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Erbium(III) Chloride: a Very Active Acylation Catalyst

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Erbium(III) chloride is a powerful catalyst for the acylation of alcohols and phenols. The reaction works well for a large variety of simple and functionalized substrates by using different kinds of acidic anhydrides (Ac_2O, $(EtCO)_2O$, $(Pr^iCO)_2O$, $(Bu^tCO)_2O$, and $(CF_3CO)_2$), without isomerization of chiral centres. Moreover, the catalyst can be easily recycled and reused without significant loss of activity.

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Introduction

Principles of green chemistry can guide the chemist to the minimization of waste in fine chemical processes, and to the reduction or avoidance of the use of organic toxic solvents. Moreover, the substitution of classical organic syntheses that employ stoichiometric amounts of reagents with clear, catalytic alternatives, which must be as efficient as possible, is another important goal towards lower environmental impact chemistry.[1]

In the last years, many of our efforts were spent to develop new environmentally friendly catalytic reagents in the strategic protection/deprotection steps of functional groups.[2–5] For example, we and other authors have already reported several useful applications of non-toxic Er(III) salts[A] as Lewis acid catalysts.[4–6]

Among the plethora of Lewis acids reported in the literature, Er(III) salts are among the most active, relative to both the values of its hydrolysis constant (K_h) and water-exchange rate constant (WERC), which are perfectly in accordance with what Kobayashi et al. reported,[7] and to the measures of complex stability constants evaluated by the use of tandem mass spectrometry,[8] which are two of the most classical ways to evaluate the efficiency of Lewis acid catalysts.

Acylation is one of the most important and widely used protection methods to preserve hydroxy functions during the course of a multi-step synthesis (Fig. 1).[9]

Generally, acylation takes place by treatment of alcohols and phenols with acid anhydrides or acid chlorides in the presence of amines, but many others methods have been proposed,[10,11] and more recently, the use of metal trifluoromethane sulfonates have been intensively developed as Lewis acid catalysts in the acylation of hydroxy groups.[3,5,12,13]

Herein, we report a simple and efficient method for the acylation of alcohols and phenols with different acid anhydrides catalyzed by erbium(III) chloride.

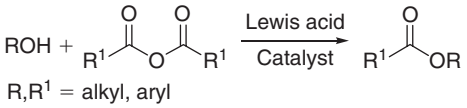

Fig. 1. Use of acylation to protect hydroxy functional groups.

Results and Discussion

First, we tested the catalytic activity of $ErCl_3$ in the acetylation of octan-1-ol at different temperatures and with different mol-% of catalyst using 1.2 equivalents of acetic anhydride in the absence of solvent. The best results were obtained by using 5 mol-% of $ErCl_3$ at 50°C, whereupon the reaction was complete within 4 h (entry 2, Table 1). In fact, room temperature seems inadequate to perform the reaction in reasonable times (entry 1, Table 1) and, when the reaction is carried out with only 1 mol-% of catalyst at 50°C (entry 3, Table 1), only partial conversion of the substrate is obtained.

The absence of water seems to be essential. In fact, the reaction is significantly faster when the catalyst is dried overnight at 140°C (entry 4, Table 1). Better results are obtained by again carrying out the reaction at 50°C, when only 90 min are enough for the complete conversion of the substrate (entry 5, Table 1). Meanwhile, higher amounts of catalyst do not seem to improve the reaction performance.

The same trend is observed for other substrates. For example, benzyl alcohol is quantitatively acetylated in 8 or 4 h, at room temperature or at 50°C, respectively, and the reaction time is further shortened (2 h) when the erbium chloride is dried beforehand. The acetylation of phenol is complete after 1.2 h, when 5 mol-% of dried $ErCl_3$ is used at 50°C, whereas an overnight reaction is necessary at room temperature with $ErCl_3 \cdot 6H_2O$ (5 mol-%). The effect is still more marked in the case of an activated aromatic substrate: only a few minutes are sufficient to

[A] Oral mouse LD_{50} $ErCl_3$ and NaCl from Sigma–Aldrich security sheets are 4417 and 4000 mg kg^{-1} respectively.

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Table 1. Setup of the reaction conditions in the acetylation of 1-octanol

Entry	Catalyst amount	Temp. [°C]	Time [h]	Yield [%]	Ref.
1	5% $ErCl_3 \cdot 6H_2O$	Room temp.	Overnight	>99	[3]
2	5% $ErCl_3 \cdot 6H_2O$	50	4	>99	[3]
3	1% $ErCl_3 \cdot 6H_2O$	50	4	83	[3]
4	Dried 5% $ErCl_3$	Room temp.	3	>99	[3]
5	Dried 5% $ErCl_3$	50	1.5	>99	[3]

perform the complete conversion of 4-nitrophenol with 5 mol-% of dried $ErCl_3$ at 50°C with respect to 1.5 h at room temperature with 5% $ErCl_3 \cdot 6H_2O$.

In order to explore the generality and the scope of erbium(III) chloride as a Lewis acid catalyst in acylation protections, we adopted a simple experimental procedure that involves stirring the solution of the substrate and acetic anhydride at 50°C in the presence of dried 5 mol-% $ErCl_3$. Primary (entries 1–5, Table 2) and secondary alcohols (entries 6, 7, Table 2), and phenols (entries 8–11, Table 2) underwent smooth acetylation with almost quantitative yields.

It is worth noting that tertiary alcohols are also smoothly acetylated (entries 12,13, Table 2). The previously reported reactions, which used cerium and erbium triflate as catalysts, showed drawbacks with these substrates. In particular, no competitive dehydration was registered in their acetylation. Even our previously proposed $Er(OTf)_3$ method needed a temperature of −10°C to avoid this competitive reaction,[5] whereas cerium triflate always gave elimination with 2-phenylpropan-2-ol.[2]

The reaction of phenols suffers from the electronic demand on the hydroxy function. Contrary to the very fast reaction observed in the cases of salicylic acid and 4-nitrophenol, *p*-cresol reacts much more slowly (entries 9–11, Table 2).

The Ac_2O–$ErCl_3$ system tolerates the presence of other functionalities on the substrates such as carbonyl and carboxylic groups (entries 3 and 9, Table 2). No rearrangement took place for allylic and propargyl substrates (entries 1 and 2, Table 2), and optically active substrates were also efficiently acetylated without any loss of optical purity (entries 6 and 7, Table 2), which demonstrates the mildness of this method.

Furthermore, no byproducts as a result of a Fries rearrangement are obtained from any phenols submitted to this acetylating procedure even after prolonged reaction time.

Unfortunately, no selective acetylation is observed when the present method is applied for the acetylation of α-D-glucose. Peracetylated sugar was exclusively recovered in almost quantitative yield (entry 14, Table 2) in the presence of 5 mol-% of catalyst after 7 h of reaction.

The acid-sensitive *t*-butyl dimethylsilyl (TBDMS) and tetrahydropyranyl (THP) protective groups did not survive under these acetylation conditions and both the functions were replaced by the acetyl group to furnish the corresponding diacetate (entries 15 and 16, Table 2), while, obviously, the acetyl group is unaffected (entry 4, Table 2).

Generally, the industrial production of aspirin consists of the acetylation of salicylic acid using mineral acids. We applied the present protocol with good advantage to obtain smoothly the aspirin in almost quantitative yield in only 15 min.

Table 2. Acetylation of alcohols and phenols at 50°C, using 5 mol-% dried $ErCl_3$ as catalyst

Entry	Substrate	Time [h]	Yield [%][A]	Ref.
1	but-2-en-1-ol	4	>99	[3]
2	Propargyl alcohol	1.2	>99	[3]
3	$CH_3COCH(Me)CH_2OH$	1	>99	[5]
4	$AcO(CH_2)_3OH$	1	>99	[3]
5	$PhCH_2OH$	2	>99	[3]
6	(+)-Menthol	6	>99	[3]
7	Cholesterol	6	>99	[3]
8	PhOH	1.2	>99	[3]
9	2-COOH-C_6H_4-OH	0.2	>99[B]	—[E]
10	4-NO_2-C_6H_4-OH	0.2	>99	[3]
11	4-Me-C_6H_4-OH	2	>99	[3]
12	$Et(Me)_2COH$	3.5	>99	[14d]
13	$Ph(Me)_2COH$	6	>99	[5]
14	α-D-Glucose	7	>99[C]	[3]
15	$HO(CH_2)_4OTBDMS$	0.2	>99[D]	[3]
16	$HO(CH_2)_4OTHP$	0.2	>99[D]	[3]

[A] Isolated yield by flash column chromatography on silica gel was reported and all products were identified by comparison of their EI-MS and ^1H NMR spectroscopic data with those of authentic compounds and literature reported data.
[B] At reflux.
[C] Only peracetate derivatives were obtained.
[D] Butan-1,4-diol diacetate was the only product obtained.
[E] Compared to an actual sample.

The catalyst can be reused in the same process several times without significant loss of activity: the salt was extracted into an aqueous phase, and after evaporation under reduced pressure, the catalyst was obtained as a white solid (85–90% recovered),[B] which could be reused after drying overnight over P_2O_5 at 140°C. The recovered catalyst was used five times in the acetylation reaction of the salicylic acid, maintaining 5 mol-% of catalyst, and the registered yields were always higher than 87%.

Considering the gentleness and efficiency of the method, we decided to explore the application of the $ErCl_3$–acid anhydride protocol to other acylations. Unfortunately, major amounts of anhydride were necessary to dissolve the reagents. When octan-1-ol is treated with 3.6 equiv. of propionic anhydride at 50°C in the presence of 5 mol-% of $ErCl_3$, the acylation proceeds smoothly in 1.5 h with almost quantitative yield (entry 1, Table 3). Surprisingly the reaction is still fast in isobutyric anhydride (entry 2, Table 3) and even with the pivalate, which is one of the most obstinate ester protecting groups because of its steric hindrance (entry 3, Table 3).

The generality of the method has been explored with structurally different alcohols and phenols, which were submitted to the action of $ErCl_3$ at 5 mol-% in 3.6 equivalents of propionic, isobutyric, or pivaloyl anhydrides. Evident differences in reactivity were not registered between primary (entries 1–3, 5–11, Table 3) and secondary alcohols (entries 13–15, Table 3), nor between the three aliphatic anhydrides, and, again, no rearrangement took place for allylic and propargyl substrates (entries 5–8, Table 3).

Thus, we extended the $ErCl_3$–anhydride protocol to the preparation of trifluoroacetate esters of alcohols and phenols.

[B] The purity of the recovered $ErCl_3$ was confirmed by comparison with the IR spectrum of the commercial product.

Table 3. Acylation of alcohols and phenols using 5 mol-% dried $ErCl_3$ as catalyst

Entry	Substrate	Acid anhydride (equiv.)	Temp. [°C]	Time [h]	Yield [%][A]	Ref.
1	octan-1-ol	$(EtCO)_2O$ (3.6)	50	1.5	>99	[5]
2	octan-1-ol	$(^iPrCO)_2O$ (3.6)	50	1.2	>99	[14a]
3	octan-1-ol	$(^tBuCO)_2O$ (3.6)	50	2	>99	[5]
4	octan-1-ol	$(CF_3CO)_2O$ (3.6)	Reflux	1.5	>99	[5]
5	but-2-en-1-ol	$(EtCO)_2O$ (3.6)	50	1	>99	[5]
6	but-2-en-1-ol	$(^iPrCO)_2O$ (3.6)	50	1.5	>99	[14b]
7	but-2-en-1-ol	$(^tBuCO)_2O$ (3.6)	50	2	>99	[5]
8	Propargyl alcohol	$(^tBuCO)_2O$ (3.6)	50	2.5	>99	[5]
9	$PhCH_2OH$	$(EtCO)_2O$ (3.6)	50	1.5	>99	[5]
10	$PhCH_2OH$	$(^iPrCO)_2O$ (3.6)	50	2	>99	[14c]
11	$PhCH_2OH$	$(^tBuCO)_2O$ (3.6)	50	2.5	>99	[5]
12	$PhCH_2OH$	$(CF_3CO)_2O$ (3.6)	Reflux	2	>99	[5]
13	(+)-Menthol	$(EtCO)_2O$ (3.6)	50	4	>99	[5]
14	(+)-Menthol	$(^iPrCO)_2O$ (3.6)	50	5	>99	[13]
15	(+)-Menthol	$(^tBuCO)_2O$ (3.6)	50	6	>99	[5]
16	(+)-Menthol	$(CF_3CO)_2O$ (3.6)	Reflux	4	>99	[5]
17	PhOH	$(EtCO)_2O$ (3.6)	50	0.5	>99	[14e]
18	PhOH	$(^iPrCO)_2O$ (3.6)	50	0.2	>99	[14g]
19	PhOH	$(^tBuCO)_2O$ (3.6)	50	0.3	>99	[14g]
20	PhOH	$(CF_3CO)_2O$ (3.6)	Reflux	0.3	>99	[14e]
21	2-COOH-C_6H_4-OH	$(EtCO)_2O$ (3.6)	Reflux	0.2	>99	[14h]
22	2-COOH-C_6H_4-OH	$(^iPrCO)_2O$ (3.6)	Reflux	0.5	>99	[14h]
23	4-Me-C_6H_4-OH	$(EtCO)_2O$ (3.6)	50	1.5	>99	[5]
24	4-Me-C_6H_4-OH	$(^tBuCO)_2O$ (3.6)	50	3	>99	[5]
25	4-Me-C_6H_4-OH	$(CF_3CO)_2O$ (3.6)	Reflux	Overnight	0	[14e]
26	4-NO_2-C_6H_4-OH	$(EtCO)_2O$ (3.6)	50	0.2	>99	[5]
27	4-NO_2-C_6H_4-OH	$(^tBuCO)_2O$ (3.6)	50	0.5	>99	[5]
28	4-NO_2-C_6H_4-OH	$(CF_3CO)_2O$ (3.6)	Reflux	3	>99	[14e]

[A] Isolated yield by flash column chromatography on silica gel was reported and all products were identified by comparison of their EI-MS and ^1H NMR spectroscopic data with those of authentic compounds and literature reported data.

Better results were obtained when the reaction was performed in the presence of 3.6 equivalents of trifluoroacetic anhydride and 5 mol-% of $ErCl_3$ at reflux temperature. The present modified method permitted us to easily obtain trifluoroacetylated derivatives of both primary and secondary alcohols (entries 4, 12, 16, Table 3) as well as phenols (entries 20, 28, Table 3) in almost quantitative yields and in very short reaction times.

Conclusions

In conclusion, the erbium(III) chloride/acyl anhydrides protocol can be considered a tangible improvement with respect to the other existing methods, which involve the use of triflate derivatives as catalysts, in the preparation of acyl esters of alcohols and phenols, especially with respect to our cerium and erbium(III) triflate method.[2,5] In fact, this protocol has comparable costs with respect to both cerium and erbium triflates, since higher charged amounts of erbium chloride are counterbalanced by its lower price. Moreover, triflate derivatives are much more toxic with respect to $ErCl_3$, which possesses an oral mouse LD_{50} comparable to NaCl.[A]

Erbium chloride is used in true catalytic amounts in the absence of any organic solvent and using only a low excess of acyl anhydride. All acylation reactions are performed smoothly and in neutral conditions. Moreover, it is possible to recover the catalyst almost quantitatively and without significant loss of activity.

This methodology only suffers from the low solubility of most of alcohols in anhydrides other than acetic anhydride, which results in the use of a large excess of the anhydrides. From an environmental chemistry point of view, the waste of large amounts of anhydrides is not attractive. Alternately, the achievement of trifluoroacetates and pivaloates is an important goal in traditional organic chemistry.

Experimental

In a model reaction octan-1-ol (500 mg, 3.85 mmol) was added to 0.463 mL of dry Ac_2O (0.472 g, 4.62 mmol) and $ErCl_3$ (52.7 mg, 0.193 mmol), the acetylation was complete in 1 h under neat conditions at 50°C to afford a quantitative yield. Acylation with propionic and pivalic anhydrides was still conducted at 50°C using the same mol-% of catalyst, but using 3.6 equivalents of anhydride. Especially after pivalation, the purification of products requires a tedious work-up to separate the esters from the remaining acyl anhydride. Therefore, methanol was added at the end of the acylation reaction in order to convert the remaining acyl anhydride to the corresponding methyl ester. Afterwards the pure product was obtained by simple filtration through a thin pad of silica gel with petroleum ether 60/80.

Acylation with trifluoroacetic anhydride was carried out under the same conditions at reflux temperature.

All known products were identified by comparison of their EI-MS and ^1H NMR spectroscopic data with those of authentic compounds (when commercially available) and literature reported data.[14]

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