high. 4-(Dimethylamino)benzaldehyde (Table 2, entry 28), however, because of deactivation of the carbonyl group, remained unaffected even when the reaction mixture was stirred at room temperature for 20 h, and the starting material was quantitatively recovered.

The utility of the present method was then extended by employing it in the formation of other *gem*-dicarboxylates.

Table 2. Iron(III) fluoride catalyzed synthesis of acylals

Entry	Substrate	Time [min]	Yield ^{A,B} [%]	Ref.
1	C ₆ H ₅ CHO	5	97	[20]
2	4-ClC ₆ H ₄ CHO	10	96	[20]
3	4-FC ₆ H ₄ CHO	10	98	[14]
4	4-MeC ₆ H ₄ CHO	10	98	[14]
5	4-MeOC ₆ H ₄ CHO	15	95	[14]
6	4-CNC ₆ H ₄ CHO	10	96	[21]
7	4-NO ₂ C ₆ H ₄ CHO	10	98	[20]
8	3-NO ₂ C ₆ H ₄ CHO	10	97	[20]
9	n-C ₃ H ₇ CHO	15	96	[6d]
10	<i>n</i> -C ₅ H ₁₁ CHO	20	95	[6e]
11	n-C7H15CHO	20	94	[5b]
12	1-C ₁₀ H ₇ CHO	35	94	[12]
13	2-C ₁₀ H ₇ CHO	35	95	[6m]
14	1-C ₁₄ H ₉ CHO	40	93	[6m]
15	2-Furaldehyde	10	96	[21]
16	Thiophene-2-carboxaldehyde	10	95	[1b]
17	(E)-PhCH=CHCHO	10	98	[21]
18	(E)-MeCH=CHCHO	10	97	[6a]
19	CH ₂ CH=CHCHO	10	97	[5b]
20	4-(OTBDMS)C ₆ H ₄ CHO	10	96	[2i]
21	3-(O-Allyl)C ₆ H ₄ CHO	8	95	_
22	3-(OPNB)C ₆ H ₄ CHO	10	98	[9]
23	3-(OBz)C ₆ H ₄ CHO	15	96	[2i]
24	3,4-(OCH2O)C6H3CHO	10	96	[14]
25	3-(OPh)C ₆ H ₄ CHO	20	97	[6a]
26	4-(NHBoc)C ₆ H ₄ CHO	15	92	[8]
27	4-(OTIPS)C ₆ H ₄ CHO	15	93	[8]
28	4-NMe ₂ C ₆ H ₄ CHO	_C	_D	_

^AYield of pure isolated product.

^BProducts were characterized by spectroscopic analysis.

^CTime in minutes.

^DThe starting material remained intact.

 Table 3. Conversion of benzaldehyde into geminal dicarboxylates with acid anhydrides

Aldehyde	Anhydride (RCO) ₂ O	Time [min]	Yield ^A [%]
РНСНО	$R = C_3H_7$	90	85
РНСНО	$R = i - C_3 H_7$	120	80
РНСНО	$R = i - C_4 H_9$	120	80

^AYield of pure isolated product.



Scheme 2.

Acylation of benzaldehyde with propionic, butyric, and *iso*butyric anhydrides resulted in 80–85% yields of the *gem*dicarboxylates (Table 3).

Next, we investigated the competitive reaction for the acylation of benzaldehyde in the presence of cyclohexanone. When a 1 : 1 mixture of benzaldehyde and cyclohexanone was allowed to react with acetic anhydride in the presence of 0.1 mol-% FeF₃ for 5 min, TLC analysis of the reaction mixture indicated complete disappearance of the benzaldehyde, while cyclohexanone remained intact, even when the mixture continued to stir for 5 h (Scheme 2). Also, in the case of acetyl benzaldehyde, the



Scheme 3.

 Table 4.
 Comparison of the effect of catalysts in the acylation of 4-nitrobenzaldehyde (1 equiv.) as an example

Catalyst	Catalyst load [mol-%]	Time [min]	Yield ^A [%]
ZrCl ₄	5	30	92 ^[8]
$Zn(BF_4)_2$	0.6	3 ^B	93[9]
$Fe_2(SO_4)_3 \cdot xH_2O$	2	1.5^{B}	85 ^[10]
$Cu(BF_4)_2 \cdot xH_2O$	1	3	92 ^[12]
InBr ₃	0.1	0.1	99 ^[14]
Sc(OTf) ₃	2	10	99 ^[2b]
Cu(OTf) ₂	2.5	4^{B}	94 ^[22]
LiOTf	20	15^{B}	99 ^[23]
AlPW12O40	0.1	45	89[16]
FeF ₃	0.1	10	99

^AYield of pure isolated product.

^BTime in hours.

aldehyde group was converted into the corresponding diacetate, while the ketone functionality remained unaffected (Scheme 3). This result suggests that the present protocol is useful for carrying out similar chemoselective reactions.

Furthermore, we studied the catalytic ability of other iron salts such as FeCl₃, FeBr₃, and FeI₃ for the synthesis of 1,1diacetates (acylals). Among these catalysts, FeF₃ is found to be more effective than the aforementioned catalysts. By using 0.1 mol-% of FeCl₃, FeBr₃, and FeI₃, benzaldehyde was converted into the corresponding 1,1-diacetate (acylal) in 50, 45, and 40% yield, respectively, when the reaction mixture was stirred for 30 min. This result clearly shows the strong catalytic ability of FeF₃ in comparison with FeCl₃, FeBr₃, and FeI₃. The catalyst FeF₃ shows better activity in comparison with FeCl₃, FeBr₃, and FeI₃, because of high activation of the carbonyl group.

While comparing the effect of catalysts on the acylation of 4-nitrobenzaldehyde, we found that FeF_3 is more efficient than some of the recently reported catalysts in terms of the amount of catalyst used, yields, and reaction times (Table 4).

In conclusion, iron(III) fluoride is a highly efficient and practical catalyst for the conversion of aldehydes into 1,1-diacetates (acylals). The advantages include the low cost, ease of catalyst handling, mild reaction conditions, short reaction times, and excellent chemoselectivity. Moreover, the solvent-free condition employed in the present method should make it 'environmentally friendly' and useful for industrial applications.

Experimental

Typical Experimental Procedure

A mixture of benzaldehyde (10 mmol) and freshly distilled Ac_2O (30 mmol) was stirred at room temperature in the presence of a catalytic amount of iron(III) flouride (0.01 mmol) for an appropriate time (Table 1). After completion of the reaction, as indicated by TLC, the reaction mixture was quenched with water and extracted with ethyl acetate. After being washed with aqueous

NaHCO₃ and brine, the organic layer was dried over Na₂SO₄. Evaporation of the solvent under reduced pressure gave almost pure product. Further purification was achieved by column chromatography or recrystallization from ethyl acetate/hexane to afford pure acetoxyphenylmethyl acetate (97%), identical (mp, IR, and ¹H NMR) to an authentic sample. The recovered catalyst was activated by heating at 100°C under vacuum for 2 h and reused for the acylation of a fresh lot of benzaldehyde (10 mmol) to afford 89% yield of acetoxyphenylmethyl acetate after 10 min. After activation, the recovered catalyst was reused for four more consecutive acylation reactions of benzaldehyde (10 mmol) to afford 88, 85, 83, and 80% yields in 15, 20, 25, and 30 min, respectively.

Spectroscopic Data for Some Compounds

Entry 1.

Mp 43–44°C (lit.^[20] 44–45°C). ν_{max} (KBr)/cm⁻¹ 700, 760, 1010, 1065, 1215, 1245, 1375, 1470, 1605, 1750, 3060. $\delta_{\rm H}$ 2.02 (s, 6H), 7.37–7.40 (m, 3H), 7.50–7.53 (m, 2H), 7.70 (s, 1H).

Entry 2.

Mp 81–82°C (lit.^[20] 82–83°C). ν_{max} (KBr)/cm⁻¹ 620, 780, 1010, 1210, 1375, 1480, 1605, 1760, 3020, 3060. $\delta_{\rm H}$ 2.12 (s, 6H), 7.38–7.42 (m, 2H), 7.43–7.46 (m, 2H), 7.65 (s, 1H).

Entry 3.

Mp 51–52°C (lit.^[14] 50–51°C). ν_{max} (KBr)/cm⁻¹ 630, 775, 1015, 1215, 1475, 1605, 1755, 3020, 3055. $\delta_{\rm H}$ 2.13 (s, 6H), 7.40–7.42 (m, 2H), 7.45–7.47 (m, 2H), 7.67 (s, 1H).

Entry 4.

Mp 81–82°C (lit.^[14] 82–83°C). ν_{max} (KBr)/cm⁻¹ 625, 780, 1015, 1210, 1250, 1490, 1650, 1755, 3020, 3055. $\delta_{\rm H}$ 2.14 (s, 6H), 2.40 (s, 3H), 7.22 (d, *J* 8.0, 2H), 7.42 (d, *J* 8.0, 2H), 7.68 (s, 1H).

Entry 5.

Mp 63–64°C (lit.^[14] 64–65°C). ν_{max} (KBr)/cm⁻¹ 925, 990, 1220, 1245, 1670, 1765, 3010, 3050. $\delta_{\rm H}$ 2.10 (s, 6H), 3.75 (s, 3H), 7.45–7.47 (m, 2H), 7.48–7.51 (m, 2H), 7.68 (s, 1H).

Entry 6.

Mp 101–102°C (lit.^[21] 100–102°C). ν_{max} (KBr)/cm⁻¹ 815, 1010, 1220, 1250, 1385, 1490, 1765, 2225, 3070. $\delta_{\rm H}$ 2.13 (s, 6H), 7.50–7.55 (m, 2H), 7.60–7.65 (m, 2H), 7.67 (s, 1H).

Entry 7.

Mp 124–126°C (lit.^[20] 125–127°C). ν_{max} (KBr)/cm⁻¹ 850, 955, 995, 1090, 1200, 1210, 1345, 1535, 1615, 1765, 2225, 3095. $\delta_{\rm H}$ 2.10 (s, 6H), 7.55 (d, *J* 9, 2H), 8.0 (d, *J* 9, 2H), 7.50 (s, 1H).

Entry 8.

Mp 64–65°C (lit.^[20] 65–66°C). ν_{max} (KBr)/cm⁻¹ 735, 820, 955, 1040, 1090, 1200, 1230, 1535, 1755, 3095. $\delta_{\rm H}$ 2.12 (s, 6H), 7.52–7.78 (m, 3H), 8.1 (d, *J* 7.2, 1H), 8.22 (s, 1H).

Entry 10.

Liquid (128–129/2).^[6e] ν_{max} (neat)/cm⁻¹ 650, 990, 1015, 1090, 1205, 1235, 1375, 1460, 1750, 2960. $\delta_{\rm H}$ 1.02 (t, *J* 5.6, 3H), 1.25–1.80 (m, 8H), 2.05 (s, 6H), 6.68 (s, 1H).

Entry 12.

Mp 90–91°C (lit.^[12] 90–92°C). ν_{max} (KBr)/cm⁻¹ 950, 995, 1090, 1210, 1535, 1615, 1755, 3095. $\delta_{\rm H}$ 2.11 (s, 6H), 7.45–7.60 (m, 3H), 7.75 (d, *J* 7.0, 1H), 7.85–7.90 (m, 2H), 8.25–8.30 (m, 2H).

Entry 13.

Mp 100–102°C (lit.^[6m] 101–102°C). ν_{max} (KBr)/cm⁻¹ 955, 1005, 1095, 1215, 1530, 1670, 1755, 3095. $\delta_{\rm H}$ 2.14 (s, 6H), 7.51 (t, 2H), 7.61 (d, 1H), 7.85 (s, 1H), 7.86–7.93 (m, 3H), 8.04 (s, 1H).

Entry 14.

Mp 196–197°C (lit.^[6m] 197–198°C). ν_{max} (KBr)/cm⁻¹ 950, 1005, 1090, 1220, 1530, 1665, 1750, 3085. $\delta_{\rm H}$ 2.15 (s, 6H), 7.51 (t, 2H), 7.58 (t, 2H), 8.01 (d, *J* 8.2, 2H), 8.54 (s, 1H), 8.64 (d, *J* 8.0, 2H), 9.22 (s, 1H).

Entry 15.

Mp 52–54°C (lit.^[21] 51–53°C). ν_{max} (KBr)/cm⁻¹ 755, 790, 935, 960, 1015, 1060, 1150, 1225, 1370, 1500, 1610, 1750, 3125, 3160. $\delta_{\rm H}$ 2.15 (s, 6H), 6.40–6.42 (m, 1H), 6.55 (d, *J* 3.4, 1H), 7.45 (s, 1H), 7.75 (s, 1H).

Entry 16.

Mp 65–66°C (lit.^[1b] 66–67°C). ν_{max} (KBr)/cm⁻¹ 855, 1015, 1245, 1465, 1750, 1765, 2950, 3025. $\delta_{\rm H}$ 2.15 (s, 6H), 7.10 (dd, *J* 5.2, 4.6, 1H), 7.32 (d, *J* 4.4, 1H), 7.40 (d, *J* 4.4, 1H), 7.85 (s, 1H).

Entry 17.

Mp 84–85°C (lit.^[21] 84–86°C). ν_{max} (KBr)/cm⁻¹ 695, 750, 945, 1010, 1110, 1210, 1245, 1375, 1490, 1610, 1655, 1765, 2930, 3090. $\delta_{\rm H}$ 2.12 (s, 6H), 5.92 (dd, *J* 16.0, 1H), 6.85 (d, *J* 16, 1H), 7.63–7.13 (m, 6H).

Entry 20.

Mp 91–92°C (lit.^[2i] 91–94°C). ν_{max} (KBr)/cm⁻¹ 690, 955, 1010, 1165, 1210, 1239, 1371, 1515, 1610, 1655, 1767, 2935. $\delta_{\rm H}$ 0.28 (s, 2H), 0.95 (s, 9H), 2.07 (s, 6H), 6.65 (d, *J* 8.2, 2H), 7.03 (d, *J* 8.2, 2H), 7.60 (s, 1H).

Entry 21.

Mp 39–40°C (lit.^[6a] 40–41°C). ν_{max} (KBr)/cm⁻¹ 925, 1010, 1165, 1210, 1250, 1370, 1430, 1525, 1625, 1767, 2990, 3035. $\delta_{\rm H}$ 2.10 (s, 6H), 4.55 (d, *J* 5.2, 2H), 5.30 (d, *J* 10.2, 1H), 5.45 (d, *J* 16.2, 1H), 5.95–6.10 (m, 1H), 6.95 (d, *J* 8.2, 2H), 7.45 (d, *J* 8.2, 2H), 7.60 (s, 1H).

Entry 23.

Mp 52–54°C (lit.^[2i] 52–55°C). ν_{max} (KBr)/cm⁻¹ 825, 1010, 1167, 1225, 1375, 1511, 1605, 1750, 2930. $\delta_{\rm H}$ 2.12 (s, 6H), 5.15 (s, 2H), 7.11 (d, *J* 8.2, 2H), 7.42 (m, 5H), 7.63 (s, 1H), 7.80 (d, *J* 8.2, 2H).

Entry 24.

Mp 79–80°C (lit.^[14] 78–79°C). ν_{max} (KBr)/cm⁻¹ 790, 825, 930, 1005, 1040, 1150, 1225, 1365, 1445, 1490, 1605, 1755, 2955. $\delta_{\rm H}$ 2.03 (s, 6H), 5.85 (s, 2H), 6.65 (m, 3H), 7.50 (s, 1H).

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