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$ZrCl_4$ as an Efficient Catalyst for a Novel One-Pot Protection/Deprotection Synthetic Methodology

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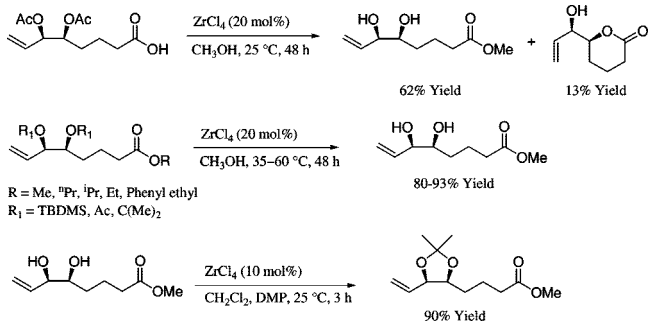
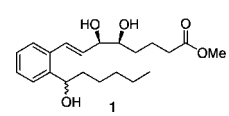
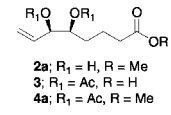


A catalytic quantity of $ZrCl_4$ (20 mol %) was found to be an efficient catalyst for the one-pot esterification and deprotection of (5*S*,6*R*)-5,6-diacetoxyoct-7-enoic acid in good yields (44−62%) with a lactone formed as a minor byproduct. $ZrCl_4$ (10−20 mol %) was also sufficient to deprotect 1,3-dioxalane, bis-TBDMS ethers, and diacetate functional groups in excellent yields of up to 93%. $ZrCl_4$ (1−10 mol %) also promoted diol protection as the acetonide in 90% yield and acted as a trans-esterification catalyst for a range of esters.

The protection or deprotection of a functional group is one of the most important and widely carried out synthetic transformations in preparative organic chemistry.[1] The use of acidic or basic conditions or hydrogenolysis are routinely used methods for the deprotection of phenolic and aliphatic esters.[1] Several catalyst systems are used for the deprotection of phenyl acetate, but these do not deprotect aliphatic acetates,[2] which can be deprotected using sodium methoxide at lower temperature[3] and by using organotin compounds[4a–c] [$^tBu_2SnOH(Cl)]_2$ or dibutyltin oxide, $Mg(OMe)_2$,[4d] $HClO_4-SiO_2$,[4e] and acetyl chloride.[4f] As part of our work on the development of compounds with potential for the resolution of inflammation, we recently reported the synthesis and biological evaluation of Lipoxin A_4 analogues of type **1**.[5] In our synthesis, we prepared (5*S*,6*R*)-methyl-5,6-dihydroxyoct-7-enoate **2a** as a key intermediate in a two-step procedure from (5*S*,6*R*)-5,6-diacetoxyoct-7-enoic acid **3** involving conversion of the acid to the methyl ester **4a** using diazomethane and subsequent diacetate deprotection under basic conditions at low reaction temperatures. In light of the ability of $ZrCl_4$ to catalyze a wide range of transformations,[6] including the esterification of acids, and its potential to promote acetate deprotection, we investigated its use in a one-pot conversion of (5*S*,6*R*)-5,6-diacetoxyoct-7-enoic acid **3** to (5*S*,6*R*)-methyl-5,6-dihydroxyoct-7-enoate **2a**.[7] We now wish to report in full the results of this investigation and related protection/deprotection studies employing $ZrCl_4$.





Our initial investigation employing $ZrCl_4$ (20 mol %) demonstrated that the desired one-pot procedure was indeed

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(5) O'Sullivan, T. P.; Vallin, K. S. A.; Shah, S. T. A.; Fakhry, J.; Maderna, P.; Scannell, M.; Sampaio, A. L. F.; Perretti, M.; Godson, C.; Guiry, P. J. *J. Med. Chem.* **2007**, *50*, 5894.

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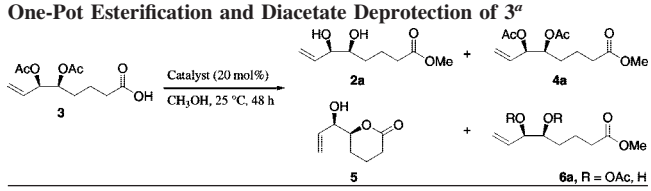
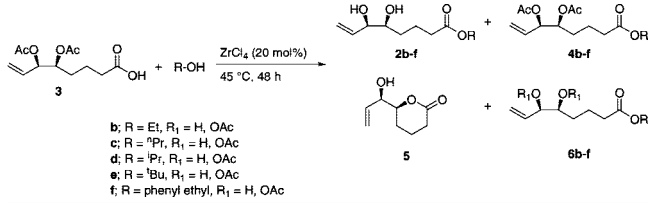
TABLE 1. Screening of Different Lewis Acid Catalysts for the One-Pot Esterification and Diacetate Deprotection of 3[a]



Entry	Catalyst	Distribution of isolated products (%)[b] 2a	4a	5	6a[e]
1	$ZrCl_4$	62		13	
2[c]	$ZrCl_4$	70		5	
3[d]	$ZrCl_4$	72		3	
4	$SnCl_2$		68		12
5	$Yb(OTf)_3$		37		30
6	$Cu(OTf)_2$		62		18
7	$FeCl_3$		55		15
8	$NH_4[Ce(NO_3)_4]$		23		24
9	CsF				
10	$ZnCl_2$				

[a] The catalyst (20 mol %) and acid **3** (0.4 mmol) were dissolved in 300 μL of MeOH and stirred for 48 h at 25 °C. [b] Isolated yield after purification by column chromatography. [c] The reaction was carried out at 60 °C for 8 h. [d] The reaction was carried out at 80 °C for 4 h. [e] Obtained as a mixture of 5-acetoxy-6-hydroxy-oct-7-enoic methyl ester and 6-acetoxy-5-hydroxy-oct-7-enoic methyl ester.

TABLE 2. Effect of Different Alcohols on the One-Pot Esterification and Diacetate Deprotection of 3[a]



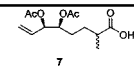
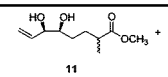
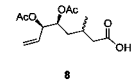
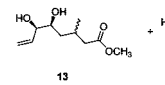
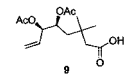
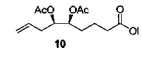
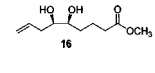
Entry	Alcohols	Distribution of isolated products (%)[b] 2b−f	4b−f	5	6b−f
1[c]	EtOH	44	27	5	
2	EtOH	54	10	13	
3	^{n}PrOH	61		5	
4	^{i}PrOH	40	21		18[d]
5	^{t}BuOH				
6	phenyl ethyl		50		

[a] The catalyst (20 mol %) and substrate 3 (0.4 mmol) were dissolved in 300 μL of MeOH and stirred for 48 h at 45 °C. [b] Isolated yield after purification by column chromatography. [c] The reaction was carried out at 25 °C. [d] Obtained as a mixture of 5-acetoxy-6-hydroxy-oct-7-enoic isopropyl ester and 6-acetoxy-5-hydroxy-oct-7-enoic isopropyl ester.

feasible, producing the required product **2a** in 62% yield, in addition to lactone **5** in 13% yield (Table 1, entry 1). We were able to increase the ratio of diol to lactone to a maximum of 72:3 by increasing the reaction temperature and decreasing the reaction time (entries 2 and 3). In addition, we have screened a range of Lewis acid catalysts in this model reaction and found that under identical reaction condition most of the catalysts were unable to deprotect the diacetate as required and instead provided methyl ester **4a** and mono deprotected diacetate **6a** as the major and minor products, respectively (entries 4−8). CsF and $ZnCl_2$ did not promote any reaction with substrate **3** (entries 9 and 10).

We have also tested the use of $ZrCl_4$ (20 mol %) for the one-pot esterification and diacetate deprotection of substrate **3** in the presence of a range of different aliphatic alcohols such as ethanol, *n*-propanol, isopropanol, and *tert*-butanol (Table 2).

TABLE 3. Use of $ZrCl_4$ for the One-Pot Esterification and Diacetate Deprotection of Different Diacetoxy Acids (7−10)[a]

Entry	Substrate[b]	Product	Isolated yield (%)[c] diol	lactone
1			48 (2:1)[d]	17 (2.1:1)[d]
2			59	11 (2.3:1)[d]
3			-	92
4			68	-

[a] The catalyst (20 mol %) and substrates **7**−**10** (0.4 mmol) were dissolved in 300 μL of MeOH and stirred for 48 h at 25 °C. [b] The diasteromeric ratio of substrate **7** and **8** was determined by ^{1}H NMR and found to be 1:1 and 0.9:1.1, respectively. [c] Isolated yield after purification by column chromatography. [d] The value in parenthesis refers to the diasteromeric ratio of products **11**, **12**, and **14** determined by ^{1}H NMR.

This afforded the corresponding esters **2b**−**e** in moderate to good yields (44−61%) with formation of lactone **5** (5−13%) and monoacetylated esters **6b**−**e** (entries 1−4). We observed that primary alcohols had increased reactivity toward esterification and deacylation compared to secondary alcohols, whereas tertiary alcohols did not undergo the required transformation at all (Table 2, entry 5).

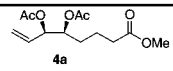
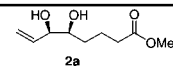
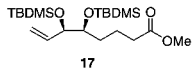
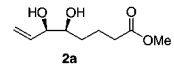
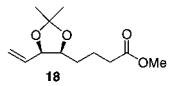
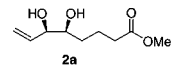
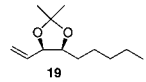
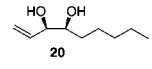
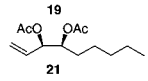
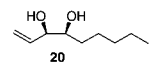
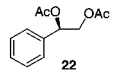
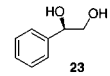
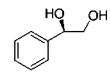
To extend our study, we have also investigated the one-pot esterification and deprotection of diacetate methodology and found it to be applicable to analogues of 5,6-diacetoxyoct-7-enoic acids (**7**−**10**), giving the corresponding dihydroxy esters and lactones (Table 3). The 2- and 3-methyl substituted 5,6-diacetoxyoct-7-enoic acids (**7** and **8**) were used as substrates for the esterification and diacetate deprotection using $ZrCl_4$ (20 mol %) as catalyst, providing dihydroxy esters **11** and **13** as the major products in 48−59% isolated yield, while lactones **12** and **14** were formed as byproducts in 11−17% yield. When we used (5*S*,6*R*)-5,6-diacetoxy-3,3-dimethyloct-7-enoicacid (**9**) as a substrate, we prepared the unexpected lactone **15** as a sole product in 92% isolated yield. We have also used (5*S*,6*R*)-5,6-diacetoxynon-8-enoic acid (**10**) as substrate and afforded 68% yield of desired product **16**.

Recently, we reported the chemoselective deprotection of TBS and bis-TBS ethers catalyzed by TMSBr.[8] We have also investigated the deprotection of a variety of bis-protected methyl esters possessing a variety of protecting groups (acetonide, diacetate, bis-TBDMS ethers) using $ZrCl_4$ (10−20 mol %) as catalyst (Table 4). The deprotection of diacetate methyl ester **4a** required 20 mol % $ZrCl_4$ under standard reaction conditions and provided **2a** in 87% yield with 6% yield of lactone **5** as byproduct within 36 h (Table 4, entry 1). In contrast, the selective deprotection of acetonide and bis-TBDMS protecting groups promoted by $ZrCl_4$ (10 mol %) provided 80−85% isolated yields of the desired product **2a** within 3−4 h, having

(7) The various 5,6-diacetoxyoct-7-enoic acid derivatives were synthesized according to reported procedure,[5] and the 2-bromoethyl-1,3-dioxanes were synthesized by using a reported method: Gérard, G. *Tetrahedron Lett.* **1984**, *35*, 3805 The spectroscopic data for all substrates are given in Supporting Information.

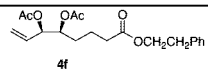
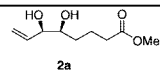
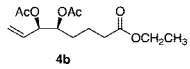
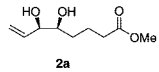
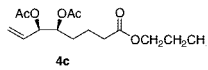
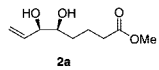
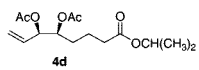
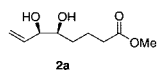
(8) Shah, S. T. A.; Guiry, P. J. *Org. Biomol. Chem.* **2008**, *6*, 2168.

TABLE 4. Deprotection of Various Protecting Groups Catalyzed by $ZrCl_4$[a]

Entry	Substrate	Product	Time (h)	Catalyst loading (mol%)	Isolated yield (%)[b]
1	 **4a**	 **2a**	36	20	87(6)[c]
2	 **17**	 **2a**	3	10	85(4)[c]
3	 **18**	 **2a**	4	10	80(1)[c]
4	 **19**	 **20**	3	10	80
5	 **21**	 **20**	6	20	89
6	 **22**	 **23**	4	20	90
7	 **24**	 **23**	3	10	93

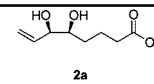
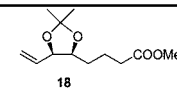
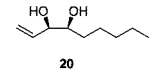
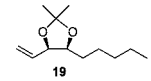
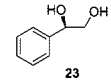
[a] The catalyst (10−20 mol %) and substrate (0.4 mmol) were dissolved in 300 μL of MeOH and stirred for the mentioned time at 35 °C. [b] Isolated yield after column chromatography. [c] The value in parenthesis refers to the ratio of lactonized product (**5**) determined by ^{1}H NMR.

TABLE 5. Transesterification of Different Esters Catalyzed by $ZrCl_4$ in Methanol[a]

Entry	Substrate	Product	Time (h)	Isolated yield (%)[b]
1	 **4f**	 **2a**	12	80
2	 **4b**	 **2a**	8	80
3	 **4c**	 **2a**	6	86
4	 **4d**	 **2a**	8	85

[a] The catalyst (20 mol %) and diol (0.5 mmol) were dissolved in 500 μL of MeOH and stirred for the indicated time at 60 °C. [b] Isolated yield after purification by column chromatography.

TABLE 6. Protection of Diol Using 2,2-Dimethoxypropane (DMP) as Protecting Reagent and $ZrCl_4$ as Catalyst[a]

Entry	Substrate	Product	Time (h)	Isolated yield (%)[b]
1	 **2a**	 **18**	3	90
2	 **20**	 **19**	2	92
3	 **23**	 **24**	2	94[c]
4			4	86[d]

[a] The catalyst (10 mol %) and diol (0.5 mmol) were dissolved in 2 mL of CH_2Cl_2 and stirred for mentioned time at 25 °C. [b] Isolated yield after purification by column chromatography. [c] The enantiomeric excess was determined chiral GC column, the ee was found to be 95%. [d] One mole percent of the catalyst was used under identical reaction conditions.

only 1−4% of lactone **5** as byproduct (Table 4, entries 2 and 3). $ZrCl_4$ (10−20%) was also able to deprotect a range of substrates possessing acetonide and acetate groups in excellent yields in 3−6 h (Table 4, entries 4−7).

During the one-pot esterification and diacetate deprotection of substrate **3** using phenylethanol, we observed the ester **4f** as the sole product. According to our initial investigations, methanol is a good choice of solvent for the deprotection of the diacetate functionality. Hence, the diacetate ester **4f** was treated with methanol using $ZrCl_4$ (20 mol %) as a catalyst, and compound **2a** was produced in 89% yield (Table 5, entry 1). These results reveal that $ZrCl_4$ could be used for the trans-esterification of the range of esters **4b**−**f**, e.g., ethyl, *n*-propyl, isopropyl, and phenyl ethyl (Table 5). $ZrCl_4$ (20 mol %) acts as a novel catalyst for the trans-esterification of the different esters and the deprotection of diacetate within 8−12 h in 80−86% isolated yields.

The protection of a 1,2-diol by a acetonide functionality is frequently used in carbohydrate and peptide chemistry because of its stability to mild acidic as well as basic conditions.[1] Classical acetonation of 1,2-diols has been achieved using acetone with various mineral acids, such as concentrated sulfuric acid or fuming HCl or phosphoric acid, in the presence or absence of Cu(II) sulfate or zinc chloride.[9] In addition, this condensation reaction can be performed by using other ac-

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etonide-forming agents, including 2,2-dimethoxypropane (DMP) and 2-methoxypropene (MP) in anhydrous solvents such as *N*,*N*-dimethylformamide (DMF) or dimethylsulfoxide with acid catalysis. So far, a diverse array of catalysts has been employed in the isopropylidenation of saccharides, including pyridinium *p*-toluenesulfonate (PPTS),[10] TESOTf,[11] HBF_4,[12] di-*p*-nitrophenyl hydrogen phosphate,[13] Lewis acidic metal salts (e.g., $ZnCl_2$,[14a] $AlCl_3$,[14b] ceric ammonium nitrate (CAN),[14c] $CuSO_4$,[14d] $FeCl_3$,[14e] $SnCl_2$,[14f] and PdX_2[14g]), iodine,[15] and heterogeneous media (e.g., ion exchange resins,[16a] morillonite clay,[16b] zeolites,[16c] and heteropolyacids (HPA)[16d]).

We have investigated our protocol for the protection of 1,2-diols by using dimethoxypropane (DMP) as a protecting reagent at room temperature with $ZrCl_4$ (10 mol %) as a novel catalyst in CH_2Cl_2, providing 90−94% isolated yields within 2−3 h (Table 6). The use of 1 mol % of catalyst still afforded a good yield (Table 6, entry 4). The dioxalane protection of 1,2-phenylethane diol (ee, 95%) was provided 1,3-dioxalane in an excellent yield without affecting the stereochemistry.

In summary, we have developed an efficient one-pot method for the esterification and deprotection of diacetates using $ZrCl_4$ as a catalyst. $ZrCl_4$ can also be used for the deprotection of different protecting groups such as acetonide, bis-TBDMS, and diacetate, giving excellent yields of diols, and it was also used as a novel catalyst for the protection of 1,2-diols as an acetonide. We have also determined that $ZrCl_4$ is an efficient catalyst for the trans-esterification of different esters and the deprotection of 1,2-diacetates. We are currently investigating this novel methodology as the key steps in a variety of natural product synthesis and the results of these studies will be reported in due course.

Experimental Section

General Procedure for $ZrCl_4$-Catalyzed Deacylation and Esterification. Diacetoxy acid **3** (0.4 mmol) was dissolved in 300 μL of MeOH, 0.08 mmol of $ZrCl_4$ was added, and resulting reaction mixture was stirred at 25 °C for 48 h. In the case of ^{n}PrOH, ^{i}PrOH, and ^{t}BuOH the reaction was carried out at 45 °C. The reaction progress was monitored by TLC using 1:1 (pentane/EtOAc) as a mobile phase. The reaction mixture was purified using column chromatography by directly loading on to silica gel. The lactone and diol were purified by flash column chromatography using CH_2Cl_2/MeOH (96:4) as eluent. All compounds were characterized by ^{1}H NMR, ^{13}C NMR, HRMS, and optical rotation.

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Supporting Information Available: Full experimental procedures, characterization data, and ^{1}H and ^{13}C NMR spectra of all intermediates and products. This material is available free of charge via the Internet at http://pubs.acs.org.

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