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Chemoselective deacylation of functionalized esters catalyzed by dioxomolybdenum dichloride

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ABSTRACT

Among five different oxidometallic species and two Lewis acids investigated, MoO_2Cl_2 shows the best catalytic and chemoselective activity for the deacylation of esters in methanol at ambient or elevated temperature. Both high efficiency and chemoselectivity were achieved for substrates bearing different ether or ester groups. Acylated mono and disaccharides can also be selectively deacetylated in good yields, leading to useful carbohydrate templates for further synthetic manipulations.

1. Introduction

The deacylations of esters, amides, and thioesters are important transformations in organic synthesis, particularly in carbohydrate chemistry.[1] In the past decade, to aid in drug discovery and biochemical research, new methodologies to achieve efficient carbohydrate synthesis expand rapidly. In the meantime, improving efficiency with minimal toxic wastes in these synthetic processes by using milder and neutral catalytic systems remains in great demands.

Several reliable protocols for deacylation have been well documented and somewhat standardized in the literature.[2] For example, K_2CO_3 in methanol,[3] $NaHCO_3$ in H_2O_2 solution,[4] KCN in ethanol,[5] N_2H_4 in methanol,[6] Bu_2SnO under reflux conditions,[7] Brønsted acids like HCl or HBF_4 in methanol,[8] and $Sc(OTf)_3$ for methyl/ethyl esters in warmed EtOH or MeOH.[9] Equal or excess amounts of Sm and I_2 were also used for the deprotection of esters and lactams.[10] Recently, triphenyl phosphite–chlorine complex was used at lower temperature to facilitate the deacylation of amides.[11] Although these reaction protocols are useful, some of them still involve Harsher reaction conditions by exposing substrates to acid, base media, or at higher temperature. Under such circumstances, functional groups sensitive to acid or base may not be fully compatible.

In total synthesis and carbohydrate chemistry, key intermediates often contain two or more ester moieties under similar steric environments that need subsequent differentiation. So far, selectively deprotecting one ester while retaining the others remains to be explored. Therefore, chemoselective deacylation of esters by milder and neutral catalysts with good functional group compatibility is highly desirable.

Enzymes are known to deprotect acetate functionality selectively with somewhat limited substrate scope.[12] Guanidine/guanidinium nitrate (ca. 10 equiv, 4/1) reagent can be used to deprotect acetate in the presence of *N*-Troc group.[13] Acetate was selectively removed in 3′-*O*-acetyl-*N*-4,5′-*O*-dibenzoylcytidin in methanolic ammonia.[14] Stoichiometric uses of Lewis acids like $BF_3{\cdot}OEt_2$[15] and lanthanide triflate[16] to facilitate the deacylation of anomeric acetates were also documented. Besides, methanolysis of methoxyacetates can be achieved by catalytic $Yb(OTf)_3$ in methanol while retaining other esters.[17]

Primary alkyl esters can be selectively unmasked by using Mg metal in methanol.[18] DBU can promote the deacylation of allylic or primary alcohol-derived acetate without cleavage of benzoate moiety within the same substrate.[19] Accordingly, we hope to establish a single catalytic system, which involves mild reaction conditions and exhibits high chemoselectivity.

Recently, we have been investigating the new catalytic profiles of vanadyl and oxidometallic species. By identifying some catalyst–substrate adducts by ESI-MS analysis from catalytic acylation of alcohols, amphoteric character of some catalysts was revealed. So far, we have examined several C–X bond forming events like acylation and phosphorylation[20a–c] of protic nucleophiles, esterification, and transesterification,[20d,e] acetal formation of diols,[20f] thioglycosylation of peracetylated sugars,[20g] conjugate additions by protic and *C*-centered nucleophiles.[20h,i] In particular, based on our experiences from catalytic transesterification and acylation, we sought to examine the feasibility of our catalytic system in chemoselective deacylation of esters.

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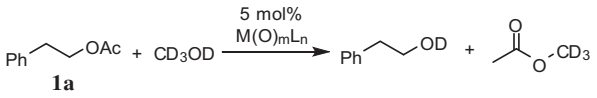
2. Results and discussion

In the initial tests on the reactivity of five different oxidometallic species and two Lewis acids (5 mol %), methanolysis of 2-phenylethyl acetate was examined in deuterated methanol. The conversion for each catalytic reaction was determined by the relative integration values of the methylene signals next to acetate and hydroxyl group, in respective ^{1}H NMR spectra (Table 1).

Table 1
Methanolysis of 2-phenylethyl acetate in CD_3OD catalyzed by five different oxidometallic species and two Lewis acids



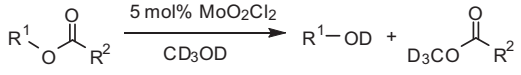
Entry	$M(O)_mL_n$	Temp, °C	Time, h	$t_{1/2}$,[a] h	Yield,[b] %
1	MoO_2Cl_2	rt	27	4.1	98
2	$Sc(OTf)_3$	rt	55	10.0	98
3	$VO(OTf)_2$	rt	44	25.3	92
4	$Yb(OTf)_3$	rt	194	65.1	94
5	$VOCl_2$	45	92	32.7	97
6	Bu_2SnO	45	194	33.0	95
7	$TiO(acac)_2$	60	469	49.0	99

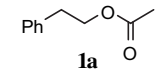
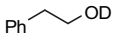
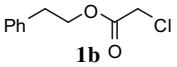
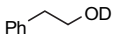
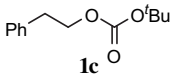
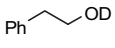
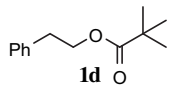
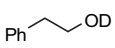
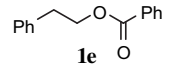
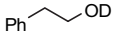
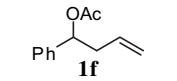
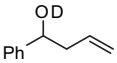
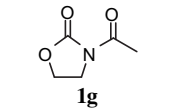
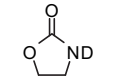
[a] The reaction time at 50% conversion.
[b] Isolated yields of purified materials.

It was found that MoO_2Cl_2 was the most effective in catalyzing the deacetylation at ambient temperature in 27 h ($t_{1/2}$, 4.1 h). The resulting 2-phenylethanol was isolated in 98% purified yield after aqueous workup. $Sc(OTf)_3$ showed also good reactivity. The methanolysis (98% yield, in 55 h) was about 2.5 times slower than that catalyzed by MoO_2Cl_2. Vanadyl triflate was about six times slower in terms of the reaction rate. The deacetylation reaction was completed in 44 h. The reaction rate ($t_{1/2}$, 65.1 h) mediated by $Yb(OTf)_3$ is 16 times slower than that catalyzed MoO_2Cl_2. Conversely, the same test reaction proceeded effective only at 45 °C with prolonged reaction time (92 h) by vanadyl chloride. Di-*n*-butyltin oxide (Bu_2SnO) has been documented as an efficient catalyst to trigger the NAS of functionalized esters in boiling methanol or ethanol.[21] As a comparison, the deacetylation proceeded sluggishly at 45 °C when catalyzed by Bu_2SnO, reaching completion in 194 h. In addition, although $TiO(acac)_2$ possesses excellent catalytic efficiency in transesterification of methyl esters in refluxed toluene,[20e] the performance was unsatisfactory in the test reaction at 60 °C. It took 469 h for completion with 99% conversion. By taking the $t_{1/2}$ values and reaction temperature factor into account, the reaction catalyzed by MoO_2Cl_2 is about 16, 16, and 96 times faster than those catalyzed by $VOCl_2$, Bu_2SnO, and $TiO(acac)_2$, respectively.

The possibility of performing chemoselective deprotection of esters with the optimal catalyst-MoO_2Cl_2 was further evaluated by first studying the rate profiles for the deacylation of a series of 2-phenylethyl esters **1a**–**e** in CD_3OD. The reaction progresses for each deacylation were monitored by ^{1}H NMR spectrometry. It was found that chloroacetyl group removal in **1b** is slower than the acetyl group removal in **1a** by a factor of 2 (entries 1 and 2 in Table 2). By taking the $t_{1/2}$ values and reaction temperature factor into account, the deacetylation of **1a** was 211–398 times faster than *t*-Boc, pivaloyl, and benzoyl group removals at 65 °C (entries 3–5). In view of the dramatic rate difference in the methanolysis of **1a**–**e** catalyzed by MoO_2Cl_2, acetate could be selectively removed without cleavage of any pivalate, benzoate, or *tert*-butyl carbonate for substrates bearing multiple ester functionalities. The rate of deacetylation also highly depends on the steric attribute of the alcohol component in the acetates. The rate for removing primary acetate in **1a** was about 28 times faster than the rate of secondary acetate removal in **1f** (entries 1 and 6, Table 2), which may be also suitable for chemoselective deacetylation in carbohydrates. Furthermore, *N*-acetylated oxazolidinone like **1g** generally may introduce chelating effect[22] toward Lewis acids and can also be smoothly removed at 45 °C with prolonged reaction time (136 h) under the new catalytic deacylation protocol (entry 7).

Table 2
Effects of acyl groups on the deacylation of selected substrates catalyzed by MoO_2Cl_2 in CD_3OD



Entry	Substrate	T, °C	t, h	$t_{1/2}$,[a] h	Product	Yield,[b] %
1	 **1a**	rt	27	4.1		98
2	 **1b**	rt	44	8.7		97
3	 **1c**	65	290	108.3		96
4	 **1d**	65	290	185.8		75
5	 **1e**	65	290	204.2		69
6	 **1f**	45	147	29.7		92
7	 **1g**	45	136	58.8		95

[a] The reaction time at 50% conversion.
[b] Isolated yields of purified materials.

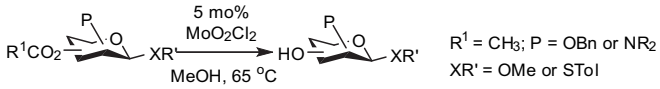
Thioglycosides serve as important building blocks for the preparation of oligosaccharides. With extension of a handy protocol for catalytic thioglycosylation of peracetylated sugars by MoO_2Cl_2,[20g,23] we selected a series of acetate-containing, mono, and disaccharides as substrates for catalytic deacetylation by MoO_2Cl_2 in MeOH (Table 3).

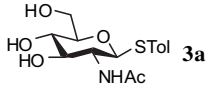
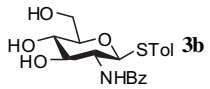
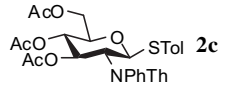
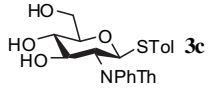
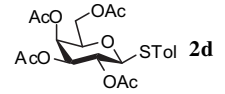
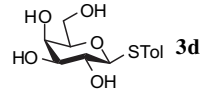
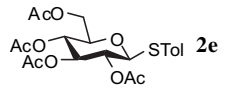
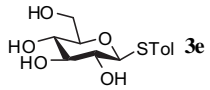
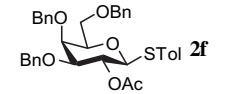
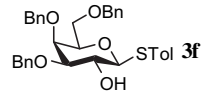
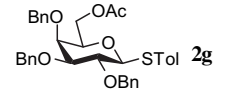
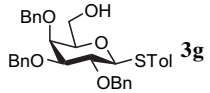
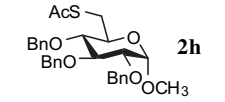
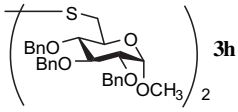
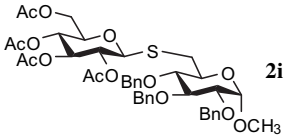
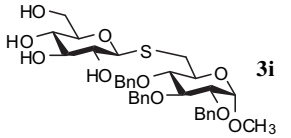
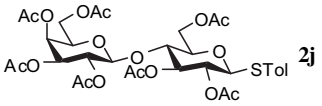
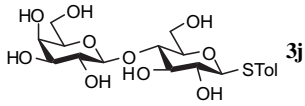
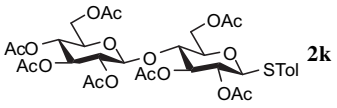
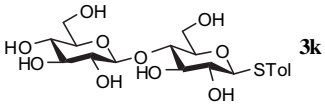
Per-*O*-acetylated glucosamine-derived thioglycosides **2a**–**c** with three different amino-protecting groups (Ac, Bz, and Phth) were first examined by the new deacylation protocol at 65 °C. To our delight, only the acetate groups in **2a**–**c** were selectively transesterified by MeOH in 11–60 h with intact amino-protecting groups at C2 substituents. The resultant triols **3a**–**c** were isolated in 94–99% yields (entries 1–3). Thioglycosides **2d** and **2e** derived from 2,3,4,6-tetra-*O*-acetylated galactose and glucose can be similarly unmasked in 87 and 97% yields, respectively.

Notably, benzyl ether as well as thioether at the glycosidic linkage is tolerant under the reaction conditions. The acetate groups in galactose-derived thioglycosides **2f** and **2g** can be smoothly and selectively removed in 86 and 97% yields (entries 6 and 7), respectively.

Besides, thioacetates are also amenable to deacetylation by this catalytic protocol. The thioacetate in **2h** was deacetylated with concomitant formation of the disulfide in 94% yield (entry 8). The desired free thiol **3h** can be obtained quantitatively by the treatment of the disulfide with $NaBH_4$. This free thiol **3h** has been further applied to the synthesis of disaccharide **2i** by thioglycosylation of β-D-glucose pentaacetate with **3h** in the presence of catalytic MoO_2Cl_2.[20g] The acetates in disaccharide **2i** can be fully unmasked to form **3i** in 94% yield (entry 9).

Table 3
Deacetylation of acetate-containing, functionalized saccharides catalyzed by MoO_2Cl_2 in CH_3OH



Entry	Substrate	*t*, h	Product	Yield,[a] %
1	 **2a**	33	 **3a**	95
2	 **2b**	60	 **3b**	94
3	 **2c**	11	 **3c**	99
4	 **2d**	36	 **3d**	87
5	 **2e**	33	 **3e**	97
6	 **2f**	69	 **3f**	86
7	 **2g**	8	 **3g**	97
8	 **2h**	112	 **3h**	94
9	 **2i**	74	 **3i**	94
10	 **2j**	61	 **3j**	97
11	 **2k**	62	 **3k**	92

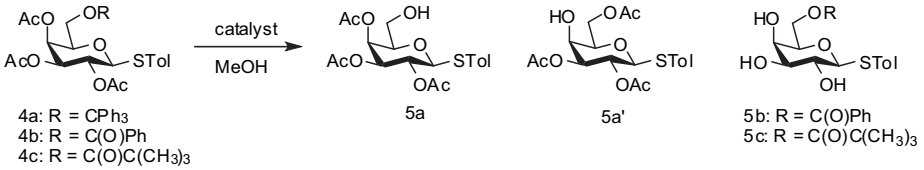
[a] Isolated yields of purified materials.

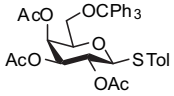
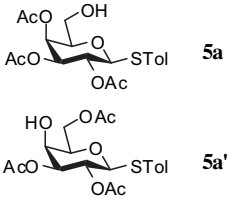
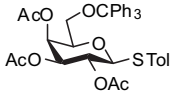
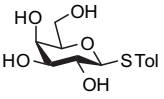
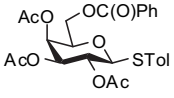
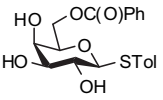
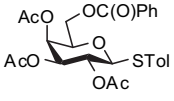
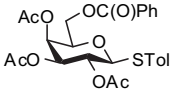
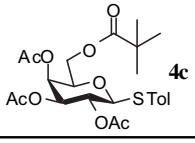
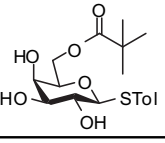
Other common peracylated disaccharides like **2j** and **2k** can also be completely deacetylated in 61–62 h to provide **3j** and **3k** in 97% and 92% yields, respectively.

The C6 position of galactose-based β-thioglycoside was further modified to trityl ether or different esters to test the feasibility for chemoselective deprotection of trityl or acetate groups in these substrates, Table 4.

Similar to our previous observation,[24] the trityl group in **4a** was cleaved along with complete deacetylation (entry 2) at 65 °C (entry 2, Table 4). Nevertheless, by lowering the reaction temperature to ambient temperature, the trityl group at C6 was selectively removed with intact secondary acetates albeit of with a discrete amount of acetyl group transfer in the products (**5a**/**5a′**, 76/24, entry 1). The acetate groups at C2, C3, and C4 positions in **4b** were completely removed in 66 h at 65 °C in MeOH with benzoate moiety remained intact, leading to **5b** in 88% yield (entry 3). In marked contrast, methanolysis of **4b** by $Sc(OTf)_3$ (5 mol %) led to **5b** (56%) along with the fully deprotected **3d** (41%) under similar reaction conditions (entry 4).[25] Treatment of **4b** in methanolic NH_3 at ambient temperature in 1.5 h also led to

Table 4
Chemoselective deprotection of galactose-based β-thioglycoside by MoO_2Cl_2

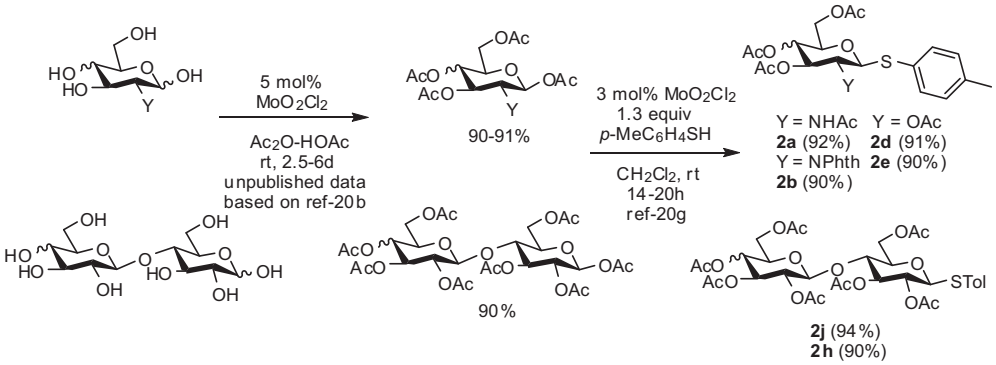


Entry	Substrate	Catalyst	*T*, °C	*t*, h	Product	Yield,[a] %
1	 **4a**	MoO_2Cl_2[b]	rt	6	 **5a** **5a'**	91 [**5a**/**5a**′ (76:24)[c]]
2	 **4a**	MoO_2Cl_2[b]	65	41	 **3d**	95
3	 **4b**	MoO_2Cl_2[b]	65	66	 **5b**	88
4	 **4b**	$Sc(OTf)_2$[b]	65	70	**5b**/**3d**	56:41
5	 **4b**	NH_3 in MeOH	rt	1.5	**5b**/**3d**	61:27
6	 **4c**	MoO_2Cl_2[b]	45	168	 **5c**	75

[a] Isolated yields of purified materials.
[b] 5 mol %.
[c] Determined by ^1H NMR spectrometry.

3d (27%) resulting from both deacetylation and debenzoylation.[25] The desired product **5b** was isolated in only 61% (entry 5). With the C6 hydroxyl group protected into a pivalate, **4c** was completely deacetylated at 45 °C in 168 h, providing **5c** in 75% yield (entry 6).

For the further application of this protocol, the important intermediates **3a**–**e** in carbohydrate synthesis can be readily prepared by sequential peracetylation,[20b] thioglycosylation,[20g] and deacetylation of glucose and galactose, respectively, in high yields by the same catalyst (i.e., MoO_2Cl_2), Scheme 1.



Scheme 1. Preparation of peracetylated thioglycosides by sequential peracetylation and thioglycosylation by MoO_2Cl_2.

3. Conclusion

In conclusion, we have established the relative rate profiles for the deacetylation of esters in the presence of five different oxidometallic species and two commonly used Lewis acids. Chemoselective deacetylation was achievable for esters with varying acyl attributes (i.e., acetyl vs *t*-Boc, pivaloyl, and benzoyl), sterics and/or electronics in the leaving groups by using a catalytic amount (1–5 mol %) of MoO_2Cl_2 in warmed MeOH, which was more effective than $Sc(OTf)_3$ or methanolic NH_3 catalyzed system. In combination with our recently developed catalytic peracetyaltion, thioglycosylation, and acetal formation of 4,6-diols,[20f] this new catalytic deacetylation protocol is thus suitable for routine synthesis of mono and disaccharides. Investigation toward oligosaccharide synthesis via a sequence of these catalytic transformations by MoO_2Cl_2 or $VO(OTf)_2$ is currently underway.

4. Experimental

4.1. General procedure for the catalytic deacylation

In a 25-mL, two-necked, round-bottomed flask equipped with an addition funnel was placed MoO_2Cl_2 (5 mol %) followed by the addition of anhydrous methanol (2 mL) under N_2 atmosphere. To this solution was slowly added a solution of an acetate-containing sugar (1 mmol) in methanol (3 mL) at ambient temperature via the addition funnel. After completion of the reaction as evidenced by TLC analysis, the reaction mixture was concentrated in vacuo and the residue was quenched with cold saturated aqueous $NaHCO_3$ (5 mL). Methylene chloride (10 mL) was added to the reaction mixture. The organic layer was separated and washed with brine, dried ($MgSO_4$), filtered, and evaporated. The crude residue was purified by column chromatography on silica gel. The product was characterized by routine spectroscopic methods.

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Supplementary data

Supplementary data related to this article can be found online version at doi:10.1016/j.tet.2010.12.024. These data include MOL files and InChIKeys of the most important compounds described in this article.

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