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Synthesis of N-Heteroaryl(trifluoromethyl)hydroxyalkanoic Acid Esters by Highly Efficient Solid Acid-Catalyzed Hydroxyalkylation of Indoles and Pyrroles with Activated Trifluoromethyl Ketones

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Abstract: The synthesis of N-heteroaryl(trifluoromethyl)hydroxyalkanoic acid esters by solid acid-catalyzed Friedel–Crafts hydroxyalkylation of indoles and pyrroles with ethyl 3,3,3-trifluoropyruvate and ethyl 4,4,4-trifluoroacetoacetate is described. The inexpensive and readily available K-10 montmorillonite is found to be an efficient catalyst for the synthesis of a wide variety of trifluoromethylated indol-3-yl- and pyrrol-2-yl-hydroxypropionic and -butanoic acid esters. Using a series of substituted indoles and pyrroles the corresponding products were isolated in excellent yield (up to 98%) and 100% selectivity under mild experimental conditions, during very short reaction times. Beyond these, the ease of product isolation, catalyst stability and handling make this process an attractive, environmentally benign alternative for the synthesis of the target compounds.

Keywords: ethyl trifluoroacetoacetate; ethyl trifluoropyruvate; Friedel–Crafts hydroxyalkylation; heterogeneous catalysis; K-10; solid acid catalysis

Introduction

Since the first publication on biologically active organofluorine compounds,[1a] the synthesis of these materials has received significant attention in the pharmaceutical and materials sciences.[1] Among these compounds the trifluoromethyl group-containing molecules are especially important due to their unique physical and biological properties.[2] Some of the most well-known drugs are Prozac® (anti-depressant), Diflucan® (anti-fungal agent), Casodex® (anti-cancer agent) and Desflurane (inhalation anesthetic).[2] Mosher's acid and its derivatives are another important class of CF_3-containing compounds, which are widely used as chiral NMR resolution agents.[3]

Indolyl-alkanecarboxylic acids including trifluoromethylated derivatives have also attracted considerable attention in recent years due to their excellent biological activity.[4] Their synthesis can be achieved by enantioselective Friedel–Crafts reactions of trifluoromethyl pyruvate with aromatic and heteroaromatic compounds catalyzed by chiral copper(II) complexes.[5a] Alternative methods include but are not limited to the superacid catalytic hydroxyalkylations with ethyl 3,3,3-trifluoropyruvate,[3c] application of Grignard reagents[5b, c] or organocuprates.[5d] Despite the several available processes[6] the development of new environmentally benign methods for the synthesis of trifluoromethylated compounds is still in great demand.

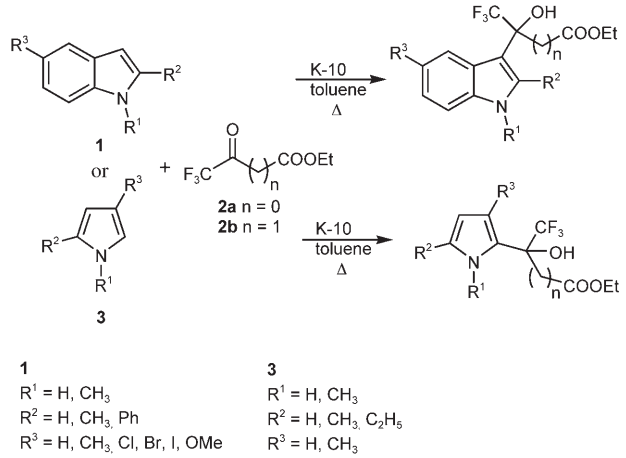
Friedel–Crafts chemistry is one of the most fundamental C–C bond forming reactions in organic chemistry.[7] Two major applications of the aromatic electrophilic substitution reaction such as acylation and alkylation, provide a wide range of highly valuable products.[8] The conventional methods for carrying out the Friedel–Crafts reaction involve the use of traditional Lewis or Brønsted acid catalysts.[1,2] Although these acids are excellent catalysts, many of them cannot meet the recent environmental and safety standards for fine chemical production. As a result, the development of environmentally benign catalysts attracted significant attention.[9] However, the search for active and selective heterogeneous acid catalytic systems is still highly desirable.

Continuing our efforts in developing environmentally friendly, heterogeneous catalytic synthetic methods, herein, we report the synthesis of trifluoromethylated hydroxyl(N-heteroaryl)alkanoic acid esters by solid acid-catalyzed hydroxyalkylations. This method is based on the application of K-10 montmorillonite and trifluoromethylated α- and considerably less reactive β-keto esters. Beyond the new procedure, several new products have been synthesized and this process provided an opportunity to explore their further chemical and biomedical potential.

Results and Discussion

Due to the extended interest in trifluoromethylated indolyl-carboxylic acid derivatives[4,5] we intended to develop a new, economic and easily adaptable solid acid-catalyzed process for the synthesis of these compounds. The general scheme of the reaction is summarized in Scheme 1.

As a first step, several solid acid catalysts have been tested in the reaction of indole with **2a** and **2b**, respectively. Some weak solid acids (e.g., Amberlyst, Dowex) could not activate **2b**, while the superacidic Nafion-H[9c] showed slow reaction rates, probably due to its limited surface area (~ 10 $m^2 g^{-1}$). Finally, K-10 montmorillonite was found to be the catalyst of choice for these transformations. It is a well-known strong solid acid for a variety of acid-catalyzed organic transformations[9b] and also used for bifunctional catalysis.[10] K-10 is prepared from natural montmorillonite by high temperature mineral acid treatment. According to solid state ^{29}Si NMR studies its main constituent is a quartz-like material, in addition to kaolinite and montmorillonite.[11] The acid strength of K-10 highly surpasses the acidity of the other solids (SiO_2, Al_2O_3, TiO_2 etc.), however, it is a significantly weaker acid than the superacidic Nafion-H.[9,12] Its Hammett acidity constant is $H_0 = -8$, this value is as high as the acidity of concentrated nitric acid.[9b,12] Besides, its BET surface exceeds 250 $m^2 g^{-1}$, which is significantly higher than that of other solid acids (~10–20 $m^2 g^{-1}$) surface area. Based on the preliminary investigations further reactions have been carried out with K-10 montmorillonite as a catalyst.



Scheme 1. K-10 montmorillonite-catalyzed hydroxyalkylation of indoles (**1**) and pyrroles (**3**) with ethyl 3,3,3-trifluoropyruvate (**2a**) and ethyl 4,4,4-trifluoroacetoacetate (**2b**).

As a next step, we have selected the hydroxyalkylation of indole with reactants **2a** and **2b**, respectively, as a probe reaction to determine optimum experimental conditions. The results are summarized in Table 1.

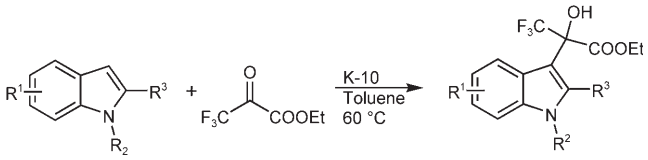
As shown, **2a** reacts with indole with a very slow rate, no product formation has been observed with **2b** even after extended reaction time (entries 1, 5). We observed that the reaction time can drastically be reduced by using K-10 montmorillonite as catalyst at room temperature in the case of indole **2a** reaction (entry 2). However, K-10 was not able to activate **2b** under identical conditions. Using elevated temperatures (60–70 °C) and microwave irradiation, respectively, we observed excellent reaction rates. Using microwave irradiation, however, the isolated yields are only moderate to good, probably due to a limited reagent loss from the open reaction vessel. Conventional heating combined with a closed pressure tube reactor excluded reagent loss and gave the maximum yields (Table 1 entries 4 and 8). As such, this system was applied in further reactions.

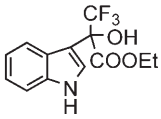
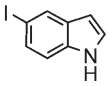
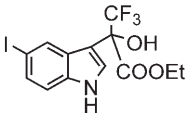
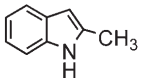
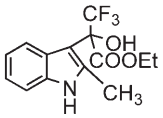
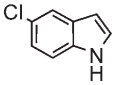
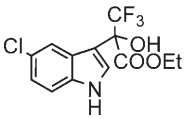
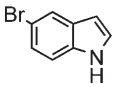
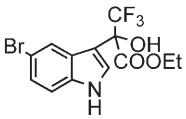
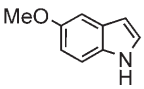
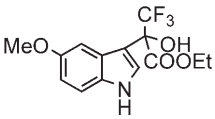
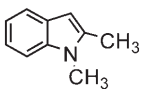
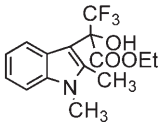
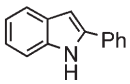
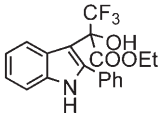
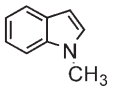
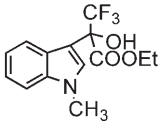
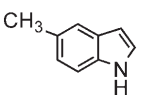
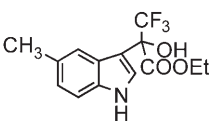
Table 1. Hydroxyalkylation of indole with ethyl 3,3,3-trifluoropyruvate (**2a**) and ethyl 4,4,4-trifluoroacetoacetate (**2b**) under various experimental conditions.

Entry	Substrate	Reactant	Catalyst	Solvent	Temp. [°C]	Time [h]	Yield [%]
1	Indole	**2a**	–	Ether	25	24	89
2	Indole	**2a**	K-10	Ether	25	1	85
3	Indole	**2a**	K-10	–	μw[a]	0.2	80
4	Indole	**2a**	K-10	Toluene	60	0.066	97
5	Indole	**2b**	–	Ether	25	24	0
6	Indole	**2b**	K-10	Ether	25	24	0
7	Indole	**2b**	K-10	–	μw	0.5	75
8	Indole	**2b**	K-10	Toluene	70	1	98

[a] μw = microwave irradiation (1200 W power).

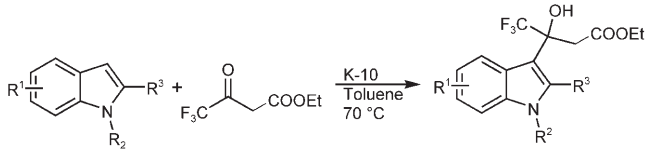
Table 2. K-10 montmorillonite-catalyzed hydroxyalkylation of substituted indoles with ethyl 3,3,3-trifluoropyruvate (**2a**) in toluene at 60 °C in a closed pressure tube.

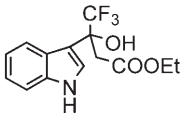
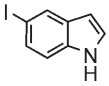
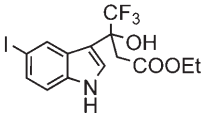
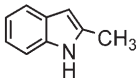
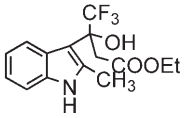
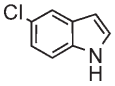
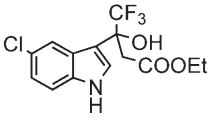
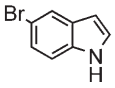
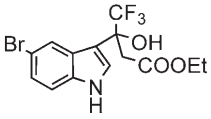
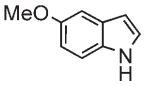
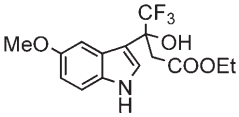
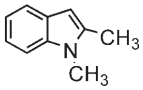
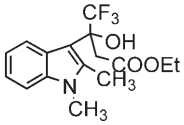
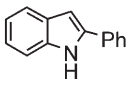
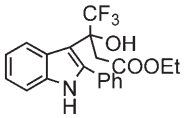
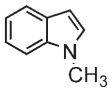
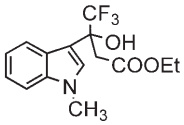
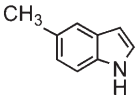
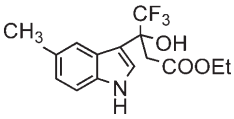


Entry	Substrate	Time [min]	Product	Yield [%][a]
1		4		98
2		9		98
3		5		97
4		6		95
5		6		98
6		5		97
7		4		98
8		6		96
9		4		95
10		4		98

[a] Isolated yield.

Table 3. K-10 montmorillonite-catalyzed hydroxyalkylation of substituted indoles with ethyl 4,4,4-trifluoroacetoacetate (**2b**) in toluene at 70 °C in a closed pressure tube.



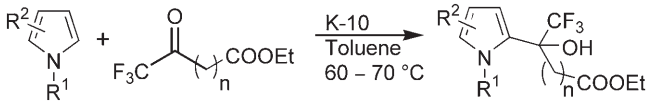
Entry	Substrate	Time [h]	Product	Yield [%][a]
1		1		98[b]
2		2		80[b]
3		0.75		98[b]
4		1		85[b]
5		1		92[b]
6		1.5		89[b]
7		1		95[b]
8		1.5		90[b]
9		1.5		88[b]
10		1		91[b]

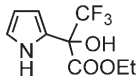
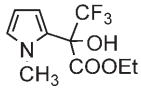
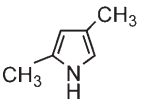
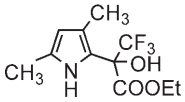
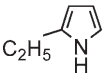
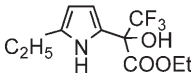
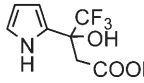
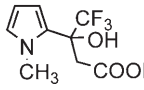
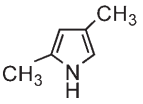
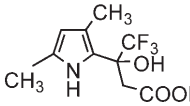
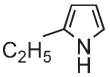
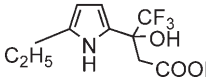
[a] Isolated yield.
[b] New compounds.

The first set of synthetic studies involved substituted indoles and **2a**. The results of K-10-catalyzed hydroxyalkylations are tabulated in Table 2.

As Table 2 clearly shows, K-10 is an excellent catalyst for the hydroxyalkylation reaction. Using a wide variety of substituted indoles, excellent yields have been observed. The substituents did not affect significantly the

Table 4. K-10 montmorillonite-catalyzed hydroxyalkylation of substituted pyrrole derivatives with ethyl 3,3,3-trifluoropyruvate (**2a**, n = 0) and ethyl 4,4,4-trifluoroactoacetate (**2b**, n = 1) in a closed pressure tube.



Entry	Substrate	Reactant	Temp. [°C]	Time [min]	Product	Yield [%][a]
1		**2a**	60	6		98
2		**2a**	60	5		97
3		**2a**	60	5		95
4		**2a**	60	6		93
5		**2b**	70	30		98[b]
6		**2b**	70	30		94[b]
7		**2b**	70	30		89[b]
8		**2b**	70	30		86[b]

[a] Isolated yield.
[b] New compounds.

reactivity of indoles, reaction times varied from 4 to 9 minutes. The reactions proceeded smoothly and most of them were completed in an average time of 5 minutes. Despite the short reaction times, the isolated yields indicated practically quantitative product formation. No by-product formation was observed.

Based on the excellent result shown in Table 2, a similar sequence of reactions was carried out with substituted indoles and **2b**. The results are provided in Table 3.

According to the optimization (Table 1), a slight increase in reaction temperature (70 °C) was necessary in this case. As **2b** is a significantly weaker electrophile than **2a**, the reactions usually require longer contact times to achieve yields similar to those listed in Table 1. However, the longest reaction still required only 2 hours and the yields obtained were excellent. Although electron-donating substituents slightly increased the reactivity of indoles, the electronic or steric nature of the substituents did not significantly affect the outcome of the reactions. The yields obtained were excellent and in the 88–98% range.

Pyrroles also readily underwent hydroxyalkylation at their α-position under the same reaction conditions. In this case, any excess of the hydroxyalkylating agents resulted in the formation of 2,5-disubstituted pyrroles. In order to avoid the formation of such by-products, equimolar amounts of these reactants have been used. Results are summarized in Table 4.

Table 4 shows that, using 1:1 pyrrole/reactant ratio, the expected mono-hydroxyalkylated products have been formed in excellent yields (86–98%). The products have easily been isolated, no significant by-product formation has been observed.

The key step in the proposed mechanism of the reaction is the adsorption of the trifluoro-keto ester on the surface of the catalyst. We propose that the carbonyl oxygen interacts with a surface Lewis acid center. This adsorption/complex formation anchors the volatile re-

actant and initiates strong electrophilic character on the carbonyl carbon, resulting in a surface-bound intermediate of carbocationic nature. Similar carbonyl-anchoring effect has been observed in the hydrogenation of cinnamaldehyde on Pt/K-10 catalyst.[10] The formation of such intermediate is clearly supported by experiments carried out with microwave irradiation in an open reaction vessel (Table 1, entries 3 and 7). As ethyl trifluoropyruvate has a low boiling point (42 °C) without such chemical adsorption a significant amount of **2a** would have evaporated and have been lost from the reaction mixture. The high yields unambiguously indicate that such extensive reactant loss does not occur even from the open vessel. After the adsorption the reaction follows the conventional Friedel–Crafts mechanism.[3]

Conclusion

In conclusion, a new solid acid-catalyzed, effective, economic and clean Friedel–Crafts hydroxyalkylation reaction has been developed to incorporate hydroxyl(trifluoromethyl)alkanoic acid moiety into indoles and pyrroles. Our method was able to provide the products in excellent yields and selectivities, under mild conditions, in short reaction times. In addition, it made possible the selective synthesis of a wide range of 4,4,4-trifluoromethyl(N-heteroaryl)hydroxybutanoic acid esters for the first time. This simple and effective process provides a novel way for the synthesis of the target compounds that might open new possibilities in their chemical and biomedical applications.

Experimental Section

Materials

All indoles, pyrroles, ethyl 3,3,3-trifluoropyruvate and ethyl 4,4,4-trifluoroacetoacetate were purchased from Aldrich and used without further purification. K-10 was a Fluka product. The $CDCl_3$ used as solvent for NMR studies and the $CFCl_3$ used as reference compound in ^{19}F NMR measurements were obtained form Aldrich. Other solvents used in synthesis were Fisher products with a minimum purity of 99.5%.

General Procedure for the Synthesis of 2-Hydroxy-2-(indol-3-yl)-3,3,3-trifluoropropionic Acid Ethyl Esters (Table 2, Entries 1–10)

Indole (0.75 mmol) and ethyl 3,3,3-trifluoropyruvate (1.125 mmol) were dissolved in 3 mL of toluene in a Teflon screw-cap pressure tube and 500 mg of K-10 montmorillonite were added. The reaction mixture was immersed into an oil bath preheated to 60 °C. The reaction mixture was stirred by magnetic stirrer and the progress of reaction was monitored by TLC (CH_2Cl_2 eluent). After satisfactory conversion, the product was separated from catalyst by filtration. The solvent and excess of TFP were removed under vacuum. The products have been isolated as crystals or oils and purified by flash chromatography when needed.

General Procedure for the Synthesis of 3-Hydroxy-3-(indol-3-yl)-4,4,4-trifluorobutanoic Acid Ethyl Esters (Table 3, Entries 1–10)

Indole (0.75 mmol) and ethyl 4,4,4-trifluoroacetoacetate (1.125 mmol) were dissolved in 3 mL of toluene in a Teflon screw-cap pressure tube and 500 mg of K-10 were added. The reaction mixture was then immersed into an oil bath preheated to 70 °C. The reaction mixture was stirred by magnetic stirrer and the progress of reaction was monitored by TLC (CH_2Cl_2 eluent). After satisfactory conversion, the product was separated from catalyst by filtration. The solvent was removed under vacuum. The oily residue was purified by flash chromatography to obtain the pure product.

General Procedure for the Synthesis of 2-Hydroxy-2-(pyrrol-2-yl)-3,3,3-trifluoropropionic Acid Ethyl Esters (Table 4, Entries 1–4)

Pyrrole (0.75 mmol) and ethyl 3,3,3-trifluoropyruvate (0.75 mmol) were dissolved in 3 mL of toluene in a Teflon screw-cap pressure tube and 500 mg of K-10 were added. The reaction mixture was then immersed into an oil bath preheated to 60 °C. The reaction mixture was stirred by magnetic stirrer and the progress of reaction was monitored by TLC (CH_2Cl_2 eluent). After satisfactory conversion, the product was separated from catalyst by filtration. The solvent and excess of TFP were removed under vacuum. The products have been isolated as oils.

General Procedure for the Synthesis of 3-Hydroxy-3-(pyrrol-2-yl)-4,4,4-trifluorobutanoic Acid Ethyl Esters (Table 4, Entries 5–8)

Indole (0.75 mmol) and ethyl 4,4,4-trifluoroacetoacetate (0.075 mmol) were dissolved in 3 mL of toluene in a Teflon screw-cap pressure tube and 500 mg of K-10 were added. The reaction mixture was then immersed into an oil bath preheated to 70 °C. The reaction mixture was stirred by magnetic stirrer and the progress of reaction was monitored by TLC (CH_2Cl_2 eluent). After satisfactory conversion, the product was separated from catalyst by filtration. The solvent was removed under vacuu,. The oily residue was purified by flash chromatography to obtain the pure product.

Product Identification and Analysis

The products were characterized by NMR (^1H, ^{13}C, ^{19}F) spectroscopy and mass spectrometry. The complete NMR and MS characterization of all products is provided in the Supporting Information

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