N—$(CH_3)_2$); 7.80 and 7.90 (both m, 2 H, H-5, H-8); the H-6 and H-7 signals are superimposed upon those of compounds **5** and **6**; the signals of the NH_2 and OH groups are considerably broadened due to exchange. ^{13}C NMR spectrum (30°C, DMSO-d_6), δ: 42.57 (q, N—$(CH_3)_2$); 118.04 and 124.78 (both s, C-9, C-10); 119.70, 119.90, 121.58 and 124.10 (all d, C-5, C-6, C-7, C-8); 125.94 and 128.03 (both s, C-2, C-3); 132.21 and 143.67 (both s, C-1, C-4).

6-Isopropoxy-9,10,11,11a-tetrahydro-8*H*-naphtho[2',1':4,5]oxazolo[3,2-*a*]pyridine-5-ol (9) was prepared by irradiating 8 mg of aminoquinone **10** dissolved in 0.5 mL of CS_2 at −80°C for 1 h. ^1H NMR spectrum (−70°C, CS_2)*, δ: 1.00 (d, 3 H, CH_3, $^3J_{H-H}$ = 5.8 Hz); 1.03 (m, H-10*a*); 1.07 (d, 3 H, CH_3, $^3J_{H-H}$ = 5.8 Hz); 1.40 (m, 2 H, H-9, H-9); 1.51 (m, 1 H, H-10*e*); 1.78—1.98 (m, 2 H, H-11*a*, H-11*e*); 2.76 (m, 2 H, H-8, H-8); 4.32 (m, 1 H, OCH_3, $^3J_{H-H}$ = 5.8 Hz); 4.71 (m, 1 H, H-11a, $J_{H(11a)-H(11a)}$ = 5.5 Hz; $J_{H(11a)-H(11e)}$ = 3.7 Hz); 5.78 (br s, 1 H, OH); 6.81 and 6.88 (both m, 1 H, H-2, H-3); 7.16 (m, 1 H, H-1); 7.47 (m, 1 H, H-4). ^{13}C NMR spectrum (−70°C, CS_2, δ(CS_2) = 192.8), δ: 21.78 and 25.14 (both t, C-10, C-9); 22.66 (q, CH_3); 22.97 (q, CH_3); 28.87 (t, C-11); 49.02 (t, C-8); 74.52 (d, OCH); 97.97 (d, C-11a); 117.01 and 119.61 (both s, C-12b, C-4a); 120.52, 122.86, 123.52 and 125.25 (all d, C-1, C-2, C-3, C-4); 129.53 and 129.53 (both s, C-5, C-6a); 139.24 and 139.76 (both s, C-6, C-12a). ^{13}C NMR spectrum (23°C, CS_2), δ: 20.96 (t, C-10); 22.57 (q, CH_3); 23.19 (q, CH_3); 24.58 (t, C-9); 28.46 (t, C-11); 48.52 (t, C-8); 74.61 (d, OCH); 96.70 (d, C-11a); 117.35 and 120.08 (both s, C-12b, C-4a); 120.54, 122.81, 123.38 and 124.97 (all d, C-1, C-2, C-3, C-4); 129.36 and 130.81 (both s, (C-5, C-6a); 139.15 (s, C-12a); 140.45 (C-6).

* Chemical shifts are referred to an external standard.

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Synthesis of 2(3)-ethoxycarbonyl-5,6,7,8-tetrafluorochromones

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The hitherto unknown ethyl pentafluorobenzoylpiruvate was prepared by condensing pentafluoroacetophenone with diethyl oxalate. Intramolecular cyclization of this ester or of its copper(II) chelate, as well as of ethyl 2-(ethoxymethylene)pentafluorobenzoylacetate affords 2- and 3-ethoxycarbonyl-5,6,7,8-tetrafluorochromones. Hydrolysis of the latter followed by decarboxylation gives 5,6,7,8-tetrafluorochromone.

Key words: intramolecular cyclization; 2- (and 3-)-ethoxycarbonyl-5,6,7,8-tetrafluorochromone, hydrolysis; 2- (and 3-)-carboxy-5,6,7,8-tetrafluorochromone, decarboxylation; 5,6,7,8-tetrafluorochromone.

One of the most significant achievements of late in the development of antibacterial agents is the emergence of fluoroquinolones as a new generation of synthetic antibiotics.[1] In this connection, fluorinated chromone-

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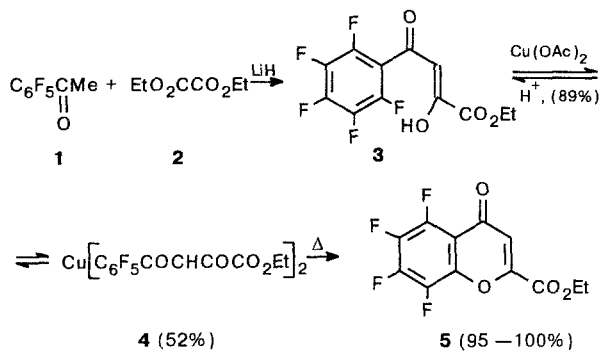
Scheme 1



carboxylic acids are of unquestionable interest as oxygen-containing analogs of fluoroquinolones. Traditionally, monofluoro-derivatives of chromonecarboxylic acids are obtained from substituted phenols.[2,3] Dicarbonyl derivatives of pentafluorobenzene are more promising for the synthesis of chromone systems, due to the facility of nucleophilic substitution of their ortho-fluorine atom which enables intramolecular cyclization. For instance, the transformation of polyfluoroaromatic β-ketoesters[4] and β-diketones[4,5] to γ-benzopyrone derivatives, as well as the synthesis of 3-ethoxycarbonyl-2-methyl-5,6,7,8-tetrafluorochromone from ethoxymagnesium acetoacetate and pentafluorobenzoyl chloride[4,6–8] have been reported. However, these procedures are not general enough for the synthesis of other derivatives of fluorinated chromone. Moreover, the employment of organomagnesium compounds involves certain operational inconveniences (see refs. [4,6–8]).

The purpose of this work was to elaborate effective methods for the synthesis of 2- (and 3-)-ethoxycarbonyl-5,6,7,8-tetrafluorochromones and their derivatives. Here we propose a synthesis of 2-ethoxycarbonyl-5,6,7,8-tetrafluorochromone based on the condensation of pentafluoroacetophenone (**1**) with diethyl oxalate (**2**) in the presence of LiH (Scheme 1). Ethyl pentafluorobenzoylpiruvate (**3**) was initially obtained and isolated *via* its copper chelate (**4**). Then compound **3**, stable at 25°C, was quantitatively transformed to chromone (**5**) on heating, by analogy with the cyclization of 2-(pentafluorophenylacetyl)pentafluorobenzoylacetic ester to 3-ethoxycarbonyl-2-pentafluorobenzoyl-5,6,7,8-tetrafluorochromone (cf. ref.[4]). The copper chelate **4** is stable to heating in water or in non-polar solvents, but undergoes cyclization to **5** in DMSO or DMF.

As in the case of polyfluoroacylpiruvates,[9] no signals of methylene protons related to the keto-form are observed in the ^{1}H NMR spectrum of compound **3**, while those of the enol form are present (a methine proton at δ 6.75 and a single set of signals of the OEt group). In the IR spectrum of **3**, absorption bands (AB) due to the valence vibrations of ester groups (1750 cm^{-1} and 1730 cm^{-1}) and conjugated carbonyls (1640 cm^{-1} and 1620 cm^{-1}) are observed. The doublet structure of these bands remains unaffected on dilution, which implies that **3** exists as an equilibrium mixture of stereoisomers. Also, an AB of the C=C bond (1585 cm^{-1}) and a broad diffuse AB of a hydrogen-bonded OH group are observed.

The IR spectrum of the chelate **4** resembles that of ester **3** and exhibits the AB characteristic of valence vibrations of ester groups (1735 cm^{-1} and 1720 cm^{-1}), and that of a C=O group at 1655 cm^{-1}. The latter, in contrast with the earlier data,[9] implies that no coordination with metal takes place. An AB typical of the C=C bond (1590 cm^{-1}) is also present.

As follows from the formation of 2-ethoxycarbonyl-5,6,7,8-tetrafluorochromone, ester **3** is enolized mainly at the carbon atom adjacent to the CO_2Et group.

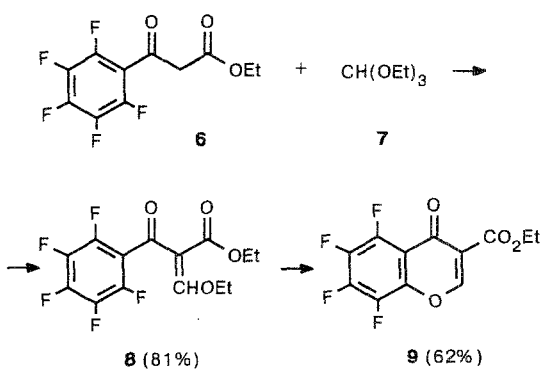
The structure of **5** is confirmed by chemical transformations as well as by IR, ^{1}H, and ^{19}F NMR spectral data. The characteristic frequencies in the IR spectrum of **5** are similar to those given in ref.[6] for 3-ethoxycarbonyl-2-methyl-5,6,7,8-tetrafluorochromone. The ^{1}H NMR spectrum of **5** exhibits the signals of ester CH_2- and CH_3- groups, and =CH group (δ 7.04).

Attempts to substitute the hydrogen atom at position 3 of compound **5** with a carboxyl group on treatment with ethyl chloroformate or with CO_2 have failed. This is probably due to the stability of the chromone ring toward an electrophilic attack. This attitude is also characteristic of unsubstituted chromone (cf. ref.[10]).

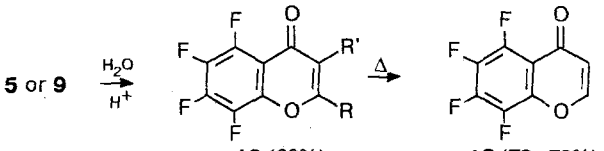
By reacting pentafluorobenzoylacetic ester (**6**) with ethyl orthoformate (**7**) by analogy with a known procedure[11] but in the absence of Ac_2O, ethyl 2-(ethoxymethylene)pentafluorobenzoylacetate (**8**) was prepared. The latter was further converted to the hitherto unknown 3-ethoxycarbonyl-5,6,7,8-tetrafluorochromone (**9**) (Scheme 2). The ^{1}H NMR spectrum of **9** differs from that of **5** in the position of the signal of the hydrogen atom in the chromone moiety (δ 9.60, H-2).

The hydrolysis of esters **5** and **9** in AcOH affords the corresponding chromonecarboxylic acids (**10**) and (**11**), which undergo decarboxylation on sublimation to give 5,6,7,8-tetrafluorochromone (**12**) (Scheme 3).

Scheme 2



Scheme 3



5, 10: R′ = H, R = COOH
9, 11: R′ = COOH, R = H

Chromone **12** could be prepared directly from **9** in refluxed AcOH. This fact points to the lower stability of **11** in comparison with that of **10**. Similar hydrolysis of **9** in formic acid results in the partial reduction of the C=C bond of the γ-pyrone ring.

In the ^{1}H NMR spectrum of **10** the signal of the pyrone =CH group is observed at δ 6.80, while in the spectrum of **11** it appears at δ 9.17. Chemical shifts of the two doublets at δ 6.26 and 8.25 in the ^{1}H NMR spectrum of **12** correspond to those of unsubstituted chromone (cf. ref.[10]). The downfield shift of these signals in compounds **5**,**10**, and **9**,**11** (as compared with the corresponding signals for chromone **12**) is possibly due to deshielding of these protons by the CO_2Et and CO_2H groups. On the other hand, the presence of fluorine atoms in the aromatic moiety of the chromone system has little effect on the circular current in the heterocycle.

Experimental

The IR spectra (400—4000 cm^{-1}) were recorded on a Specord 75-IR spectrometer for suspensions in vaseline oil (for **3** — in CCl_4 solution; $C = 10^{-1} \div 10^{-2}$ mol L^{-1}; d = 50÷280 μm). The ^{1}H NMR spectra were obtained in $CDCl_3$ on a Tesla BS-567 A spectrometer (100 MHz, $SiMe_4$ as the reference); the ^{19}F NMR spectra were taken on a Tesla BS-587 instrument (75 MHz, $CFCl_3$ as the reference).

Pentafluoroacetophenone (1) and ethyl pentafluorobenzoylacetate (6) were obtained as described in ref.[8]

Bis(ethyl 2-hydroxy-4-oxo-4-pentafluorophenyl-2-butenoato)copper (II) (4). A round-bottom flask (250 mL), equipped with an effective water-cooled reflux condenser protected with a drying tube ($CaCl_2$), was charged with finely ground LiH (2.46 g, 0.31 mol), ketone **1** (60.6 g, 0.29 mol), and ester **2** (81.1 g, 0.56 mol). The mixture was heated until an energetic reaction began. Then the reaction mixture was cooled and filtered, and the filtrate was shaken with an excess aqueous solution of $Cu(OAc)_2$ until a persistent blue color of the water layer developed. The crude chelate **4** was filtered off, dissolved in ether, and reprecipitated with hexane to give 51 g (52 %) of **4**, mp 230°C (ether—hexane). IR spectrum, ν (cm^{-1}): 1735, 1720 (C=O, ester); 1655 (C=O); 1590 (C=C). Found (%): C 42.34; H 1.94; F 27.47. Calculated for $C_{24}H_{12}CuF_{10}O_8$ (%): C 42.27; H 1.77; F 27.86.

Ethyl 2-hydroxy-4-oxo-4-pentafluorophenyl-2-butenoate (3). A mixture of **4** (10.0 g, 14.7 mmol), 150 mL of CH_2Cl_2, and 100 mL of 10 % HCl was shaken until the discoloration of the organic layer. The latter was separated, and the solvent was removed in a vacuum to leave 8 g (89 %) of ester **3** (pure). IR spectrum, ν (cm^{-1}): 1750, 1730 (C=O, ester); 1640, 1620 (C=O); 1580 (C=C); 3450 (OH). ^{1}H NMR spectrum, δ: 1.43 (t, 3 H, $OCH_2\underline{CH_3}$, J = 7 Hz); 4.42 (q, 2 H, $O\underline{CH_2}CH_3$, J = 7 Hz); 6.75 (s, 1 H, CH). Found (%): C 46.72; H 2.26; F 30.48. Calculated for $C_{12}H_7F_5O_4$ (%): C 46.47; H 2.28; F 30.62.

2-Ethoxycarbonyl-5,6,7,8-tetrafluorochromone (5). A mixture of **4** (41.0 g, 60.0 mmol) with 150 mL of DMSO was heated for 20 min on a boiling water bath. After cooling, water (300 mL) was added, the white precipitate was filtered off, washed with 10 % HCl (20 mL) and water, and dried in a vacuum to yield 33 g (95 %) of **5**, mp 125°C. IR spectrum, ν (cm^{-1}): 1745 (C=O, ester); 1665 (C=O); 3070, 1620 (C=C). ^{1}H NMR spectrum, δ: 1.44 (t, 3 H, $OCH_2\underline{CH_3}$, J = 7 Hz); 4.48 (q, 2 H, $O\underline{CH_2}CH_3$, J = 7 Hz); 7.04 (s, 1 H, CH). ^{19}F NMR ($CDCl_3$), δ: −158.88 (t), −155.49 (dd), −145.49 (dt), −141.42 (m). Found (%): C 49.48; H 2.27; F 26.10. Calculated for $C_{12}H_6F_4O_4$ (%): C 49.67; H 2.08; F 26.19.

Ethyl 2-ethoxymethylene-3-oxo-3-pentafluorophenylpropionate (8). A mixture of **6** (20 g, 71.0 mmol) and **7** (50.0 g, 340 mmol) was boiled for 5 h, the EtOH formed being distilled off. Vacuum distillation gave 19.5 g (81 %) of **8** as the fraction with bp 160—162°C (1—2 Torr). IR spectrum, ν (cm^{-1}): 1720, 1700 (C=O, ester); 1665 (C=O); 1610, 1570 (C=C). ^{1}H NMR spectrum, δ: 1.2 (dt, 3 H, $CHOCH_2\underline{CH_3}$, J = 12, 2.2 Hz); 1.41 and 1.47 (both t, 3 H, $CO_2CH_2\underline{CH_3}$, J = 11 Hz); 4.14 (q, 2 H, $CHO\underline{CH_2}CH_3$, J = 12 Hz); 4.35 and 4.37 (both q, 2 H, $CO_2\underline{CH_2}CH_3$, J = 11 Hz); 7.8 (d, 1 H, CH, J = 2.2 Hz). Found (%): C 49.37; H 3.24; F 27.68. Calculated for $C_{14}H_{11}F_5O_4$ (%): C 49.71; H 3.28; F 28.09.

3-Ethoxycarbonyl-5,6,7,8-tetrafluorochromone (9). A mixture of **8** (3.0 g, 8.9 mmol) with 10 mL of water was refluxed for 15—20 min. After cooling, the precipitate was filtered off, washed with water (20 mL) and hexane (20 mL), and dried to give 1.6 g (62 %) of **9**, mp 104—105°C. IR spectrum, ν (cm^{-1}): 1730, (C=O, ester); 1670, 1645 (C=O); 1585 (C=C). ^{1}H NMR spectrum, δ: 1.40 (t, 3 H, $OCH_2\underline{CH_3}$, J = 7.5 Hz); 4.40 (q, 2 H, $O\underline{CH_2}CH_3$, J = 7.5 Hz); 8.60 (s, 1 H, CH). Found (%): C 49.43; H 2.08; F 26.35. Calculated for $C_{12}H_6F_4O_4$ (%): C 49.67; H 2.08; F 26.19.

2-Carboxy-5,6,7,8-tetrafluorochromone (10). A 250 mL flask equipped with a water-cooled reflux condenser was charged with 10.0 g (34.5 mmol) of **5**, 150 mL of AcOH, and 10 mL of conc. HCl. The mixture was boiled for 6 h, and AcOH was distilled off until the crystallization of the pot liquor began. Ice water (70 mL) was added, the precipitate was filtered off, washed with 50 mL of water, and dried to give 7.2 g (80 %) of **10**, mp 209—210°C (subl.). IR spectrum, ν (cm^{-1}): 1735 (C=O, ester); 1660, 1645 (C=O); 3090, 1610 (C=C). ^{1}H NMR spectrum (acetone-d_6), δ: 6.75 (br.s, 1 H, OH); 6.80 (s, 1 H, CH). ^{19}F NMR spectrum (D_2O), δ: −159.96 (t), −156.77 (dd), −145.75 (dt), −141.42 (m). Found (%): C 45.70; H 0.50; F 29.20. Calculated for $C_{10}H_2F_4O_4$ (%): C 45.82; H 0.77; F 28.99.

3-Carboxy-5,6,7,8-tetrafluorochromone (11). A mixture of **9** (4.0 g, 13.8 mmol), glacial AcOH (50 mL), and conc. HCl (10 mL) was heated at 40—45°C for 20 h. The AcOH was removed in a vacuum at 50°C until the crystallization of the pot liquor began. The precipitate was filtered, washed with CCl_4, reprecipitated from AcOH with water, and vacuum dried at 50°C to yield 2.5 g (69 %) of **11**, mp 172—173°C. IR spectrum, ν (cm^{-1}): 1735 (C=O, ester); 1660, 1645 (C=O); 1610 (C=C).

^{1}H NMR spectrum (acetone-d_6), δ: 9.17 (s, 1 H, CH); 12.58 (br.s, 1 H OH); ^{19}F NMR (D_2O), δ: −158.97 (t), −157.45 (dd), −145.50 (dt); −140.50 (m). Found (%): C 45.94; H 0.61; F 29.40. Calculated for $C_{10}H_2F_4O_4$ (%): C 45.82; H 0.77; F 28.99.

5,6,7,8-Tetrafluorochromone (12).

Method *1*. Compound **10** (5.0 g, 19.0 mmol) was sublimed at 230—250°C under atmospheric pressure to afford 3.0 g (72 %) of **12**, mp 95—96°C. IR spectrum, ν (cm^{-1}): 1670, 1650 (C=O); 3050, 1595, 1630 (C=C). ^{1}H NMR spectrum (acetone-d_6), δ: 8.25 (d, 1 H, CH, J = 6.25 Hz), 6.26 (d, 1 H, CH, J = 6.25 Hz); ^{19}F NMR ($CHCl_3$), δ: −161.46 (t), −158.50 (dd), −148.49 (dt), −142.77 (m). Found (%): C 49.37; H 1.22; F 34.99. Calculated for $C_9H_2F_4O_2$ (%): C 49.56; H 0.92; F 34.84.

Method *2*. A mixture of **9** (2.0 g, 6.9 mmol), AcOH (50 mL), and conc. HCl (10 mL) was refluxed for 6 h, then concentrated under a water aspirator vacuum until the crystallization of the residue began. The residue was suspended in water, filtered off, dried and sublimed to yield 1.1 g (73 %) of **12**, mp 95—96°C. Elemental analysis and spectral data of the product corresponded to structure **12**.

Method *3*. Compound **11** (0.5 g, 1.9 mmol) was sublimed at 190—200°C under atmospheric pressure to give 0.33 g (79 %) of **12**, mp 95—96°C. Elemental analysis and spectral data of the product correspond to structure **12**.

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A convenient sonochemical synthesis of vicinally substituted 3-hydroxylaminopyridines

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A method of synthesis of vicinally substituted N-(3-pyridyl)hydroxylamines by reducing the corresponding nitropyridines with Zn/NH_4Cl/EtOH under ultrasonication is proposed. Ultrasound irradiation increases the yields of these hydroxylamines and facilitates their isolation.

Key words: vicinally substituted N-(3-pyridyl)hydroxylamines, synthesis; 3-nitropyridines; reduction, ultrasound-promoted.

N-Hetarylhydroxylamines vicinally substituted with a «good» leaving group are bifunctional compounds that are hard to attain. On the other hand, they are promising starting materials for the synthesis of fused cyclic systems.

The most common and efficient method, and in some cases the only expedient method for the synthesis of aryl- and hetaryl hydroxylamines involves the reduction of related nitro compounds. Although such transformations are known,[1—4] few of them are of wide scope.

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