Reaction of pentafluorobenzoylpyruvic acid with amines

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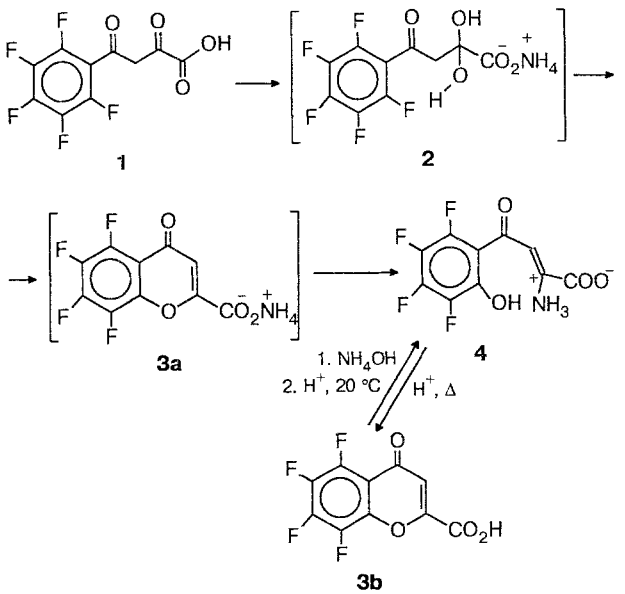
Reactions of pentafluorobenzoylpyruvic acid with amines afford the respective enamines. The intramolecular cyclization of the latter results in *N*-substituted 4-quinolone-2-carboxylic acids. Ammonia and triethylamine favor the cyclization of pentafluorobenzoylpyruvic acid to 2-carboxychromone.

Key words: pentafluorobenzoylpyruvic acid; primary amines; intramolecular cyclization; nucleophilic substitution of *ortho* fluorine atom; 2-carboxy-5,6,7,8-tetrafluorochromone; 5,6,7,8-tetrafluoro-1,4-dihydro-4-oxoquinoline-2-carboxylic acid.

The reaction of ethyl pentafluorobenzoylpyruvate with amines readily gives 5,6,7,8-tetrafluoro-2-ethoxycarbonylchromone, which is resistant to the further attack by the nucleophile.[1] The reaction of pentafluorobenzoylpyruvic acid with *N*-nucleophiles has not been studied. However, the synthetic potential of this compound should be similar to that of nonfluorinated aroylpyruvic acids, which react with amines at the α-carbonyl and carboxyl groups.[2—4] However, unlike the nonfluorinated analogs, pentafluorobenzoylpyruvic acid is also capable of intramolecular cyclization owing to the ease of nucleophilic substitution of the *ortho* fluorine atom.

Scheme 1



In the present work we studied the reaction of pentafluorobenzoylpyruvic acid (**1**) with ammonia, isopropylamine, cyclohexylamine, ethanolamine, triethylamine, and aniline.

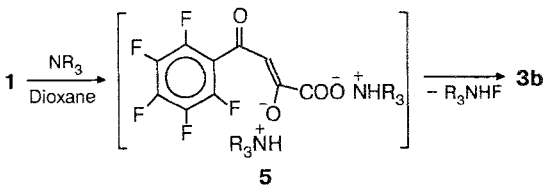
The reaction of compound **1** with ammonium hydroxide gives amino acid **4**, probably *via* intermediates **2** and **3a** (Scheme 1). It is known that when nonfluorinated analogs of **1** react with amines in ethanol,[2,3] the *O*-nucleophile is added at the α-carbonyl carbon atom, but subsequent nucleophilic substitution of the *ortho* fluorine atom to give chromone **3** is typical of compound **1**. Heating compound **4** in an acid medium results in its cyclization into 5,6,7,8-tetrafluoro-2-carboxychromone (**3b**) (*cf.* Ref. 1).

2-Carboxychromone **3b** is also formed (in 65—68 % yield) in the reaction of compound **1** with anhydrous NH_3 or Et_3N in dioxane (Scheme 2).

Thus, irrespective of the solvent, the reaction of compound **1** with NH_3 predominantly results in the intramolecular cyclization. These reactions involve the intermediate formation of salt **5**.

Ammonium salt **7** obtained from methyl trifluoroacetylpyruvic acid (**6**) (Scheme 3) does not change on heating in toluene.

Scheme 2



R = H, Et

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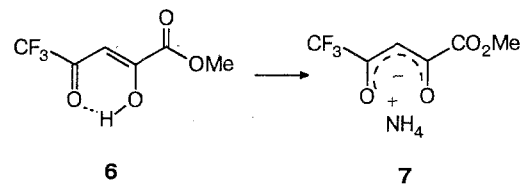
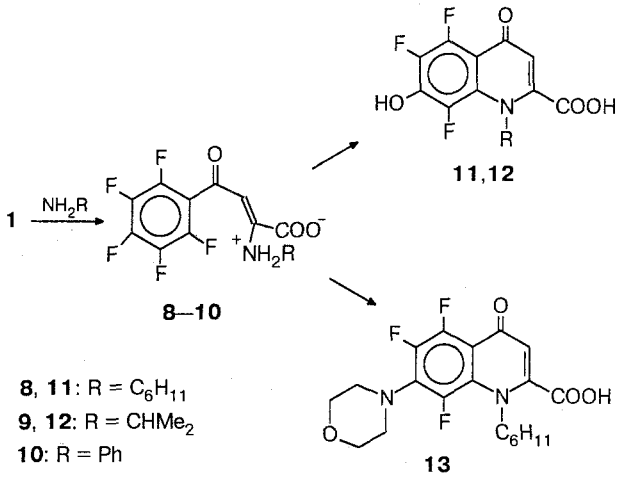
Scheme 3



Scheme 4



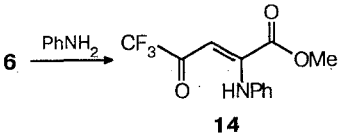
8, 11: R = C_6H_{11}
9, 12: R = $CHMe_2$
10: R = Ph

The reaction of acid **1** with isopropylamine, cyclohexylamine, or aniline in dioxane proceeds by a different route and gives enamines **8—10** (Scheme 4). The presence of water in the reaction medium does not affect the yields of compounds **8—10**.

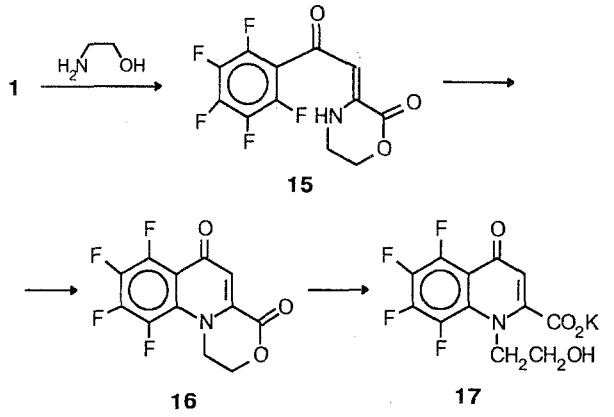
Under alkaline conditions, cyclization of compounds **8** and **9** and nucleophilic substitution of the fluorine atom at C-7, typical of fluorine-containing compounds of this type,[5] occur. The replacement of this active fluorine atom by a morpholine moiety and subsequent cyclization make it possible to transform compound **8** into derivative **13**.

The formation of enamines **8—10** in the above reactions is determined probably by the increasing role of steric factors resulting both in a decrease in the stability of compounds **5** and **7** and a decrease in the hardness of the reacting amine. Obviously, this results in orbital control of the reaction rather than charge control as in the case of NH_3.[6] This behavior of acid **1** is similar to that in the series of fluorine-containing derivatives of acetylpyruvic acid. For example, **6** smoothly reacts with aniline to give amino-compound **14** (Scheme 5).

Scheme 5



Scheme 6



Like aroylpyruvic acids,[4] acid **1** reacts with ethanolamine in dioxane to give a derivative of 1,4-oxazin-2-one **15**, which can then undergo cyclization to compound **16** owing to the presence of an *ortho* fluorine atom in the aromatic ring. Alkaline hydrolysis of **16** occurs with lactone ring opening and results in quinolonecarboxylic acid **17** (Scheme 6).

Thus, the reaction of pentafluorobenzoylpyruvic acid with *N*-nucleophiles primarily involves the α-carbonyl group, but intramolecular cyclization by the replacement of the *ortho* fluorine atom in the aromatic ring to give heterocyclic compounds of novel types is also possible. This kind of cyclization is not characteristic of fluorine-less hydrocarbon analogs.

Experimental

IR spectra of suspensions in vaseline oil were recorded on a Specord 75 IR spectrophotometer in the range 400—4000 cm^{-1}. ^1H NMR spectra were obtained on a Tesla BS-567 A spectrometer (^1H, 100 MHz, relative to TMS, in DMF-d_7). ^{19}F NMR spectra were obtained on a Tesla BS-587 spectrometer (^{19}F, 75 MHz, in DMF-d_7, relative to $CFCl_3$). The digital resolution was 0.5 Hz per point, which corresponds to 0.01 ppm precision in measuring the chemical shifts. The ^{13}C NMR spectrum was recorded on a BS-587A spectrometer (^{13}C, 20 MHz, in $CDCl_3$, relative to TMS).

Ethyl pentafluorobenzoylpyruvate and methyl trifluoroacetylpyruvate **6** were obtained by the known procedures (*cf.* Refs. 7 and 8, respectively).

2,4-Dioxo-4-pentafluorophenylbutyric acid (1). A mixture of ethyl pentafluorobenzoylpyruvate (40.0 g, 129.0 mmol), AcOH (200 mL), and conc. HCl (10 mL) were kept at 35—40 °C for 6 days. The mixture was poured into water (600 mL), then hexane (150 mL) was added, and the mixture was vigorously stirred. The precipitate was filtered off and dried *in vacuo* at 30—40 °C to give 23.7 g (65 %) of compound **1**, m.p. 79 °C (subl.). IR, ν/cm^{-1}: 3540, 3420, 2000 (OH), 1680 (C=O, COOH), 1710 sh. (C=O, keto), 1640, 1625 (C=O, enol), 1585, 1520 (C=C), 1000 (CF). ^1H NMR (CD_3OD), δ: 3.45 (m, 2 H, CH_2, keto); 5.3 (br.s, OH); 6.66 (t, J = 1.6 Hz, 1 H, CH, enol). ^{19}F NMR (CD_3OD), δ, keto): −162.11÷−161.37 (m, 2 F, *meta*-, keto form);

−161.71÷−160.98 (m, 2 F, *meta*-, enol); −150.96 (t.t, J = 20.0 Hz; J = 4.1 Hz, 1 F, *para*-, keto form); −150.03 (t t, J = 20.0 Hz; J = 4.1 Hz, 1 F, *para*-, enol); −141.11÷−140.56 (m, 1 F, *ortho*-, keto form); −140.70÷−140.16 (m, 2 F, *ortho*-, enol). Found (%): C, 42.59; H, 1.10; F, 33.47. $C_{10}H_3F_5N_4$. Calculated (%): C, 42.57; H, 1.07; F, 33.67.

2-Amino-3-(2-hydroxy-3,4,5,6-tetrafluorobenzoyl)acrylic acid (4). Compound **1** (0.8 g, 1.06 mmol) in 25 % NH_4OH (50 mL) was heated to boiling, concentrated to half the original volume, and cooled to 20 °C. HCl was added to pH ~1—2; the precipitate was filtered off, washed with water, and recrystallized from acetonitrile to give 0.15 g (51 %) of compound **4**, m.p. 223—225 °C. IR, ν/cm^{-1}: 1710 (C=O, COOH); 1640 (C=O); 1610 (C=C); 2650, 2500 (OH, NH_3^+); 1575 (COO^-); 3315, 3455 (NH). ^{1}H NMR (acetone-d_6), δ: 6.63 (d, J_{H-F} = 1.1 Hz, 1 H, CH,); 7.92 (br.s, 1 H, NH); 9.6 (br.s, 1 H, NH); 11.1 (br.s, 2 H, 2 OH). ^{19}F NMR, δ: −137.49 (dd d, 1 F); −151.22 (dd d, 1 F); −164.31 (dd d, 1 F); −172.13 (dd.d, 1 F). Found (%): C, 43.11; H, 2.05; F, 26.86; N, 4.90. $C_{10}H_5F_4NO_4$. Calculated (%): C, 43.03; H, 1.81; F, 27.23; N, 5.02.

5,6,7,8-Tetrafluoro-2-carboxychromone (3b). A. Compound **4** (1.0 g, 3.58 mmol) in a mixture of AcOH (30 mL) and conc. HCl (10 mL) was refluxed for 10 h. The acetic acid was distilled off until crystallization of a residue began, and the mixture was cooled to 20 °C. The precipitate was filtered off and washed with water to give 0.6 g (64 %) of **3b**, m.p. 210—212 °C. Its physicochemical constants are in agreement with those reported earlier.[7]

B. Dry NH_3 was passed through a solution of compound **1** (0.4 g, 1.42 mmol) in dioxane (15 mL), initially at 20 °C and then at the boiling point of the solvent for 1 h. The reaction mixture was cooled and neutralized with 15 % HCl (50 mL). The precipitate was filtered off, washed with water, and dried to give 0.25 g (68 %) of compound **3b**, m.p. 210—212 °C. The physicochemical constants are in agreement with those reported earlier.[7]

C. A mixture of compound **1** (0.1 g, 0.355 mmol) in dioxane (4 mL) and Et_3N (1 mL, 0.73 g, 7.2 mmol) was kept for 15 min at 18 °C. The reaction mixture was poured into dilute HCl (10 mL), and the residue was filtered off to give 0.04 g (43 %) of compound **3b**. The extraction of the filtrate with ethyl acetate (15 mL) followed by treatment with hexane gave an additional amount (0.02 g) of **3b**, overall yield 0.06 g (65 %), m.p. 210—212 °C. The physicochemical constants are in agreement with those reported earlier.[7]

[Methyl(trifluoroacetylpyruvato)]ammonium (7). Ammonia was passed for 1 h through a solution of compound **6** (2.0 g, 10.0 mmol) in benzene (50 mL). The precipitate was filtered off and dried in the air to give 2.0 g (93 %) of compound **7**, m.p. 84—86 °C. IR, ν/cm^{-1}: 1725 (C=O in CO_2Me); 1630 (C=O); 1510 (C=C); 3170, 3070, 1495 (NH). ^{1}H NMR (CD_3OD), δ: 3.8 (s, 3 H, CH_3); 4.9 (s, 4 H, NH_4^+); 5.86 (s, 1 H, CH). Found (%): C, 33.11; H, 3.66; F, 26.69; N, 7.07. $C_6H_5F_3O_4 \cdot NH_3$. Calculated (%): C, 33.50; H, 3.75; F, 26.49; N, 6.51.

2-Cyclohexylamino-3-pentafluorobenzoylacrylic acid (8). A mixture of compound **1** (3.0 g, 10.6 mmol) in dioxane (20 mL) and cyclohexylamine (1.05 g, 10.6 mmol) was refluxed for 1 h. The solution was cooled and poured into water (200 mL), and the product was precipitated with hexane (100 mL). The precipitate was filtered off and recrystallized from CCl_4 to give 2.5 g (65 %) of compound **8**, m.p. 155—157 °C. IR, ν/cm^{-1}: 3250 (NH); 1680 (C=O in COOH); 2700, 1565 (COO^-, NH_2^+); 1640 (C=O); 1510 (C=C). ^{1}H NMR, δ: 1.05—2.1 (m, 10 H, 5 CH_2); 3.85 (m, 1 H, NCH); 5.62 (s, 1 H, CH=); 6.22 (br.s, 1 H, OH); 10.8 (br.s, 1 H, NH). ^{19}F NMR, δ: −162.37÷−161.7 (m, 2 F, *meta*-); −154.29 (t, J = 20.7 Hz, 1 F, *para*-); −142.71÷−142.29 (m, 2 F, *ortho*-). Found (%): C, 52.58; H, 4.20; F, 26.77; $C_{16}H_{14}F_5NO_3$. Calculated (%): C, 53.00; H, 3.88; F, 26.20.

2-(Isopropylamino)-3-pentafluorobenzoylacrylic acid (9). In a similar way, 1.6 g (47 %) of compound **9** was obtained from compound **1** (3.0 g, 10.6 mmol) and isopropylamine (0.63 g, 10.7 mmol); m.p. 158—160 °C. IR, ν/cm^{-1}: 3240 (NH); 1690 (C=O in COOH); 2700, 1600—1565 (COO^-, NH_2^+); 1650 (C=O); 1515 (C=C). ^{1}H NMR, δ: 1.32 (d, J = 6.6 Hz, 6 H, 2Me); 3.91—4.25 (m, 1 H, NCH); 5.56 (s, 1 H, CH=); 6.1 (br.s, 1 H, OH); 10.6 (br.s, 1 H, NH). ^{19}F NMR, δ: −162.41÷−161.66 (m, 2 F, *meta*-); −154.33 (t, J = 20.5 Hz, 1 F, *para*-); −142.74÷−142.33 (m, 2 F, *ortho*-). Found (%): C, 46.60; H, 3.55; F, 28.74; $C_{13}H_{10}F_5NO_3 \cdot 0.5H_2O$. Calculated (%): C, 47.00; H, 3.34; F, 28.60.

2-Anilino-3-pentafluorobenzoylacrylic acid (10). In a similar way, 0.6 g (78 %) of crude **10** was obtained from compound **1** (0.6 g, 2.13 mmol) and aniline (0.2 g, 2.14 mmol); m.p. 176—178 °C. IR, ν/cm^{-1}: 3200 (NH); 1680 (C=O in COOH); 2700, 1550 (COO^-, NH_2^+); 1640 (C=O); 1510 (C=C). ^{1}H NMR (CD_3COCD_3), δ, stereoisomers A : B in 8 : 1 ratio): 5.97 (t, J = 1.6 Hz, 1 H, CH=, A); 6.06 (t, J = 1.6 Hz, 1 H, CH=, B); 7.2—7.6 (m, 5 H, Ph); 11.9 (br.s, 1 H, NH). ^{19}F NMR (CD_3COCD_3), δ, A : B in 8 : 1 ratio): −161.84 (m, 2 F, *meta*-, isomer A); −161.67 (m, 2 F, *meta*-, isomer B); −153.17 (tt, 1 F, *para*-, A); −152.44 (tt, 1 F, *para*-, B); −141.98 (m, 2 F, *ortho*-, A); −141.25 (m, 2 F, *ortho*-, B). Found (%): C, 53.88; H, 2.60; F, 26.20; N, 4.01. $C_{16}H_8F_5NO_3$. Calculated (%): C, 53.80; H, 2.26; F, 26.59; N, 3.92.

1-Cyclohexyl-5,6,8-trifluoro-7-hydroxy-4-quinolone-2-carboxylic acid (11). A mixture of compound **8** (7.0 g, 19.3 mmol) and KOH (8.0 g, 143.0 mmol) in water (200 mL) was heated for 1 h at 90—95 °C on a water bath. The mixture was cooled and poured dropwise with stirring into a solution of conc. HCl (25 mL) in water (100 mL). The precipitate was filtered off, washed with water and 2-propanol, and dried to give 4.8 g (74 %) of compound **11**, m.p. 295—297 °C. IR, ν/cm^{-1}: 2650 (OH, COO^-, NH^+); 1725 (C=O in COOH); 1640 (C=O); 1610, 1520 (C=C); 1565 (COO^-). ^{1}H NMR, δ: 1.25—2.12 (m, 10 H, 5 CH_2); 3.95 (m, 1 H, NCH); 6.41 (s, 1 H, CH=); 9.1 (br.s, 1 H, OH). ^{19}F NMR, δ: −161.20 (d.d, 1 F, F-6); −147.36 (d.d, 1 F, F-5); −140.95÷−140.55 (m, 1 F, F-8); J_{5-6} = J_{6-5} = 19.5 Hz; J_{5-8} = 11.5 Hz; J_{6-8} = 8.1 Hz. Found (%): C, 56.18; H, 4.46; F, 16.80. $C_{16}H_{14}F_3NO_4$. Calculated (%): C, 56.31; H, 4.13; F, 16.70.

5,6,8-Trifluoro-7-hydroxy-1-isopropyl-4-quinolone-2-carboxylic acid (12). In a similar way, compound **9** (0.5 g, 1.55 mmol) was heated with KOH (0.5 g, 90 mmol) in water (10 mL). The solution was acidified with dilute HCl (1 : 5, 60 mL). The precipitate was filtered off, washed with water, and dried to give 0.35 g (75 %) of compound **12**, m.p. 210—212 °C. IR, ν/cm^{-1}: 2500 (OH, COO^-, NH^+); 1730 (C=O in COOH); 1640 (C=O); 1590 (COO^-); 1505 (C=C). ^{1}H NMR, δ: 1.57 (d d, J_{H-H} = 5.8 Hz, J_{H-F} = 2.8 Hz, 6 H, 2 Me); 4.4—4.6 (m, 1 H, NCH); 6.14 (br.s, 2 H, OH); 6.36 (s, 1 H, CH=). ^{19}F NMR, δ: −161.1 (d d, 1 F, F-6); −147.16 (d d, 1 F, F-5); −139.83 (m, 1 F, F-8); J_{5-6} = 19.6 Hz; J_{5-8} = 11.5 Hz; J_{6-8} = 7.8 Hz. Found (%):

C, 51.67; H, 3.49; F, 19.13; $C_{13}H_{10}F_3NO_4$. Calculated (%): C, 51.83; H, 3.35; F, 18.92.

1-Cyclohexyl-5,6,8-trifluoro-7-morpholino-4-quinolone-2-carboxylic acid (13). A mixture of compound **8** (9.0 g, 24.8 mmol) and morpholine (12.0 g, 138.0 mmol) in DMSO (40 mL) was heated for 1 h at 90—100 °C. A solution of KOH (9.0 g, 160.0 mmol) in water (150 mL) was added to the reaction mixture, and the solution was heated for an additional 1 h at 90—100 °C. The mixture was cooled and mixed with a solution of dilute HCl (1 : 3, 200 mL). The precipitate was filtered off, precipitated with water from DMF, and reprecipitated with acetonitrile from DMF to give 3.6 g (35 %) of compound **13,** m.p. 176—178 °C. IR, ν/cm^{-1}: 3300, 3400, 2000 (OH, COO^-, NH^+); 1710 (C=O in COOH); 1630 (C=O); 1590 sh. (COO^-); 1610 (C=C). ^1H NMR (DMF-d_7 + CD_3COOD), δ: 0.9—2.2 (m, 10 H, 5 CH_2); 3.44 (br.s, 4 H, CH_2NCH_2); 3.80 (t, J = 4.0 Hz, 4 H, CH_2OCH_2); 4.00 (m, 1 H, NCH); 6.36 (s, 1 H, CH=). ^{19}F NMR, δ: −151.34 (d d, 1 F, F-6); −147.14 (d d, 1 F, F-5); −128.84 (d, 1 F, F-5); J_{5-6} = 18.6 Hz; J_{5-8} = 12.2 Hz; J_{6-8} = 4.4 Hz; J_{8-5} = 10.8 Hz. Found (%): C, 58.61; H, 5.20; F, 13.40; N, 6.91. $C_{20}H_{21}F_3N_2O_4$. Calculated (%): C, 58.53; H, 5.16; F, 13.89; N, 6.83.

Methyl 2-anilino-5,5,5-trifluoro-4-oxo-2-pentenoate (14). A mixture of compound **6** (2.0 g, 10.0 mmol) and $PhNH_2$ (0.93 g, 10.0 mmol) in MeOH (10 mL) was stirred for 8 h, the MeOH was evaporated, and the residue was recrystallyzed from pentane to give 1.6 g (59 %) of compound **14**, m.p. 60—61 °C. IR, ν/cm^{-1}: 1730 (C=O in CO_2Me); 1620 (C=O); 1580 (C=C); 3380, 3250, 1560 (NH). ^1H NMR ($CDCl_3$), δ: 3.72 (s, 3 H, CH_3); 5.91 (s, 1 H, CH=); 7.0—7.4 (m, 5 H, Ph); 11.8 (br.s, 1 H, NH). ^{13}C NMR, δ: 53.23 (s, Me); 91.41 (s, CH=); 154.50 (s, =CNPh); 163.05 (s, C=O in COOMe); 116.71 (q, J = 288.1 Hz, CF_3); 178.32 (q, J = 34.8 Hz, C=O). Found (%): C, 53.04; H, 4.01; F, 21.20; N, 4.92. $C_{12}H_{10}F_3NO_3$. Calculated (%): C, 52.78; H, 3.69; F, 20.86; N, 5.13.

3-Pentafluorobenzoylmethylenemorpholin-2-one (15). A mixture of compound **1** (3.0 g, 10.6 mmol) and ethanolamine (0.65 g, 10.7 mmol) in dioxane (25 mL) was refluxed for 1 h. The reaction mixture was poured into water. The precipitate was filtered off and recrystallized from MeOH to give 1.5 g (46 %) of compound **15,** m.p. 175—177 °C. IR, ν/cm^{-1}: 3260, 1580 (NH); 1735 (OC=O); 1640 (C_6F_5C=O); 1625, 1510 (C=C). ^1H NMR (CD_3COCD_3), δ: 3.48 (dt, J_{H-H} = 5.0 Hz, J_{H-F} = 3.5 Hz, 2 H, CH_2N); 4.74 (t, J = 5.0 Hz, 2 H, CH_2O); 6.1 (t, J = 1.6 Hz, 1 H, CH=); 10.7 (br.s, 1 H, NH). ^{19}F NMR (CD_3COCD_3), δ: −162.38÷−161.62 (m, 2 F, *meta*-); −153.99 (tt, 1 F, *para*-); −142.74÷−142.20 (m, 2 F, *ortho*-). Found (%): C, 46.51; H, 2.40; F, 30.36. $C_{12}H_6F_5NO_3$. Calculated (%): C, 46.92; H, 1.97; F, 30.92.

7,8,9,10-Tetrafluoro-4-oxo-1,2,4,5-tetrahydro[1,4]oxazino-[4,3-*b*]-4-quinolone (16). A solution of compound **15** (5.6 g, 18.2 mmol) in DMSO (35 mL) was refluxed for 25 min, then water (100 mL) was added dropwise with stirring. The precipitate was filtered off and recrystallized from acetonitrile to give 2.4 g (46 %) of compound **16,** m.p. 208 °C. IR, ν/cm^{-1}: 1740 (C=O in OC=O); 1630 (C=O); 1600, 1515 (C=C). ^1H NMR, δ: 4.7—4.9 (m, 4 H, 2 CH_2); 6.67 (s, 1 H, CH=). ^{19}F NMR, δ: −162.51 (d d, 1 F, F-6); −150.06 (dd d, 1 F, F-7); −146.24 (dd t, 1 F, F-8); −143.99 (dd d, 1 F, F-5); J_{6-7} = 21.1 Hz; J_{7-6} = 21.4 Hz; J_{6-5} = 19.9 Hz; J_{5-6} = 19.97 Hz; J_{7-8} = 19.2 Hz; J_{8-7} = 19.6 Hz; J_{7-5} = 7.0 Hz; J_{5-7} = 7.4 Hz; J_{8-5} = J_{5-8} = 12.9 Hz. Found (%): C, 49.86; H, 2.22; F, 26.16. $C_{12}H_5F_4NO_3$. Calculated (%): C, 50.19; H, 1.75; F, 26.46.

Potassium 5,6,7,8-tetrafluoro-1-(2-hydroxyethyl)-4-quinolone-2-carboxylate (17). A mixture of 0.29 *N* KOH (5.8 mL, 1.689 mol) and compound **16** (0.5 g, 1.741 mmol) was stirred for 20 min. The mixture was diluted with water to 15 mL, the residue of compound **16** was filtered off, and the filtrate was concentrated to 70 °C to give 0.45 g (76 %) of compound **17**, m.p. 240 °C (dec.). IR, ν/cm^{-1}: 3310 (OH); 1640 (C=O); 3050, 1510, 1590 (C=C); 1610 (COO^-). ^1H NMR (DMF-d_7+D_2O), δ: 3.91 (d t, J_{H-F} = 2.0 Hz, 2 H, CH_2N); 4.65 (m, 2 H, CH_2O); 6.18 (s, 1 H, CH=). ^{19}F NMR (DMF-d_7+D_2O), δ: −163.78 (t, 1 F, F-6); −150.63 (dd.d, 1 F, F-7); −145.59 (dd.t, 1 F, F-8); −143.79 (ddd, 1 F, F-5); J_{6-5} = J_{5-6} = 21.5 Hz; J_{7-5} = J_{5-7} = 6.7 Hz; J_{7-8} = J_{8-7} = 19.2 Hz; J_{5-8} = J_{8-5} = 12.5 Hz; J_{8F-H} = 1.9 Hz. Found (%): C, 42.17; H, 1.98; F, 21.92. $C_{12}H_6F_4NO_4$. Calculated (%): C, 41.98; H, 1.76; F, 22.14.

References

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