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An Efficient and Green Procedure for the Preparation of *gem*-Dicarboxylates from Aldehydes Catalyzed by $Fe_2(SO_4)_3{\cdot}xH_2O$

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Abstract: An efficient and environmentally benign conversion of aldehydes into the corresponding *gem*-dicarboxylates was realized by using hydrated ferric sulfate as a heterogeneous catalyst. In addition to its high efficiency, the catalyst can be recovered simply and reused efficiently for at least seven times.

Keywords: *gem*-Dicarboxylates, hydrated ferric sulfate, protection of aldehydes, green chemistry.

Conversion of aldehydes into their corresponding *gem*-dicarboxylates is gaining importance in organic synthesis. This is due to the stability of *gem*-dicarboxylates in neutral as well as in moderate acidic media, which makes acylals complementary to acetals as carbonyl protecting groups[1]. In addition, *gem*-dicarboxylates are also important starting materials in organic synthesis, especially for the preparation of acyloxydienes and vinyl acetates through Diels-Alder reactions[2]. As a result, many methods have been examined for this transformation and they usually necessitate the use of strong protic acids[3] or Lewis acids[4] as catalysts. Recently, $Sc(OTf)_3$[5a], $LiBF_4$[5b] and WCl_5[5c] have also been employed for this purpose. However, these methods have not been entirely satisfactory because the use of conventional Bronsted or Lewis acid catalysts as well as excess organic solvents usually entails the problems of corrosiveness, tedious work-up and effluent pollution. Therefore, there are still genuine needs for the development of efficient and environmentally benign catalytic methods for this transformation by using inexpensive and non-pollution reagents.

As a continuation of our research work in using $Fe_2(SO_4)_3{\cdot}xH_2O$ as a mild, efficient and heterogeneous Lewis acid in organic synthesis[6], herein we wish to report an efficient and green procedure for the conversion of aldehydes into *gem*-diacetates catalyzed by hydrated ferric sulfate (shown in **Scheme 1**).

When a mixture of benzaldehyde (10 mmol), acetic anhydride (12 mmol) and catalytic amount of $Fe_2(SO_4)_3{\cdot}xH_2O$ (0.10 g, 0.2 mmol) was stirred in a flask at ambient temperature, exothermic reaction took place immediately. Several minutes later, the

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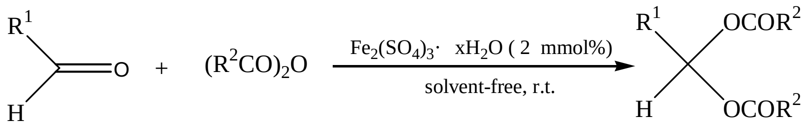
temperature of the reaction mixture fell down to r. t. and the mixture solidified. At this stage, TLC analysis showed that benzaldehyde has been completely consumed and the corresponding benzal diacetate was formed. Thus, 1 mL CH_2Cl_2 was added to the mixture to dissolve the product and the catalyst remains as a solid. The catalyst was filtered off and subsequent removal of the solvent under reduced pressure, the corresponding benzal diacetate was obtained in 97% yield. In a similar manner, other substrates with various substitution types also reacted smoothly with acetic anhydride and afford the corresponding acylals in fairly good yields (**Table 1**). The products were characterized by ^1H NMR, IR, MS and by comparison with authentic samples. In addition, it should be noted that when the catalytic reaction completed, $Fe_2(SO_4)_3{\cdot}xH_2O$ could be recovered conveniently from the reaction mixture through filtration and subsequent washing with CH_2Cl_2. Efforts on the examination of the reusability of $Fe_2(SO_4)_3{\cdot}xH_2O$ by using benzaldehyde as a model substrate showed that successive reuses of the recovered catalyst gave the product with yields almost as high as that of the first run. Even in the seventh run, the yield of product was 92%.

Scheme 1



R^1= aromatic or aliphatic group R^2= CH_3, CH_3CH_2

Table 1 Preparation of acylals catalyzed by $Fe_2(SO_4)_3{\cdot}xH_2O$

Entry	Substrate R^1	Mole ratio Substrate/anhydride	Reaction time (min)	Yield[a,b] (%)
1	C_6H_5	1:1.2	3	97
2	C_6H_5	1:1.2	15	97[c]
3	C_6H_5	1:1.2[d]	10	90
4	$C_6H_5CH{=}CH$	1:1.2	20	93
5	*p*-$MeOC_6H_4$	1:1.2	10	94
6	*p*-ClC_6H_5	1:3[e]	8	98
7	*o*-ClC_6H_5	1:3[e]	20	79
8	*m*,*p*-$(OCH_2O)C_6H_3$	1:2[e]	8	92
9	*p*-$NO_2C_6H_5$	1:2[e]	90	85
10	*m*-$NO_2C_6H_5$	1:3[e]	90	90
11	*p*-$OHCC_6H_5$	1:2.4	5	98[f]
12	*o*-HOC_6H_5	1:4	20	94[g]
13	*m*-MeO-*p*-HOC_6H_5	1:2	30	92
14	$CH_3CH{=}CH$	1:1.2	25	90
15	$CH_3CH_2CH_2$	1:1.2	30	85

[a] Isolated yields; [b] amount of catalyst used: 0.10 g; [c] amount of catalyst used: 0.02 g; [d] propionic anhydride was used; [e] excessive amount of anhydride used as solvents; [f] Yield of tetraacetate; [g] Yields of triacetate.

Several other Fe(Ⅲ) compounds, like $FeCl_3$[7], Fe^{3+}-montmorillonite[8] and PVC-$FeCl_3$[9], have also been used for this transformation. However, compared with above Fe(Ⅲ) compounds, the significant advantage of hydrated ferric sulfate is stable to air and moisture, easy operational, without any carrier and activation, as well as efficient and reusable. We predict that it will find useful application for the preparation of gem-diacetate in modern synthetic chemistry.

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References

1. T. W. Greene, P. G. M. Wuts, *Protective Groups in Organic Synthesis*, 3rd ed., Wiley, New York, **1999**, p.306.
2. R. E. Banks, J. A. Miller, M. J. Nunn, P. Stanley, *et al., J. Chem. Soc., Perkin Trans., 1* **1981**, 1096.
3. (a) M. Tomita, T. Kikuchi, K. Bessho, T. Hori, Y. Inubushi, *Chem. Pharm. Bull.,* **1963**, *11*, 1484.
   (b) W. Davey, J. R. Gwilt, *J. Chem. Soc*., **1957**, 1008.
4. (a) I. Scriabire, *Bull. Chem. Soc. Fr.,* **1961**, 1194.
   (b) J. K. Michie, J. A. Miller, *Synthesis*, **1981**, 824
5. (a) V. K. Aggarwal, S. Fonquerna, G. P. Vennall, *Synlett*, **1998**, 849.
   (b) N. Sumida, K. Nishioka, T. Sato, *Synlett*, **2001**, 1921..
   (c) B. Karimi, G. R. Ebrahimiam, H. Seradj, *Synth. Commun.*, **2002**, *32*, 669.
6. (a) G. Zhang, H. Gong, *Synth. Commun.*, **1999**, *29*, 1547.
   (b) G. Zhang, *Synth. Commun.*, **1999**, *29*, 607.
7. K. S. Kochhar, B. S. Bal, R. P. Deshpande, *et al., J. Org. Chem.*, **1983**, *48*, 1765.
8. T. S. Li, Z. H. Zhang, Y. J. Gao, *Synth. Commun.*, **1998**, *28*, 4665.
9. Y. Q. Li, *Synth. Commun*., **2000**, *30*, 3913.

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