RSC Advances

COMMUNICATION

Cite this: RSC Advances, 2013, 3, 3848

Received 9th December 2012, Accepted 22nd January 2013

DOI: 10.1039/c3ra00132f

www.rsc.org/advances

Efficient direct ester condensation between equimolar amounts of carboxylic acids and alcohols catalyzed by trifluoromethanesulfonic acid (TfOH) in Solkane365mfc[†]

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A simple, practical, and environmentally benign esterification protocol has been devised on the basis of TfOH as the catalyst and Solkane365mfc as the reaction medium. The direct condensation of equimolar amounts of various carboxylic acids and alcohols was conveniently carried out without recourse to any additional water removal technique, giving the desired carboxylic esters in excellent yields.

Introduction

The ester condensation reaction is one of the most fundamental transformations in various fields of organic synthesis.¹ Conventional esterifications are conducted with excess carboxylic acids (or alcohols) against a counterpart in the presence of an acid catalyst, or with stoichiometric dehydrating reagents or activated carboxylic acid derivatives in the presence of a stoichiometric base. In view of the rapidly increasing demands of green and sustainable chemistry, more environmentally benign alternative approaches to those currently used by the chemical industry are in strong demand. Recently, much attention has been focused on developing different efficient catalysts, which can activate the ester condensation of equimolar mixtures of carboxylic acids and alcohols. Impressive examples, mainly including metal salt catalysts² and Brønsted acid catalysts,³ have been exploited by different groups. The principal drawbacks of the majority of metallic catalysts are moisture-sensitivity, high cost, and toxicity. Many esterification methods require the azeotropic removal of water, or at least the presence of a drying agent. For Brønsted acid catalysts, it is not necessary to remove water, but most of them suffer from complex structures and are not commercially available. It is still highly desirable to search for a simpler, facile, inexpensive and efficient catalyst. In 2008, Ishihara and co-workers reported that catalytic amounts of sulfonic acids (5 mol%), such as

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p-toluenesulfonic acid (TsOH) and 10-camphorsulfonic acid (CSA), can efficiently catalyze ester condensation under solvent-free and drying agent-free conditions.⁴ Sulfonic acid is a promising candidate for the esterification reaction in process chemistry due to its simplicity, ready availability and low cost. We present herein another sulfonic acid, trifluoromethanesulfonic acid (TfOH), as an efficient catalyst in the esterification reaction. The unique property of TfOH⁵ makes it more active than other sulfonic acids, and in most cases only 0.2 mol% of TfOH is sufficient for excellent conversion.⁶

The reaction medium is also very important for practical catalytic esterification. Solvents, which are usually used in great quantities, define a major part of the environmental performance of processes in the chemical industry and also have an impact on cost, safety and health issues.7 Conventionally, ester condensations were performed in flammable and toxic non-polar solvents, such as heptane, toluene and xylene. Replacing these solvents with more environmentally acceptable alternatives appeared to be a subject of significant academic and commercial interest. Up to now, the most commonly explored green solvents for the esterification reaction are ionic liquids.^{3e,i,8} However, whether ionic liquids can be classed as green solvents is still highly debateable.⁹ The esterification reaction in other environmentally benign solvents water^{3c,d,k,10} and fluorinated phases^{2d,f,3j,11} have been primarily investigated. Although solvent-free conditions¹² seem to be a good alternative, in most cases, a solvent is often required to assist in working-up processes and transporting of materials. Thus, the development of other green media for an extremely practical catalytic esterification is still worthy of investigation. Recently, fluorous organic hybrid solvents have received more and more attention to be green substitutes for traditional organic solvents.¹³ Solkane365mfc, 1,1,1,3,3-pentafluorobutane, is a typical fluorous organic hybrid solvent developed by Solvay Fluoro GmbH.14 It is non-toxic and has no impact on the ozone layer. Although Solkane365mfc has a flash point below -27°C, it is difficult to ignite. Its thermal and chemical stability make it a good alternative solvent. Previously, we proved that Solkane365mfc was an environmentally benign solvent for several transformations.¹⁵ To further explore the reaction range, we

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[†] Electronic supplementary information (ESI) available: experimental details. See DOI: 10.1039/c3ra00132f



Scheme 1 Ester condensation between equimolar amounts of carboxylic acids **1** and alcohols **2** catalyzed by TfOH in Solkane365mfc.

present here the first thermal reaction with Solkane365mfc as the medium. The ester condensation between different carboxylic acids **1** and alcohols **2** can proceed efficiently when catalyzed by TfOH in Solkane365mfc, giving the product carboxylic esters **3** in excellent yields (Scheme 1).

Results and discussion

Initially, several reported catalysts (1.0 mol%) were evaluated in the condensation reaction of equimolar amounts of 3-phenylpropanoic acid (**1a**) and octan-1-ol (**2a**) in Solkane365mfc at 100 °C (Table 1, entries 1–6). Neither the metal salt catalyst [$\{Cl(C_6F_{13}C_2H_4)_2SnOSn(C_2H_4C_6F_{13})_2Cl\}_2$] (Otera's cat.)^{2d} or HfCl₂·2THF^{2c} gave good results (entries 1 and 2). Ammonium triflate (DPAT)^{3b} worked well giving the desired product **3aa** in 87% yield (entry 3). All the sulfonic acids TsOH·H₂O, CSA, and methanesulfonic acid (MsOH)⁴ promoted the condensation in high conversion (entries 4–6). This result encouraged us to search for a more efficient sulfonic acid catalyst. TfOH was then chosen



| Entry | Catalyst | Temp. (°C) | Conv. (%) ^{<i>a</i>} | Yield (%) ^b |
|------------|-------------------------|------------|-------------------------------|------------------------|
| 1 | Otera's cat. | 100 | 6 | _ |
| 2 | HfCl ₂ ·2THF | 100 | 16 | _ |
| 3 | DPAT | 100 | 88 | 87 |
| 4 | $TsOH \cdot H_2O$ | 100 | 93 | 93 |
| 5 | CSA | 100 | 70 | 70 |
| 6 | MsOH | 100 | 96 | 91 |
| 7 | TfOH | 100 | 99 | 96 |
| 8 | TfOH | 80 | 99 | 98 |
| 9 | TfOH | 60 | 97 | 94 |
| 10 | TfOH | 50 | 96 | 93 |
| 11^{c} | TfOH | 80 | 98 | 98 |
| $12^{c,d}$ | TfOH | 80 | 96 | 95 |
| $13^{c,e}$ | TfOH | 80 | 93 | 93 |
| 14 | HCl | 80 | complex | _ |

 a Determined by crude ¹H NMR. b Isolated yield by silica-gel column chromatography. c TfOH (0.2 mol%) was used as the catalyst. d The reaction was carried out in toluene. e The reaction was carried out in heptane.

taking advantage of its mildness, nonoxidative character, and ease of handling. The result of TfOH was exciting since the conversion reached as high as 99% at 100 °C, and even at 80 °C (entries 7 and 8). Decreasing the temperature to 60 or 50 °C, both the conversion and yield dropped slightly (entries 9 and 10). To our delight, excellent conversion and yield were obtained when only 0.2 mol% of TfOH was used at 80 °C (entry 11). It is noteworthy that when the reaction was performed in toluene or heptane, slightly lower conversion and yield were obtained (entries 12 and 13). The most conventional acid, HCl, was not effected and furnished a complex mixture (entry 14).

Under the optimized reaction condition, the ester condensation of various carboxylic acids **1** and alcohols **2** was carried out in the presence of 0.2 mol% TfOH in Solkane365mfc at 80 °C to explore the generality and scope of the substrates. First, the esterification of phenylpropanoic acid **1a** and a variety of alcohols **2a–g** were investigated. As shown in Table 2, alcohols **2a–c** with different chain lengths (C_8 , C_6 , and C_2) were converted to ester **3aa–ac** in excellent yields. Several functionalities in alcohols such as an allylic group (**2d**), a phenyl group (**2e**), and a halogen (**2f**) were tolerated. The short chain alcohol (**2c**) and sterically crowded secondary alcohol (**2g**) required more catalyst and/or longer time.

Then, the esterification of different carboxylic acids **1b**-**o** and octan-1-ol **2a** was examined. The results are shown in Table 3. 2-Unsubstituted carboxylic acids, 2-monosubstituted carboxylic acid, and sterically demanding 2,2-disubstituted carboxylic acid were smoothly condensed to produce the corresponding esters **3ba-ea** in excellent yields. 4-Oxopentanoic acid (**1f**) was selectively esterified without a protecting ketone moiety. The reactions using α , β -unsaturated carboxylic acid (**1g**) and benzoic acid (**1h**) were also successful, although more catalyst and/or a longer time was needed. A wide range of functional groups, including electron-donating, electron-withdrawing, and neutral groups in carboxylic

 Table 2 Ester condensation between phenylpropanoic acid 1a and various alcohols 2 catalyzed by TfOH in Solkane365mfc



 a Isolated yield by silica-gel column chromatography. b TfOH (1.0 mol%) was used. c The reaction was carried out for 48 h.

 Table 3 Ester condensation between various carboxylic acids 1 and octan-1-ol

 2a catalyzed by TfOH in Solkane365mfc





^a Isolated yield by silica-gel column chromatography.
 ^b TfOH (1.0 mol%) was used. ^c The reaction was carried out for 48 h.

acids **1i–o** were well tolerated, and all the ester condensation products **3ia–oa** were obtained in excellent yields.

To further investigate the substrate generality, ester condensation of either diacid (**1p**) or diol (**2h**) was investigated (Scheme 2). Both of them were smoothly converted to the corresponding diesters **3pa** or **3ah** in excellent yields without a prolonged reaction time.

Finally, we examined the ester condensation reactions in commercially available Solkane365/227 blend solvent (Solkane227: 1,1,1,2,3,3,3-heptafluoropropane). It is disclosed that Solkane365mfc has a flash point ≤ -27 °C; however, its blend form (93/7 mixture of Solkane365mfc and Solkane227) as Solkane365/227 is known to have no flash point (non-flammable) and could provide the benefits of Solkane365mfc.¹⁶ As shown in



Scheme 2 Ester condensation with diacid (1p) or diol (2h)



Scheme 3 Ester condensation reaction catalyzed by TfOH in Solkane365/227.

Scheme 3, several different carboxylic acids and octan-1-ol **2a** reacted under the catalysis of TfOH in Solkane365/227 giving the corresponding carboxylic esters in excellent yields.

Conclusions

We have developed a new practical and environmentally benign method for the esterification reaction. Only 0.2-1.0 mol% TfOH could efficiently catalyze the ester condensation of equimolar mixtures of various carboxylic acids and alcohols at 80 °C with Solkane365mfc as the medium (23 examples), although tertiary alcohols are not acceptable as partners of carboxylic acids. All of the desired carboxylic esters were obtained in excellent yields (92-99%). Even in Solkane365/227, a non-flammable solvent, the ester condensation reaction also proceeded efficiently. Note that the present method did not necessitate the use of a dehydration reagent and/or technique for the removal of azeotropic water. We hope that Solkane365mfc can be the green organic solvent of choice after water and ionic liquids in industrial process chemistry. The extension to other ubiquitous organic reactions with Solkane365mfc as the medium is currently under investigation.

Experimental

Typical procedure for ester condensation in Solkane365mfc

A mixture of phenylpropanoic acid **1a** (750.9 mg, 5.00 mmol), octan-1-ol **2a** (784.5 μ L, 5.00 mmol), TfOH (2.2 μ L, 0.01 mmol), and Solkane365mfc (5.0 mL) in a sealed tube was stirred at 80 °C for 18 h. After cooling, the solvent was evaporated, and the residue was purified by column chromatography on silica-gel (*n*-hexane/ethyl acetate = 20/1) to give ester **3aa** as a clear oil (1.2834 g, 98%).

Acknowledgements

This study was financially supported in part by Grants-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology (Project name: Advanced Molecular Transformation by Organocatalysts). We thank Dr Max Braun, Solvay Fluor GmbH for the generous gift of Solkane365mfc and thank Professor Junzo Otera for providing us with Otera's catalyst.

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Communication

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