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Diels–Alder reactions of trifluoromethyl alkenes with 5-ethoxyoxazoles: synthesis of trifluoromethylated pyridine derivatives

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Abstract

Cycloaddition reactions between 5-ethoxyoxazole derivatives [2,4-dimethyl 5-ethoxyoxazole and 4-methyl 5-ethoxyoxazole] and various trifluoromethyl alkenes [ethyl 4,4,4-trifluorocrotonate $CF_3CH{=}CHCO_2Et$, 3,3,3-trifluoro 1-(phenylsulfonyl)-1-propene $CF_3CH{=}CHSO_2Ph$ and 2-(trifluoromethyl) propenoic acid $CF_3(HO_2C)C{=}CH_2$] gave several trifluoromethyl-substituted pyridine systems in moderate yield (20–56%). Their structures were determined by multinuclear NMR techniques including ^{1}H-^{13}C HETCOR spectroscopy.

Keywords: Cycloaddition; Diels–Alder; Fluorinated pyridine; Fluoroalkene; Oxazole

1. Introduction

Development of efficient methodology for the synthesis of trifluoromethylated aromatic heterocycles is an active area of research and, in particular, routes to trifluoromethylated pyridines have been developed for applications in the preparation of a number of valuable medicinal [1] and plant protection targets [2–5].

Trifluoromethyl groups may be introduced into a pyridine ring system by reaction of an appropriately functionalised pyridine substrate with either a fluorinating agent (synthesis of carbon–fluorine bonds) or a trifluoromethylating reagent (synthesis of carbon–carbon bonds) [6]. For example, halogen exchange processes involving transformation of trichloromethyl- to trifluoromethyl-groups upon reaction with a source of fluoride ion [7] or copper catalysed coupling processes between heteraryl iodides and trifluoromethyl iodide [8] have been utilised recently to provide access to these valuable products. In contrast, however, the construction of a trifluoromethylated pyridine ring from non-pyridine precursors using cycloaddition methodology is an approach that remains relatively undeveloped.

There are only a limited number of publications that report the syntheses of trifluoromethyl pyridine systems using cycloaddition methodology and, generally, these involve reactions of trifluoromethyl diene substrates. Viehe and co-workers [9] prepared a series of 2-trifluoromethylpyridine derivatives by performing cycloaddition reactions between trifluoromethyl oxazinone and a variety of electron-poor alkynes whilst Schlosser reported that 1-ethoxy-3-trifluoromethyl-1,3-butadiene [10] underwent cycloaddition with a range of imines to give various trifluoromethylpyridine products.

[4+2]-Cycloaddition reactions between oxazoles and electron poor alkenes are well established, typically yielding functionalised 3-hydroxypyridine systems [11,12]. Most commonly, symmetrical alkenes are utilised as dienophilic substrates, for example, in the pyridoxine synthesis from a maleate ester (Scheme 1) [13].

In contrast, there are fewer reported examples of cycloaddition methodology that involve reactions of oxazoles with mono-substituted [14,15] and unsymmetrical 1,2-disubstituted alkenes [16–18] as dienophiles. Generally, in these cases, pyridine systems bearing the most electron-withdrawing substituent of the dienophile at the 4-position are the major products formed. This regioselectivity can be rationalised by Frontier Orbital theory [19]. The presence of an electron withdrawing group attached to the alkene increases the LUMO coefficient at the CH_2 site, making overlap with the C-2 oxazole position, which has a large HOMO coefficient due to the electron donating ethoxy group, very favourable.

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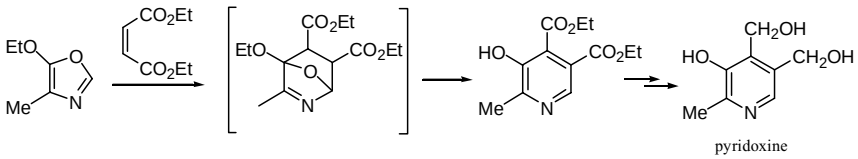


Scheme 1.

Whilst trifluoromethylated alkenes are known to participate in various Diels–Alder reactions [20] and *N*-arylfluoroalkylamines give trifluoromethyl quinoline derivatives by aza Diels–Alder processes [21], syntheses involving oxazoles as the diene partner have not been described. In this paper, we report our studies concerning reactions between various oxazoles and trifluoromethyl alkenes with a view to establishing the utility of cycloaddition methodology for the synthesis of functionalised trifluoromethyl pyridine systems.

2. Results and discussion

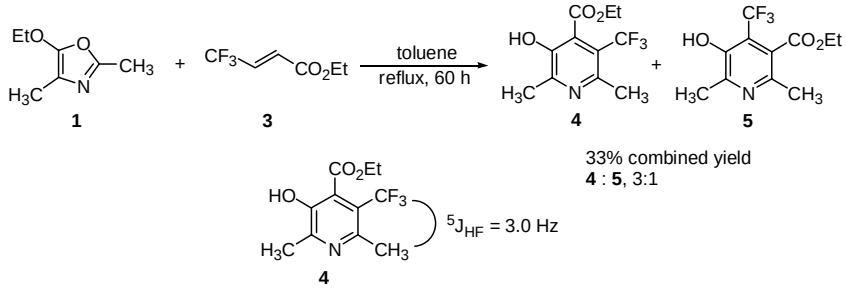
5-Ethoxyoxazoles **1** and **2** were prepared in the usual manner from DL-alanine ethyl ester hydrochloride by *N*-acylation [22] and *N*-formylation [23], respectively, followed by cyclodehydration using phosphorous pentoxide [24].

Reaction of 2,4-dimethyl-5-ethoxyoxazole **1** with ethyl 4,4,4-trifluorocrotonate **3** in refluxing toluene for 60 h yielded two trifluoromethylated pyridine derivatives **4** and **5** in 33% combined yield (Scheme 2). Analysis of the crude material by ^{19}F NMR spectroscopy and integration of the signals attributed to the trifluoromethyl resonances, indicated that **4** and **5** were formed in a 3:1 ratio. Separation and purification of pyridines **4** and **5** from the resinous crude product by silica gel chromatography was very difficult but an analytically pure sample of **4** was eventually obtained.

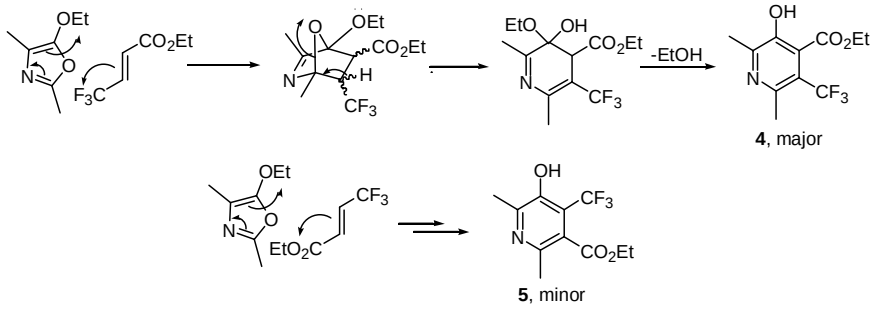
Structural assignments of **4** and **5** were made by a consideration of the ^{1}H NMR spectra. The resonance attributed to the hydrogen atoms of the C(6)-CH_3 methyl group of **4** was observed as a distinct quartet ($^{5}J_{HF}$ 3 Hz), due to coupling with the fluorine atoms of the neighbouring CF_3 group, whilst this coupling was, of course, absent from the ^{1}H NMR spectrum of minor isomer **5**. The mechanism for the formation of pyridines **4** and **5** is outlined in Scheme 3.

Heating oxazole **2** together with an excess of **3** at 120 °C in the absence of solvent for 48 h was necessary for cycloaddition to occur and two different trifluoromethylated products, pyridine **6** (25%) and pyrrole derivative **7** (8%), were obtained after purification by column chromatography (Scheme 4).

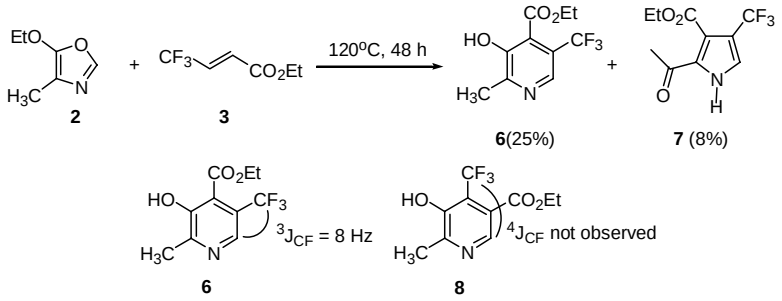
The structure of **6** was deduced by ^{1}H-^{13}C HETCOR spectroscopy, which allowed the unambiguous identification of the resonance attributed to the C-6 carbon atom as a multiplet with three-bond carbon–fluorine coupling



Scheme 2.



Scheme 3.



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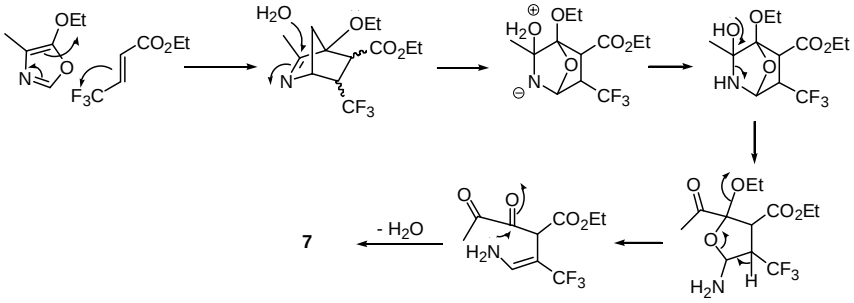

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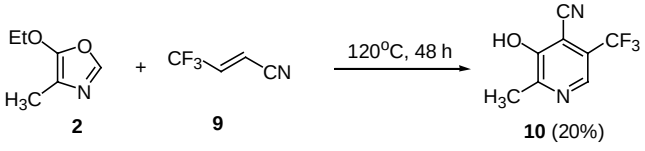
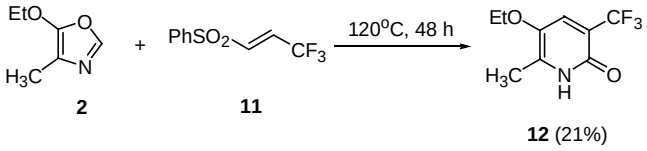


Scheme 6.



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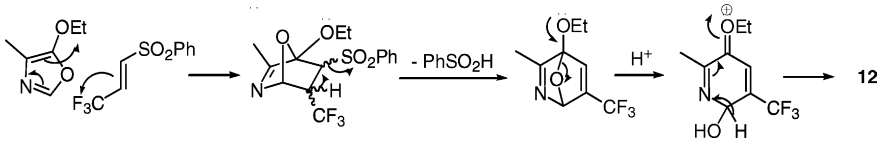
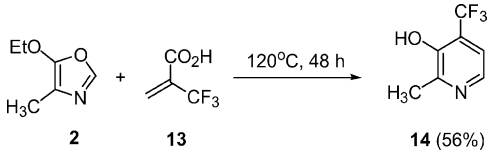


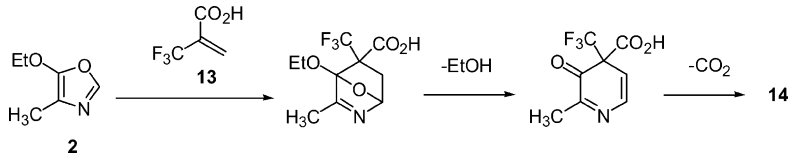
Scheme 8.

(δ 137.7, $^3J_{CF}$ 8 Hz), which is consistent with the presence of the *ortho*-CF_3 group. Alternative product isomer **8** would give a resonance with four-bond carbon–fluorine coupling, which is typically only 0–3 Hz in magnitude.

Immediately distinctive of pyrrole derivative **7** was the multiplet centred at 7.26 ppm attributed to the hydrogen attached to the pyrrole ring. The possibility that **7** was a pyridine derivative was excluded on the basis that resonances for only four aromatic carbon atoms were visible in the ^{13}C spectrum. The signal at 123.4 ppm was identified as C-5 from the ^1H-^{13}C HETCOR spectrum and the multiplicity of this signal ($^3J_{CF}$ 5 Hz) confirmed that the ring hydrogen and CF_3 were *ortho* to each other. Furthermore, the ^{13}C signal of the carbonyl group was particularly noticeable at 188.4 ppm. Compound **7** also exhibited a D_2O-exchangeable proton and a characteristic sharp NH stretching band in the infrared spectrum (3422 cm^{-1}). It appears that **7** was formed as a result of hydrolysis of the intermediate Diels–Alder adduct in the work-up stage, analogous to reported processes involving other non-fluorinated substrates [15] and a mechanism for the formation of **7** is given in Scheme 5.



Scheme 9.



Scheme 10.

By comparing the two experiments already described, we see that alkene **3** reacted regiospecifically with oxazole **2**, the products **6** and **7** arising from a common cycloadduct intermediate followed by elimination of ethanol or hydrolysis, respectively. Conversely, the modest regioselectivity seen in reaction between **3** and oxazole **1** may be ascribed to a steric clash of the oxazole C(2)CH_3 and the CF_3-group of **3** in the initial cycloaddition step.

Oxazole **2** also reacted regiospecifically with 4,4,4-trifluorocrotonitrile **9** in refluxing toluene (48 h) to furnish pyridine **10** in modest yield after column chromatography (Scheme 6). No other regioisomeric pyridines or fluorine containing products were observed by NMR spectroscopy. The structure of **10** was confirmed by ^{1}H-^{13}C HETCOR spectroscopy, which identified C-6 as a broadened signal at 135.5 ppm due to coupling with the adjacent CF_3 group.

Treatment of **2** with 3,3,3-trifluoro 1-(phenylsulfonyl)-1-propene **11** in refluxing toluene gave pyridin-2-one **12** as the only product in modest yield (Scheme 7). A mechanism for the formation of **12**, involving loss of the very good phenylsulfonyl leaving group is outlined in Scheme 8.

In contrast to the sluggish reactivity of 1,2-disubstituted alkenes **3**, **9** and **11**, 2-(trifluoromethyl)propenoic acid **13** reacted rapidly with oxazole **2** at room temperature. The reaction was accompanied by a strong exotherm and evolution of a gas. Column chromatography afforded pyridine **14** as the sole product in good yield (Scheme 9). Here, the presence of two electron withdrawing groups makes the orbital coefficient at the CH_2 site larger and overlap with the C-2 oxazole site more favourable, allowing the reaction to proceed very readily with high regioselectivity.

The *ortho* relationship of the ring hydrogens in **14** was evident from the doublet located at δ 7.34 ppm (J 5 Hz). *Meta*-couplings in pyridines typically have much smaller J values (<1 Hz). Formation of **14** can be explained by regiospecific cycloaddition of oxazole **2** to alkene **13**, followed by ring opening and decarboxylation (Scheme 10). An analogous result was reported by Matsuo from the reaction between methacrylic acid $CH_2{=}C(CH_3)CO_2H$ and oxazole **2** [17].

3. Conclusions

The cycloaddition of trifluoromethyl alkenes with 5-ethoxyoxazoles provides routes to various trifluoromethylated pyridines and pyridone derivatives depending upon the nature of the substituent present on the alkene. The regioselectivity in the cycloaddition step proceeded to give the pyridine product having the stronger electron group (i.e. CO_2Et, CN, SO_2Ph) orientated *para* to the ring nitrogen.

4. Experimental

4.1. General

2,4-Dimethyl 5-ethoxyoxazole **1** and 4-methyl 5-ethoxyoxazole **2** were prepared by literature procedures [22–24]. Other starting materials were obtained commercially (Sigma–Aldrich) and solvents were dried using literature procedures. NMR spectra were recorded in deuteriochloroform, unless otherwise stated, on a Varian VXR 400S spectrometer with tetramethylsilane and trichlorofluoromethane as internal standards. Spectral assignments were made with the aid of data collected by ^{1}H-^{1}H COSY and ^{1}H-^{13}C HETCOR experiments and coupling constants are given in hertz. Mass spectra were recorded on either a VG 7070E spectrometer or a Fissons VG Trio 1000 spectrometer coupled with a Hewlett Packard 5890 series II gas chromatograph. Accurate mass measurements were performed by the EPSRC National Mass Spectrometry service, Swansea, UK. Elemental analyses were obtained on either a Perkin-Elmer 240 or a Carlo Erba Elemental Analyser. Melting points were recorded at atmospheric pressure and are uncorrected. Column chromatography was carried out on silica gel (Merck No. 1-09385, 230-400 mesh) and TLC analysis was performed on silica gel plates.

4.2. 2,6-Dimethyl-3-hydroxy- 5-trifluoromethyl isonicotinic acid ethyl ester (*4*)

5-Ethoxy-2,4-dimethyl oxazole (1 g, 7 mmol), ethyl 4,4,4 trifluorocrotonate (2.44 g, 14 mmol) and toluene (20 ml) were heated together at reflux temperature for 72 h. After cooling, volatile materials were removed at reduced pressure to yield a brown oily solid. ^{19}F NMR analysis indicated a mixture of two trifluoromethylated products in ratio 3:1. Purification by column chromatography on silica gel (eluent 10:1 hexane-ethyl acetate) gave 3-hydroxy-2,6-dimethyl-5-trifluoromethyl isonicotinic acid ethyl ester **4** (0.34 g, 18.5%) as a yellow solid; mp 106–107 °C (found: C, 49.8; H, 4.6; N, 5.2, $[M]^+$, 263.076517. $C_{11}H_{12}NO_3F_3$ requires: C, 50.2; H, 4.6; N, 5.3%, $[M]^+$, 263.076928); δ_H 1.38 (3H, t, J 8 Hz, CH_2CH_3), 2.53 (3H, s, C(2)-CH_3), 2.62 (3H, q, $^{5}J_{HF}$ 3.0 Hz, C(6)-CH_3), 4.42 (2H, q, J 7 Hz,

CH_2CH_3), 8.23 (1H, br s, OH); δ_C 13.9 (s, CH_2CH_3), 19.9 (s, C(2)-CH_3), 23.7 (q, $^4J_{CF}$ 3.5, C(6)-CH_3), 63.5 (s, OCH_2), 119.4 (q, $^2J_{CF}$ 31, C–CF_3), 121.2 (m, C-4), 123.9 (q, $^1J_{CF}$ 273, CF_3), 147.8 (s, C-2), 148.3 (s, C-3), 152.8 (s, C-6), 168.0 (s, C=O); δ_F −56.4 (s); *m/z* (EI) 263 ($[M]^+$, 38%), 218 ($[M\text{-}OCH_2CH_3]^+$, 26%), 217 ($[M\text{-}OCH_2CH_3]H^+$, 100%), 189 ($[M\text{-}CO_2CH_2CH_3\text{-}H]^+$, 66%), 120 ($[M\text{-}CO_2CH_2CH_3\text{-}CF_3\text{-}H]^+$, 34%); and a mixture (ratio **4**:**5**, 1:2) containing 3-hydroxy-2,6-dimethyl-4-trifluoromethyl nicotinic acid ethyl ester **5** (0.27 g); δ_H 1.37 (3H, t, *J* 7 Hz, CH_2CH_3), 2.45 (3H, s, CH_3), 2.53 (3H, s, CH_3), 4.39 (2H, q, *J* 7Hz, CH_2CH_3); δ_F −58.95 (m); *m/z* (EI) 263 ($[M]^+$, 58%), 218 ($[M\text{-}CH_3CH_2O]^+$, 100%).

4.3. 2-Methyl-3-hydroxy- 5-trifluoromethyl isonicotinic acid ethyl ester (**6**)

4-Methyl-5-ethoxy-oxazole (0.5 g, 3.9 mmol) and ethyl 4,4,4 trifluorocrotonate (2.70 g, 16 mmol) were heated together at 120 °C for 48 h. Volatile materials were removed at reduced pressure to yield a brown oily solid, which after purification by column chromatography on silica gel (eluent 5:1 hexane-ethyl acetate) gave 2-methyl-3-hydroxy-5-trifluoromethyl isonicotinic acid ethyl ester **6** (0.24 g, 25%) as a waxy solid; (found $[M]^+$ 249.062180. $[C_{10}H_{10}NO_3F_3]^+$ requires 249.061278); δ_H 1.36 (3H, t, *J* 7 Hz, CH_2CH_3), 2.53 (3H, s, C(2)-CH_3), 4.21 (2H, q, *J* 7 Hz, CH_3CH_2O), 8.35 (1H, s, H-6), 10.80 (br s, OH); δ_F −58.6 (s); δ_C 13.8 (s, CH_2CH_3), 20.2 (s, C(2)-CH_3), 63.7 (s, CH_2), 115.3 (m, C-4), 121.3 (q, $^2J_{CF}$ 32 Hz, C-5), 123.4 (q, $^1J_{CF}$ 272 Hz, CF_3), 137.7 (q, $^3J_{CF}$ 8 Hz, C-6), 154.3 (s, C-2), 156.5 (s, C-3), 168.5 (s, C=O); *m/z* (EI) 249 ($[M]^+$, 6%), 203 ($[M\text{-}OEt\text{-}H]^+$, 14%), 175 ($[M\text{-}CO_2Et\text{-}H]^+$, 20%), 156 ($[M\text{-}CO_2Et\text{-}H\text{-}F]^+$, 26%); and, 2-(acetyl)-3-(carboethoxy)-4-trifluoromethyl pyrrole **7** (0.08 g, 8%) as an oily solid; (found $[M]^+$ 249.061537. $[C_{10}H_{10}NO_3F_3]^+$ requires 249.061278); δ_H 1.33 (3H, t, *J* 7.0, CH_2CH_3), 2.51 (3H, s, $CH_3C{=}O$), 4.34 (2H, q, *J* 7.0, CH_3CH_2O), 7.60 (1H, m, H-5), 12.8 (br m, NH); δ_F –57.7 (s); δ_C 13.7 (s, CH_2CH_3), 27.7 (s, $CH_3C{=}O$), 61.3 (s, CH_2), 113.2 (q, $^2J_{CF}$ 36.0, C-4), 117.5 (m, C-3), 122.8 (q, $^1J_{CF}$ 267.0, CF_3), 123.4 (q, $^3J_{CF}$ 5.0, C-5), 131.8 (s, C-2), 163.7 (s, OC=O), 188.4 (s, $CH_3C{=}O$); *m/z* (EI) 249 ($[M]^+$, 6%), 204 ($[M\text{-}OEt]^+$, 88%), 203 ($[M\text{-}OEt\text{-}H]^+$, 100%), 188 ($[M\text{-}OEt\text{-}H\text{-}CH_3]^+$, 60%), 184 ($[M\text{-}OEt\text{-}H\text{-}F]^+$, 90%), 175 ($[M\text{-}CO_2Et\text{-}H]^+$, 26%).

4.4. 3-Hydroxy-2-methyl-5-trifluoromethylisonicotinonitrile (**10**)

4-Methyl-5-ethoxy-oxazole (0.5 g, 3.9 mmol), 4,4,4 trifluorocrotonitrile (0.94 g, 7.8 mmol, 2 eq) and toluene (20 ml) were heated at reflux for 48 h. Volatile materials were removed at reduced pressure to yield a brown residue, which after column chromatography on silica gel (eluent 3:1 hexane-ethyl acetate) gave 3-hydroxy-2-methyl-5-trifluoromethyl-isonicotinonitrile **10** (0.16 g, 20%) as an orange solid; mp 156 °C (decomp.) (found $[M]^+$ 202.035398. $[C_8H_5N_2OF_3]^+$ requires 202.034501); δ_H 2.61 (3H, s, CH_3), 4.2 (br m, OH), 8.48 (1H, s, H-6); δ_F –60.3 (s); δ_C 21.1 (s, CH_3), 102.8 (s, C-4), 113 (s, CN), 123 (q, $^1J_{CF}$ 272 Hz, CF_3), 123.6 (q, $^2J_{CF}$ 31.5 Hz, C-5), 135.5 (m, C-6), 155.6 (s, C-2), 156.2 (s, C-3); *m/z* (EI) 203 ($[MH]^+$, 8%), 202 ($[M]^+$, 100%), 183 ($[M\text{-}F]^+$, 10%).

4.5. 5-Ethoxy-6-methyl-3-trifluoromethyl 1H-pyridin-2-one (**12**)

4-Methyl-5-ethoxy-oxazole (0.25 g, 1.97 mmol), 3,3,3-trifluoro 1-(phenylsulfonyl)-1-propene (0.93 g, 3.94 mmol) and toluene were heated at reflux for 48 h. Volatile materials were removed at reduced pressure to yield a black residue, which after column chromatography on silica gel (eluent 3:1 hexane-ethyl acetate) and recrystallisation from hexane-ethyl acetate, gave 5-ethoxy-6-methyl-3-trifluoromethyl 1H-pyridin-2-one **12** (90 mg, 21%) as a brown solid; mp 119–120 °C (found: C 48.9, H 4.6%, N 6.3, $[M]^+$, 221.066418. $C_9H_{10}NO_2F_3$ requires: C 48.9%, H 4.6%, N 6.3%, $[M]^+$, 221.066363); δ_H 1.28 (3H, t, *J* 7 Hz, CH_2CH_3), 2.45 (3H, s, C(6)CH_3), 4.20 (2H, q, *J* 7 Hz, CH_3CH_2O), 7.26 (1H, s, H-4), 11.87 (1H, br s, NH); δ_F −55.2 (s); δ_C 13.9 (s), C(6)CH_3, 15.0 (s, CH_2CH_3), 60.1 (s, CH_2), 108.8 (s, C-6), 113.5 (q, $^2J_{CF}$ 36 Hz, C-3), 120.3 (q, $^3J_{CF}$ 6.5 Hz, C-4), 124.5 (q, $^1J_{CF}$ 266 Hz, CF_3), 139.2 (s, C-5), 164 (s, C=O); *m/z* (EI) 221 ($[M]^+$, 28%), 176 ($[M\text{-}OEt]^+$, 100%).

4.6. 2-Methyl 4-trifluoromethyl pyridin-3-ol (**14**)

2-(Trifluoromethyl)propenoic acid (1.1 g, 3.9 mmol) was added to 4-methyl 5-ethoxyoxazole (0.5 g, 3.9 mmol). After gas evolution had subsided the viscous red oil was adsorbed onto silica gel and purification by column chromatography (eluent 2:1 hexane-ethyl acetate) gave 2-methyl 4-trifluoromethyl pyridin-3-ol **14** (0.46 g, 56%) as a white solid; mp 175 °C (decomp.) (found: C 47.4, H 3.4, N 7.6, $[M]^+$177.040139. $[C_7H_6NOF_3]^+$ requires: C 47.5, H 3.5, N 7.9%, $[M]^+$ 177.040149); δ_H 2.46 (3H, s, CH_3), 7.34 (1H, d, *J* 5 Hz, H-5), 8.09 (1H, m, H-6), 9.97 (1H, br s, OH); δ_F −62.0 (m); δ_C 20.9 (s, CH_3), 118.9 (m, C-5), 124.0 (q, $^2J_{CF}$ 31 Hz, C-4), 124.1 (q, $^1J_{CF}$ 272 Hz, CF_3), 141 (s, C-6), 149.5 (s, C-2), 150.4 (s, C-3); *m/z* (EI) 177 ($[M]^+$, 100%), 157 ($[M\text{-}H\text{-}F]^+$, 34%).

Acknowledgements

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