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Highly efficient and versatile acetylation of alcohols catalyzed by cerium(III) triflate

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Abstract—Cerium(III) triflate is a powerful catalyst for the acetylation of alcohols. The reaction works well for a large variety of simple and functionalized alcohols, without isomerisation of chiral centres. Changes of hydroxyl protective groups are possible in a one-pot procedure. The catalyst can be easily recycled.

The acylation of hydroxyl groups is one of the most frequently used transformations in organic synthesis. Among the various protecting groups used for the hydroxyl function, acetyl is the most common group in view of its easy introduction, being stable to the acidic reaction conditions, and also easily removable by mild alkaline hydrolysis.[1] Typically, acylation of alcohols and phenols is performed under homogeneous catalysis with acetic acid or acetyl chloride or anhydride, in the presence of a convenient basic catalyst such as triethylamine or pyridine.[2] In addition, 4-(dimethylamino) pyridine, 4-pyrrolidinopyridine,[3] *N*,*N*,*N*′,*N*′-tetramethylethylenediamine,[4] tertiary phosphines,[5] carbon tetrabromide in ethyl acetate,[6] *p*-toluenesulfonic acid,[7] zinc chloride,[8] iodine,[9] sulfamic acid,[10] magnesium bromide,[11] cobalt chloride,[12] tantalum chloride,[13] $La(OPr^i)_3$,[14] silica gel-supported sodium hydrogen sulfate,[15] montmorillonite K-10 and KSF,[16] alumina,[17] yttria-zirconia with acetic acid,[18] Ac_2O-pyridine/basic alumina under microwave irradiation,[19] KF-Al_2O_3 with Ac_2O/AcCl,[20] vanadyl(V) acetate,[21] distannoxane,[22] zeolite HSZ-360,[23] *Pseudomonas cepacia* PS lipase adsorbed on Celite,[24] and twisted amides[25] have also been applied for the acetylation of alcohols and phenols.

Another important development has been the introduction of trifluormethanesulfonate (triflate) derivatives, such as TMSOTf,[26] $Yb(OTf)_3$,[27] $La(OTf)_3$,[27a,c] $Lu(OTf)_3$,[27c] $Cu(OTf)_2$,[28] $Sc(OTf)_3$,[27a,29] $In(OTf)_3$,[30] and $Bi(OTf)_3$,[31] as efficient catalysts in acetylation with acetic acid, or anhydride or acetyl chloride.

Cerium(III)[32] and (IV)[33] salts have already been used as Lewis acid catalysts in protection/deprotection protocols, so we decided to test the $Ce(OTf)_3$ in the acetylation reaction.

In this communication we report $Ce(OTf)_3$ as an efficient and very mild catalyst for acylation of alcohols using acetic anhydride as acetylating agent.

1-Octanol was chosen as a model substrate for the acetylation reaction. It was treated with 1.5 equiv. of acetic anhydride in the presence of 1.0 mol% of $Ce(OTf)_3$ in different dry solvents at room temperature (Table 1). The reaction in acetonitrile was very clean and complete in only 1 h by GC/MS analysis. Similar results were registered in dry toluene, but in longer reaction times, and they were quite unsatisfactory in the other solvents tested.

Table 1. Attempted acetylation of 1-octanol in various solvents

Entry	Solvent	Time (min)	Yield (%)
1	THF	90	25
2	CH_2Cl_2	90	35
3	CH_3NO_2	90	10
4	Toluene	90	90
5	CH_3CN	60	>98

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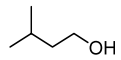
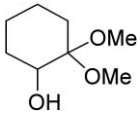
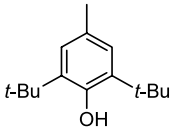
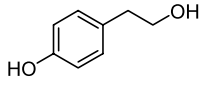
Table 2. Acetylation of alcohols using Ce(OTf) as catalyst

Entry	Substrate	$Ce(OTf)_3$ (%)	Time (h)	Yield (%)
1	Octanol	None	12	0
2	Octanol	1.0	1.0	>98
3	Octanol	10	0.5	>98
4	(+)-Menthol	None	12	0
5	(+)-Menthol	0.5	1.0	>98
6	(+)-Menthol	1.0	0.5	>98
7	(+)-Menthol	1.0	0.2	>98[a]
8	(+)-Menthol	1.0	12	0[b]
9		1.0	0.5	>98
10	*t*-BuOH	1.0	24	>98
11		1.0	24	>98
12		1.0	1.1	0[a,c]
13		1.0	6.0	>98[a,d]
14	$PhCH_2OH$	None	12	0[a]
15	$PhCH_2OH$	1.0	0.2	>98
16	Crotyl alcohol	1.0	2.5	>98
17	Propargyl alcohol	1.0	1.0	>98
18	$AcO(CH_2)_3OH$	1.0	6.0	>98
19	Benzoin	1.0	1.5	>98
20	Cinnamyl alcohol	1.0	48	0
21	Cinnamyl alcohol	10	2.5	>98
22	Cholesterol	1.0	5	93
23	α-D-Glucose	1.0	2.5	>98[a,e]
24	Glycerol	1.0	12	>98[e]
25	$HO(CH_2)_4OTBDMS$	1.0	4.0	>98[e]
26	$HO(CH_2)_4OTHP$	1.0	4.0	>98[e]
27	$TBDMSOCH(Me)$-$(CH_2)_5OH$	1.0	1.0	>98[e]
28		1.0	0.2	>98[f]
29	PhOH	1.0	2.5	>98
30	$4\text{-}NO_2\text{-}C_6H_4\text{-}OH$	1.0	0.2	>98
31	$4\text{-}Me\text{-}C_6H_4\text{-}OH$	1.0	3.0	>98
32	$4\text{-}MeO\text{-}C_6H_4\text{-}OH$	1.0	0.5	>98
33		2.0	24	>98[g]
34		1.0	0.2	>98[e]
35		1.0	0.2	73[h]
36		1.0	0.2	82[i]

[a] Ac_2O as solvent.
[b] In no-dry conditions.
[c] 2,4-Diphenyl-4-methyl-1-pentene was the only product obtained.
[d] At −10°C.
[e] Only peracetate derivatives were obtained with the removal of the previous protecting group.
[f] Only 2-acetoxycyclohexanone was obtained.
[g] At 50°C.
[h] Yield is referred to the major product 2-(4-hydroxyphenyl) ethyl acetate at −10°C.
[i] Yield is referred to the major product 2-(4-acetoxyphenyl) ethanol at −30°C.

In order to extend the scope of this acetylation reaction, it was carried out on a variety of substrates using a typical procedure where 1.0 mol% of $Ce(OTf)_3$ and 1.5 equiv. of acetic anhydride were added, at room temperature, to 2.0 ml of 1.0–1.5 M substrate dry acetonitrile solution (Table 2). Work-up and isolation of the product were quite easy and, although a slight excess of Ac_2O is used for complete conversion of the substrate, methanolysis can be applied to transform the remaining acylating agent to methyl ester, avoiding tedious separation. Partition work-up with ethyl ether and water leads to the acetylated products, as essentially single products which required, very often, no further purification as tested by ^1H NMR and GC–MS standard analytical techniques.

In control experiments without any catalyst, for several substrates (entries 1, 4, and 14, Table 2) no acetylation was observed over the same or prolonged reaction time, also by using the Ac_2O as solvent (entry 14, Table 2). Higher quantities of catalyst, up to 10 mol% entry 3, Table 2, were tested without evident advantages. On the other hand, a lower catalyst loading, such as 0.5 mol%, is still sufficient to give acetylated products although longer reaction times are needed for quantitative yields (entry 5, Table 2).

Dry reaction conditions are necessary; in fact, no reaction was observed when (+)-menthol was left to react in no-dry solvent (entry 8, Table 2). Acetic anhydride can be used as solvent (entry 7, Table 2), but work-up of the reaction becomes more difficult.

It is very interesting to note that tertiary alcohols such as *t*-butanol and 2-methyl-2-butanol (entries 10 and 11, Table 2) can also be acetylated with satisfactory yields and there was no elimination product in the mixture as shown by ^1H NMR and GC–MS analysis. However, in the case of 2-phenyl-2-propanol, the only product obtained at room temperature was 2,4-diphenyl-4-methyl-1-pentene in 83% yield.[34] Nevertheless, the acylation of 2-phenyl-2-propanol can be obtained quantitatively in 6 h at −10°C by using acetic anhydride as solvent and 1.0 mol% of catalyst (entry 13, Table 2).

This method tolerates the presence of other functionalities on the substrate such as double and triple bonds, carbonyl and acetyl groups. It was, in fact, possible to obtain easily the quantitative acetylation of crotyl and propargyl alcohols (entries 16 and 17, Table 2) or 3-acetyl-1-propanol and 2-phenyl-2-hydroxyacetophenone, or benzoin, (entries 18 and 19, Table 2). However, the acetate of cinnamyl alcohol was obtained only by raising up to 10 mol% the quantity of $Ce(OTf)_3$, because no reaction was observed in the usual reaction conditions (entries 20 and 21, Table 2).

The method presented here showed to be appropriate for the easy acetylation of chiral molecules such as (+)-menthol and cholesterol in very high yields (entries 5–7 and 22, Table 2).

No selective acetylation among different hydroxyl groups was experienced with our procedure, so in the case of α-D-glucose (entry 23, Table 2) the peracetylated glucose was the only product collected and attempt to obtain selective acetylation of the primary hydroxyl group by using only 1.5 equiv. of acetic anhydride in dry CH_3CN gave a messy mixture of partially acetylated products. Likewise, the only product obtained in the acetylation of the glycerol was its triacetylated derivative (entry 24, Table 2).

The acid-sensitive TBDMS and THP protective groups did not survive during the acetylation in these conditions, and both functions were replaced by the acetyl group to furnish the corresponding diacetate (entries 25–27, Table 2).

Also, the dimethyl acetal group was removed under the usual experimental conditions used in the present method, as could be expected on the basis of our previous work (entry 28, Table 2).[32g]

$Ce(OTf)_3$ can be reused several times without significant loss of activity. After work-up, the aqueous phase can be evaporated under reduced pressure to furnish the Ce(III) salt as a white solid, which can be reused after drying overnight over P_2O_5.

In order to extend the scope of the catalyst further, the acetylation of phenols was investigated. As shown in Table 2 (entries 29–33), phenol and differently substituted phenols were easily acetylated in the usual way. In all the cases, quantitative yields were obtained even for a phenol as highly crowded as the 2,6-di-*t*-butyl-*p*-cresol, which required simply to raise the percentage of catalyst up to 2 mol% and the reaction temperature to 50°C.

Furthermore, no by-products arising from Fries rearrangement were obtained from any phenols submitted to this acetylating procedure even after prolonged reaction time.

Differentiation between alcoholic and phenolic functionalities was tested submitting 2-(*p*-hydroxyphenyl) ethanol to the general acetylation conditions. Only the diacetate product was collected after very short reaction times at room temperature (entry 34, Table 2),[35] although the initially selective formation of acetylated derivative was detected by ^1H NMR and GC–MS analysis. The same reaction conducted at −10°C gave only 2-(*p*-hydroxyphenyl) ethyl acetate (entry 35, Table 2),[36] whereas 2-(*p*-acetoxyphenyl) ethanol was obtained at −30°C (entry 36, Table 2), as confirmed by ^1H NMR and GC–MS analysis.[37]

The behaviour of cerium(III) triflate is very surprising. It is generally known that aromatic alcohols are predominantly acylated in the presence of aliphatic alcohols under basic or nucleophilic conditions, whereas aliphatic alcohols are more nucleophilic under acidic conditions. Moreover electron-withdrawing groups on the aromatic ring increase nucleophilicity under basic conditions.[29b] The results reported in Table 2, both regarding substituted phenols (entries 29–32) and selective acetylation (entries 34–36) seem to justify both behaviours. Cerium might act as a Lewis acid at higher temperatures favouring the formation of an incipient acetylium ion, which better reacts with strong electron donating substituted phenols and aliphatic alcohols. Wheras, at lower temperatures, the triflate ion might play the role of base, favouring alkoxide ion formation with strong electron withdrawing substituted phenols and aromatic over aliphatic hydroxyl functions.

In conclusion, a powerful and versatile acetylating method has been developed based on $Ce(OTf)_3$ and acetic anhydride. $Ce(OTf)_3$ is a very cheap and easy to handle catalyst easily prepared starting from the commercial $CeCl_3{\cdot}7H_2O$.[32g,38] It appeared much more active than $CeCl_3{\cdot}7H_2O$ in the acetylation reaction, even if the selectivity toward the polyols was lost. Thus, only 1.0% instead of 10%[32c,f] of catalyst is sufficient in most cases and shorter reaction times are always sufficient. Moreover the use of acetic anhydride as the only acetyl source and the chance to recycle the catalyst underscore the use of $Ce(OTf)_3$ as an environmentally acceptable catalyst for economic transformations.

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34. Control experiments without acetyl anhydride demonstrated that 2,4-diphenyl-4-methyl-1-pentene arose from the acylated product, which could form a tertiary benzylic carbocation by acetate elimination or give elimination to α-methylstyrene, followed by dimerization. 2,4-Diphenyl-4-methyl-1-pentene: δ_H (300 MHz, $CDCl_3$) 1.21 (s, 6H, Me); 2.82 (s, 2H, CH_2); 4.77 (t, 1H, *J* 0.82, =CH); 5.13 (d, 1H, *J* 1.98, =CH); 7.2–7.4 (m, 10H, ArH). δ_C (75 MHz, $CDCl_3$) 28.40 (Me); 28.81 (Me); 38.63 (C); 49.54 (CH_2); 116.98 (CH_2); 125.61 (CH); 126.14 (CH); 126.22 (CH); 126.70 (CH); 128.03 (CH); 128.22 (CH); 143.42 (C); 146.65 (C); 149.35 (C).
35. 2-(*p*-Acetoxyphenyl) ethyl acetate: δ_H (300 MHz, DMSO-d_6) 1.96 (s, 3H, Me); 2.25 (s, 1H, Me); 2.75 (t, 2H, *J* 7.07, CH_2); 4.12 (t, 2H, *J* 7.07, CH_2); 6.60–7.18 (A_2B_2 system, 4H, *J* 8.49, ArH). δ_C (75 MHz, DMSO-d_6) 20.66 (Me); 20.77 (Me); 33.58 (CH_2); 64.74 (CH_2); 121.67 (CH); 127.88 (CH); 135.50 (C); 149.08 (C); 169.23 (C=O); 170.28 (C=O).
36. 2-(*p*-Hydroxyphenyl) ethyl acetate: δ_H (300 MHz, DMSO-d_6) 1.97 (s, 3H, Me); 2.88 (t, 2H, *J* 6.87, CH_2); 4.20 (t, 2H, *J* 6.87, CH_2); 7.00–7.40 (A_2B_2 system, 4H, *J* 8.49, ArH); 9.40 (s, 1H, OH). δ_C (75 MHz, DMSO-d_6) 20.65 (Me); 33.68 (CH_2); 64.27 (CH_2); 115.18 (CH); 129.78 (CH); 135.52 (C); 155.91 (C); 170.28 (C=O).
37. 2-(*p*-Acetoxyphenyl) ethanol δ_H (300 MHz, DMSO-d_6) 2.24 (s, 1H, Me); 2.71 (t, 2H, *J* 6.89, CH_2); 3.56 (dt, 2H, *J* 6.89 and 5.02, CH_2); 4.67 (t, 1H, *J* 5.02, OH); 7.02–7.32 (A_2B_2 system, 4H, *J* 8.36, ArH). δ_C (75 MHz, DMSO-d_6) 20.88 (Me); 38.32 (CH_2); 62.10 (CH_2); 121.43 (CH); 129.84 (CH); 137.16 (C); 148.74 (C); 169.36 (C=O).
38. $CeCl_3 \cdot 7H_2O$ which is the starting material for preparing cerium(III) triflate can be purchased from Fluka (500 g, 1.34 mol, 155.50 €). Meanwhile, the price of Bi_2O_3, the starting material for preparing $Bi(OTf)_3$, also commercially available from Fluka, is 103.30 € for 500 g (1.07 mol) and the price of $Sc(OTf)_3$, sold by Fluka, is 144.10 € for 5.0 g (0.01 mol).