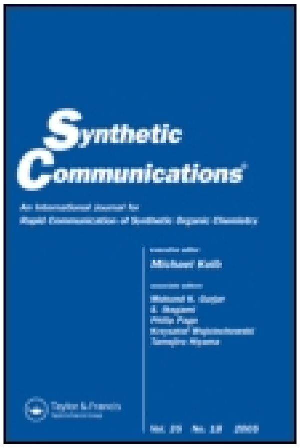

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CERIC(IV) AMMONIUM NITRATE MEDIATED TRANSESTERIFICATION AND ESTERIFICATION

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ABSTRACT

The transesterification of carboxylic esters and the esterification of carboxylic acids are effected under mild conditions in the presence of ceric(IV) ammonium nitrate (CAN).

Transesterification and esterification represent powerful methods to synthesise a variety of organic esters.[1] Typically, the reactions are catalysed by strong acids or bases[1,2] and enzymes.[3] There are reports on using titanium(IV) alkoxides,[4] tetraalkyldistannoxanes,[5] aluminium oxide,[6] ZrO_2 or binary Mo-ZrO_2[7] oxide, and ferric perchlorate adsorbed on silica gel[8] as catalysts for transesterification and esterification.

As a part of our continuous efforts concerning reactions of hydrazides and their derivatives,[9] we have recently reported on the application of ceric(IV) ammonium nitrate as a reagent for the conversion of hydrazides to esters.[10] We would like to report herein the first application of ceric(IV)

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$$\underset{\mathbf{1}}{RCOOR^1} \xrightarrow[\text{r.t.}]{CAN/R^2OH\ (\mathbf{2})} \underset{\mathbf{3}}{RCOOR^2}$$

Scheme 1.

ammonium nitrate for transesterification and esterification reactions (Scheme 1).

Initially, transesterification of ethyl hypurate was studied (Table 1, Entries 1 and 2). In order to achieve a high conversion of the starting ester in reasonable time, two equivalents of CAN were required. Similar transformations with different starting esters and alcohols were carried out. In all cases, the reaction led to a single product and after evaporation, followed by extraction with dichloromethane, we isolated esters in pure form and high yields.

Having demonstrated that CAN served efficiently in the transesterification reactions, we decided to investigate the use of CAN for esterification reactions. As it is evident from Table 2, CAN can also be applied for esterification of carboxylic acids.

Although the precise mechanism of transesterification of carboxylic esters and esterification of carboxylic acids with CAN remains unclear, the reaction might be explained by the initial coordination of carboxylic oxygens by Ce(IV), which is followed by nucleofilic attack by alcohol, deriving carboxylic esters.

The method cannot be applied to substrates containing thiol and sulphide groups or to 1,3-ketoesters due to oxidation of substrates. Furthermore, mandelic acid undergoes decarboxylation and oxidation leading quantitatively to benzaldehyde (Table 2, Entry 10).

In conclusion, the fact that metals often behave as the equivalents of hydrogen has long been recognized by chemists. As Davies said:[11] "Anything hydrogen can do, a metal can do better." Cerium (IV) ammonium nitrate is introduced herein for this purpose. The described approach seems to be a method of choice for a simple preparation of various esters employing mild reaction conditions and giving high yields of the desired products.

EXPERIMENTAL

In a typical experiment, CAN (2 mmol) was added at room temperature to a suspension of carboxylic acid or to a solution of ester **1** (1 mmol) in the appropriate alcohol **2** (5–8 ml). The reaction mixture was stirred at r.t. for the time indicated in Tables 1 and 2, evaporated to dryness, treated with water

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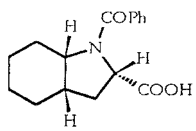
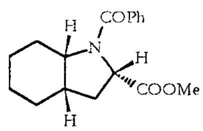
Table 1. Transesterifications Mediated by CAN

Entry	Starting Material	Product[a]	Reaction Time (h)	Yield (%)[b]
1	$PhCONHCH_2CO_2Et$	$PhCONHCH_2CO_2Me$	53	85
2	$PhCONHCH_2CO_2Et$	$PhCONHCH_2CO_2Bu^i$	366	92
3	4-Cl, 3-$NO_2C_6H_3CO_2Me$	4-Cl, 3-$NO_2C_6H_3CO_2Et$	144	98
4	$PhCONHCH(Me)CO_2CH_2CH{=}CH_2$	$PhCONHCH(Me)CO_2Me$	36	87
5	$PhCONHCH(CH_2Ph)CO_2CH_2C{\equiv}CH$	$PhCONHCH(CH_2Ph)CO_2Me$	54	95
6	4-$NO_2C_6H_4CONHCH(Me)CO_2Pr^i$	4-$NO_2C_6H_4CONHCH(Me)CO_2Me$	336	83
7	4-$NO_2C_6H_4CONHCH(Me)CO_2Pr^i$	4-$NO_2C_6H_4CONHCH(Me)CO_2Bu^i$	366	75
8	$EtOCH{=}C(CO_2Et)_2$	$EtOCH{=}C(CO_2Me)_2$	120	89
9	$EtOCH{=}C(CN)CO_2Et$	$EtOCH{=}C(CN)CO_2Me$	120	91

[a]All products are identical with those available from commercial sources and those from the literature.
[b]Yields of isolated products are given.

Table 2. Esterifications Mediated by CAN

Entry	Starting Material	Product[a]	Reaction Time (h)	Yield (%)[b]
1	$PhCONHCH_2CO_2H$	$PhCONHCH_2CO_2Me$	36	97
2	4-$PyCONHCH_2CO_2H$	4-$PyCONHCH_2CO_2Me$	40	90
3	4-$NO_2C_6H_4CO_2H$	4-$NO_2C_6H_4CO_2Me$	408	88
4	4-Cl, 3-$NO_2C_6H_3CO_2H$	4-Cl, 3-$NO_2C_6H_3CO_2Me$	336	95
5	4-$ClC_6H_4CH_2CO_2H$	4-$ClC_6H_4CH_2CO_2Me$	360	86
6	4-$PyCO_2H$	4-$PyCO_2Me$	240	73
7	$PhCH{=}CHCO_2H$	$PhCH{=}CHCO_2Me$	240	99
8	$PhCONHCH_2CO_2H$	$PhCONHCH_2CO_2Et$	360	92
9	$PhCONHCH_2CO_2H$	$PhCONHCH_2CO_2Bu^i$	192	81
10	$PhCH(OH)CO_2H$	PhCHO	0.5	99
11			53	97

[a]All products are identical with those available from commercial sources and those from the literature.
[b]Yields of isolated products are given.

($10\,cm^3$) and product extracted with dichloromethane ($6 \times 15\,cm^3$). The organic phase was dried over anhydrous sodium sulfate and evaporated to yield the corresponding ester **3**. Selected examples are listed in Tables 1 and 2.

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