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Reactions of 4-hydroxy-5,6,7,8-tetrafluorocoumarin derivatives with S-nucleophiles

I.T. Bazyl′, S.P. Kisil′, Ya.V. Burgart, V.I. Saloutin*

Institute of Organic Synthesis, Urals Division, Russian Academy of Sciences, 620219, GSP-147, Ekaterinburg, Russia

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Abstract

In the reactions with *o*-aminothiophenol, 4-hydroxy-(3-(imino)acetyl)-5,6,7,8-tetrafluorocoumarins give products of S-substitution at the C-7 atom. 7-Substituted 5,6,8-trifluorocoumarins form benzothiazole as a result of heterocyclic ring opening; 3-ethoxycarbonyl-2-methyl-5,6,7,8-tetrafluorochromone undergoes acid splitting to 2-(2-hydroxy-3,4,5,6-tetrafluorophenyl)benzothiazole. Under alkaline conditions, S-substituted coumarins decompose to acetophenone. In an acid medium, 4-hydroxy-3-iminoacetyl-5,6,8-trifluoro-7-(2-aminophenylthio)-coumarin affords 7-(2-aminophenylthio)-2-methyl-5,6,8-trifluorochromone. 4-Hydroxy-5,6-difluoro-2-H-pyrano[6,5-a]phenothiazin-2-one was isolated from condensation of 7-(2-aminophenylthio)-4-hydroxy-5,6,8-trifluorocoumarin in the presence of NaH.

Reactions of 3-acetyl(iminoacetyl)-4-hydroxy-5,6,7,8-tetrafluorocoumarins and 3-ethoxycarbonyl-2-methyl-5,6,7,8-tetrafluorochromone with 2-mercaptoethanol result in the formation of 5,7,8-trisubstituted derivatives. Interaction of 3-ethoxycarbonyl-2-methyl-5,6,7,8-tetrafluorochromone with 2-mercaptoethanol, mercaptoacetic acid and 1,2-ethanedithiol leads to the formation of the 7-substituted products. Acyl-lactone rearrangement of mono- and trisubstituted chromones gives the corresponding coumarins.

Keywords: Fluorocoumarin; Fluorochromone; S-nucleophile; *o*-Aminothiophenol; 2-Mercaptoethanol; Displacement; Opening of cycle; Acid splitting; Cyclization; Acyl-lactone rearrangement

1. Introduction

Coumarin derivatives are of significant interest for study as so many of them are biologically active compounds [1]. 4-Hydroxy-5,6,7,8-tetrafluorocoumarin derivatives were synthesized previously [2] and their reactions with amines were studied [3]. Thus, 3-acetyl- and 3-iminoacetyl-4-hydroxy-5,6,7,8-tetrafluorocoumarins react with ammonia and morpholine to form 7-substituted products. Under similar conditions, 3-methyl-6,7,8,9-tetrafluorobenzopyranoisoxazole-4-one undergoes opening of the pyrone ring to give the corresponding amides [3]. Data on the reactions of 4-hydroxy-5,6,7,8-tetrafluorocoumarin derivatives with S-nucleophiles are absent.

The reactions of fluoroquinoline-3-carboxylic acids with S-nucleophiles are known to result in the formation of 7-substituted quinolinones. Thus, interaction of 4-oxo-5,6,7-trifluoro-1-ethylquinoline-3-carboxylic acid with 2-mercaptoethanol leads to 7-alkylthio-derivatives [4–6]. Mono-substituted products are formed in the reactions of 6,7-difluoro- and 6,7,8-trifluoroquinolones with 2-mercaptoethanol and *o*-aminothiophenol [7]. Displacement of the fluorine atom at the position 5 or 8 in quinolones is possible when the heterocycle already has the substituent at the C-7 atom [8–10].

In this paper, reactions of 4-hydroxy-5,6,7,8-tetrafluorocoumarin derivatives with *o*-aminothiophenol and 2-mercaptoethanol is described.

2. Experimental details

Melting points were measured in open capillaries and are reported uncorrected. Infrared spectra were measured on a Specord 75 IR spectrometer. ^{1}H- and ^{19}F-NMR spectra were recorded on a Tesla BS-587A instrument (^{1}H: 80 MHz, using TMS as an internal standard, ^{19}F: 75 MHz, using $CFCl_3$ as an internal standard). Microanalyses were performed with a Carlo Erba CHNS-O EA 1108 elemental analyzer. Thin-layer chromatography was performed on 'Silufol-UV 254' plates.

* Corresponding author. Fax: +7-3432-745954.
E-mail address: fc@ios.uran.ru (V.I. Saloutin).

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2.1. Materials

Coumarins **1–4** were prepared by the method described previously [2]. Compound **7** was prepared from coumarin **1** via a described procedure [3]. Chromone **10** was prepared according to the literature methods [11].

2.2. Reactions of 4-hydroxy-5,6,7,8-tetrafluorocoumarin derivatives with o-aminothiophenol

2.2.1. 7-(2-Aminophenylthio)-4-hydroxy-5,6,8-trifluorocoumarin (5) (nc)

(a) *o*-Aminothiophenol (4.5 g, 36 mmol) was added to a solution of coumarin **1** (2.3 g, 10 mmol) in 100 ml of methanol. The mixture was refluxed for 1 h. The resulting precipitate was filtered off, washed with hot methanol and dried in vacuum to give compound **5** (1.38 g, 41%) as white crystals (m.p. 263–265°C). ^{1}H NMR ($(CD_3)_2SO$) δ: 5.31 (2H, s, NH_2); 5.64 (1H, s, =CH); 6.43–7.60 (4H, m, C_6H_4); 11.03 (1H, br.s, OH) ppm. ^{19}F NMR ($(CD_3)_2SO$) δ: −143.40 (1F, d-d, F-5, $J_{(5\text{-}6)} = 23.4$, $J_{(5\text{-}8)} = 14.7$ Hz); −138.65 (1F, δ, F-6, $J_{(6\text{-}5)} = 23.4$, $J_{(6\text{-}8)} = 0$ Hz); −131.94 (1F, δ, F-8, $J_{(8\text{-}5)} = 14.7$, $J_{(8\text{-}6)} = 0$ Hz) ppm. IR: 3340, 3280 (NH_2); 3070 (=CH); 1720 (C=O); 1600, 1540 (C=C, C=N, NH); 1000 (CF) cm^{-1}. Analysis: Found: C, 53.16; H, 2.48; F, 16.69; N, 4.33. Calc. for $C_{15}H_8F_3NO_3S$: C, 53.10; H, 2.38; F, 16.80; N, 4.14%.

(b) In a similar manner, compound **5** (1.7 g, 50%) was obtained from coumarin **2** (2.76 g, 10 mmol). The physicochemical data were identical to those listed above.

2.2.2. 7-(2-Aminophenylthio)-4-hydroxy-3-iminoacetyl-5,6,8-trifluorocoumarin (6) (nc)

(a) A mixture of coumarin **3** (3.9 g, 14.2 mmol) and *o*-aminothiophenol (5.3 g, 42.4 mmol) in 50 ml of methanol was refluxed for 3 h. After cooling, the resulting precipitate was collected by filtration. Recrystallization of ppt from methanol gave **6** (3.0 g, 56%) as white crystals (m.p. 221–223°C). ^{1}H NMR ($(CD_3)_2SO$) δ: 2.54 (3H, s, CH_3); 5.41 (2H, s, NH_2); 6.43–7.37 (4H, m, C_6H_4); 10.14 (1H, br.s, =NH); 11.73 (1H, br.s, OH) ppm. ^{19}F NMR ($(CD_3)_2SO$) δ: −147.07 (1F, d-d, F-5, $J_{(5\text{-}6)} = 23.0$, $J_{(5\text{-}8)} = 15.6$ Hz); −139.86 (1F, d-d, F-6, $J_{(6\text{-}5)} = 23.0$, $J_{(6\text{-}8)} = 2.0$ Hz); −132.77 (1F, d-d, F-8, $J_{(8\text{-}5)} = 15.6$, $J_{(8\text{-}6)} = 2.0$ Hz) ppm. IR: 3360, 3285 (NH_2); 1715 (C=O); 1630, 1600, 1550 (C=C, C=N, NH); 1000 (CF) cm^{-1}. Analysis: Found: C, 53.62; H, 3.11; F, 14.76; N, 7.45. Calc. for $C_{17}H_{11}F_3N_2O_3S$: C, 53.68; H, 2.92; F, 14.99; N, 7.51%.

(b) A mixture of compound **4** (0.55 g, 2.01 mmol) and *o*-aminothiophenol (1.2 g, 9.68 mmol) was refluxed in 30 ml of benzene for 6 h. The solvent was removed. A solution of 10% HCl acid (10 ml) was added to the resulting oil. The precipitate was filtered off, dried and recrystallized from methanol to give compound **6** (2.7 g, 50%). The physicochemical data were identical to those listed above.

2.2.3. Reaction of 3-methyl-6,7,8,9-tetrafluoro-4H-benzopyrano[3,4-d]isoxazol-4-one (4) with o-aminothiophenol

A mixture of compound **4** (0.55 g, 2.01 mmol) and *o*-aminothiophenol (0.3 g, 2.42 mmol) was refluxed in 20 ml of benzene for 5 h. The solvent was removed. A solution of HCl (10 ml, 10%) was added to the resulting oil. The precipitate was collected by filtration, dried and recrystallized from toluene to give compound **3** (0.2 g, 36%) as white crystals (m.p. 171–172°C; compare Ref. [2]).

2.2.4. 2-(2-Hydroxy-2-(2-hydroxy-(2-aminophenylthio)-3,5,6-trifluoro)phenyl)vinylbenzothiazole (8) (nc)

A mixture of compound **5** (1 g, 2.95 mmol) and *o*-aminothiophenol (1.84 g, 14.7 mmol) in 30 ml of toluene was refluxed for 3 h. The resulting precipitate was collected by filtration, dried and recrystallized from isopropyl alcohol to give compound **8** (1.1 g, 83%) as white crystals (m.p. 268–270°C). ^{1}H NMR ($(CD_3)_2SO$) δ: 5.64 (1H, s, =CH); 6.43–7.38 (10 H, m, 2 C_6H_4, NH_2) ppm. ^{19}F NMR ($(CD_3)_2SO$) δ: −143. 40 (1F, d-d, F-6, $J_{(6\text{-}5)} = 23.0$, $J_{(6\text{-}3)} = 14.4$ Hz); −138.64 (1F, d, F-5, $J_{(5\text{-}6)} = 23.0$, $J_{(5\text{-}3)} = 0$ Hz); −132.95 (1F, d, F-3, $J_{(3\text{-}6)} = 14.4$, $J_{(3\text{-}5)} = 0$ Hz) ppm. IR: 3350, 3280 (NH_2); 1630, 1530 (C=C, C=N); 990 (CF) cm^{-1}. Analysis: Found: C, 56.42; H, 3.05; F, 12.89; N, 5.91; S, 14.01. Calc. for $C_{21}H_{13}F_3N_2O_2S_2$: C, 56.37; H, 3.15; F, 12.74; N, 6.26; S, 14.33%.

2.2.5. 2-(2-Hydroxy-2-(2-hydroxy-4-(4-morpholinyl)-3,5,6-trifluoro)phenyl)vinylbenzothiazole (9) (nc)

In a similar manner, compound **9** (0.6 g, 50%) as white crystals (m.p. 222–224°C) was obtained from compound **7** (1 g, 2.92 mmol) and *o*-aminothiophenol (2.1 g, 16.8 mmol). ^{1}H NMR ($(CD_3)_2SO$) δ: 3.20–3.43 (4H, m, CH_2–N–CH_2); 3.64–3.76 (4H, m, CH_2–O–CH_2); 6.73 (1H, br.s, =CH); 7.20–7.93 (4H, m, C_6H_4); 13.24, 14.95 (2H, br.s, 2 OH) ppm. ^{19}F NMR ($(CD_3)_2SO$) δ: −161.55 (1F, d, F-5, $J_{(5\text{-}6)} = 22.5$, $J_{(5\text{-}3)} = 0$ Hz); −153.48 (1F, d, F-3, $J_{(3\text{-}6)} = 11.0$, $J_{(3\text{-}5)} = 0$ Hz); −141.65 (1F, d-d, F-6, $J_{(6\text{-}5)} = 22.5$, $J_{(6\text{-}3)} = 11.0$ Hz) ppm. IR: 3220–3000 (OH); 1630, 1530 (C=C, C=N); 990 (CF) cm^{-1}. Analysis: Found: C, 55.92; H, 3.73; F, 14.28; N, 7.07; S, 7.69. Calc. for $C_{19}H_{15}F_3N_2O_3S$: C, 55.93; H, 3.68; F, 13.97; N, 6.86; S, 7.89%.

2.2.6. 2-(2-Hydroxy-3,4,5,6-tetrafluorophenyl)-benzothiazole (11) (nc)

A mixture of compound **10** (0.5 g, 1.64 mmol) and *o*-aminothiophenol (0.8 g, 6.4 mmol) was refluxed in 20 ml of toluene for 6 h. After cooling, the resulting precipitate was filtered off and recrystallized from toluene to give compound **11** (0.2 g, 41%) as white crystals (m.p. 193–195°C). ^{1}H NMR ($(CD_3)_2SO$) δ: 7.0–8.3 (4H, m, C_6H_4); 12.1, 13.7 (2H, br.s, 2OH) ppm. ^{19}F NMR ($(CD_3)_2SO$) δ: −171.17 (1F, d-d-d); −162.58 (1F, d-d-d); −153.07 (1F, d-d-d); −140.15 (1F, d-d-d) ppm. IR: 2770 (OH); 1510, 1500 (C=C, C=N);

990 (CF) cm^{-1}. Analysis: Found: C, 52.12; H, 1.64; F, 25.64; N, 4.80; S, 10.86. Calc. for $C_{13}H_5F_4NOS$: C, 52.17; H, 1.67; F, 25.42; N, 4.62; S, 10.70%.

2.2.7. 4-(2-Aminophenylthio)-2-hydroxy-3,5,6-trifluoroacetophenone (**12**) (nc)

(a) Compound **5** (0.5 g, 1.47 mmol) was dissolved in 10 ml of 10% aqueous solution of NaOH. The mixture was refluxed for 2 h. After cooling, the resulting precipitate was dissolved in water. The solution was treated with conc. HCl to pH ~ 2. The resulting precipitate was collected by filtration and recrystallized from heptane to give compound **12** (0.2 g, 43%) as white crystals (m.p. 89–90°C). ^{1}H NMR ($(CD_3)_2SO$) δ: 2.66 (3H, s, CH_3); 4.17 (2H, br.s, NH_2); 6.57–7.59 (4H, m, C_6H_4); 12.39 (1H, br.s, OH) ppm. ^{19}F NMR ($(CD_3)_2SO$) δ: −145.24 (1F, d-d, F-5, $J_{(5\text{-}6)} = 24.4$, $J_{(5\text{-}3)} = 3.9$ Hz); −138.1 (1F, d-d, F-6, $J_{(6\text{-}3)} = 13.6$, $J_{(6\text{-}5)} = 24.4$ Hz); −134.87 (1F, d-d, F-3, $J_{(3\text{-}6)} = 13.6$, $J_{(3\text{-}5)} = 3.9$ Hz) ppm. IR: 3460, 3370 (NH_2); 1650 (C=O); 1550 (C=C, NH); 1000 (CF) cm^{-1}. Analysis: Found: C, 53.76; H, 3.34; F, 18.54; N, 4.58; S, 10.44. Calc. for $C_{14}H_{10}F_3NO_2S$: C, 53.67; H, 3.19; F, 18.21; N, 4.47; S, 10.22%.

(b) By analogy, product **12** (0.12 g, 48%) was obtained from compound **6** (0.3 g, 0.79 mmol). The physicochemical data were identical to those listed above.

2.2.8. 7-(2-Aminophenylthio)-2-methyl-5,6,8-trifluorocoumarin (**13**) (nc)

A mixture of compound **6** (0.5 g, 1.31 mmol), conc. H_2SO_4 (5 ml) and water (5 ml) was refluxed for 4 h. The reaction mass was cooled and treated with 10% aqueous solution of NaOH to pH ~ 7. The resulting precipitate was filtered off, dried and recrystallized from heptane to give compound **13** (0.15 g, 34%) as white crystals (m.p. 162–164°C). ^{1}H NMR ($(CD_3)_2SO$) δ: 2.34 (3H, s, CH_3); 4.38 (2H, br.s, NH_2); 6.07 (1H, s, =CH); 6.57–7.61 (4H, m, C_6H_4) ppm. ^{19}F NMR ($(CD_3)_2SO$) δ: −144.80 (1F, d-d, F-5, $J_{(5\text{-}6)} = 21.0$, $J_{(5\text{-}8)} = 16.5$ Hz); −135.78 (1F, d, F-6, $J_{(6\text{-}5)} = 21.0$, $J_{(6\text{-}8)} = 0$ Hz); −130.40 (1F, d, F-8, $J_{(8\text{-}5)} = 16.5$, $J_{(8\text{-}6)} = 0$ Hz) ppm. IR: 3350, 3270 (NH_2); 3070 (=CH); 1640 (C=O); 1510 (C=C); 1000 (CF) cm^{-1}. Analysis: Found: C, 56.85; H, 2.89; F, 16.89; N, 4.17; S, 9.88. Calc. for $C_{16}H_{10}F_3NO_2S$: C, 56.97; H, 2.99; F, 16.90; N, 4.15; S, 9.50%.

2.2.9. Cyclization of compound (**5**)

Finely ground NaH (0.3 g, 12.5 mmol) was added to a solution of compound **5** (1 g, 2.95 mmol) in 15 ml of anhydrous DMF under argon. The reaction mixture was heated at 80°C under argon for 3 h, then cooled to 20°C and poured into a mixture of conc. HCl (20 ml) and water (100 ml). The resulting precipitate was collected by filtration and dried in vacuum at 90°C to give a mixture of compounds **14** and **15** (0.75 g, 80%).

2.2.10. 4-Hydroxy-5,6-difluoro-2-H-pyrano[6,5-α]phenothiazin-2-one (**14**) (nc)

The mixture of compounds **14** and **15** (0.5 g, 1.5 mmol) was dissolved in 10 ml of *o*-xylene and refluxed for 5 min. The reaction mixture was cooled to 10°C. The resulting precipitate was collected by filtration and dried to give compound **14** (0.2 g, 21%) as white crystals (m.p. > 270°C). ^{1}H NMR ($(CD_3)_2SO$) δ: 5.66 (1H, s, =CH); 6.8–7.4 (4H, m, C_6H_4); 8.7 (2H, br.s, OH, NH) ppm. ^{19}F NMR ($(CD_3)_2SO$) δ: −150.07 (1F, d, $J_{(\text{ortho-F-F})} = 22.0$ Hz); −145.46 (1F, d, $J_{(\text{ortho-F-F})} = 22.0$ Hz) ppm. IR: 3280 (NH); 3070 (=CH); 1710 (C=O); 1640, 1600, 1510 (C=C, NH); 1000 (CF) cm^{-1}. Analysis: Found: C, 56.16; H, 2.54; F, 11.17; N, 4.53; S, 10.22. Calc. for $C_{15}H_7F_2NO_3S$: C, 56.43; H, 2.21; F, 11.90; N, 4.38; S, 10.44%.

2.3. Reactions 4-hydroxy-5,6,7,8-tetrafluorocoumarin derivatives with 2-mercaptoethanol

2.3.1. 4-Hydroxy-7-(2-hydroxyethylthio)-5,6,8-trifluorocoumarin (**16**) (nc)

To a solution of coumarin **1** (1.15 g, 4.78 mmol) in 16 ml of DMSO, 2-mercaptoethanol (3.7 g, 47.8 mmol) and triethylamine (3.7 ml) were added. The reaction mixture was heated at 80°C for 3 h, cooled to 20°C and poured into a solution of conc. HCl (15 ml) in 70 ml of water. The solution was extracted by ether (3× 20 ml). The extract was washed with water and dried under $MgSO_4$. The solvent was removed in vacuum. The residue was recrystallized from acetonitrile to give compound **16** (0.25 g, 18%) as white crystals (m.p. 160–165°C). ^{1}H NMR ($(CD_3)_2SO$) δ: 3.07–3.20 (2H, m, SCH_2); 3.50–3.63 (2H, m, OCH_2); 5.64 (1H, s, =CH); 9.6, 11.4 (2H, br.s, 2OH) ppm. ^{19}F NMR ($(CD_3)_2SO$) δ: −143.7 (1F, d-d, F-5, $J_{(5\text{-}6)} = 23.4$, $J_{(5\text{-}8)} = 14.6$ Hz); −137.7 (1F, d, F-6, $J_{(6\text{-}5)} = 23.4$, $J_{(6\text{-}8)} = 0$ Hz); −131.1 (1F, d, F-8, $J_{(8\text{-}5)} = 14.6$, $J_{(8\text{-}6)} = 0$ Hz) ppm. IR: 3240, 2640 (OH); 1700, 1680 (C=O); 1620, 1600, 1550 (C=C); 1000 (CF) cm^{-1}. Analysis: Found: C, 45.09; H, 2.37; F, 19.46; S, 10.63. Calc. for $C_{11}H_7F_3O_4S$: C, 45.21; H, 2.41; F, 19.50; S, 10.97%.

2.3.2. 3-Acetyl-4-hydroxy-5,7,8-tri(2-hydroxyethylthio)-6-fluorocoumarin (**17**) (nc)

In a similar manner, compound **17** (0.4 g, 23%), white crystals (m.p. 165–170°C) from coumarin **2** (1.15 g, 4.16 mmol), 2-mercaptoethanol (3.7 g, 47.8 mmol) and triethylamine (3.7 ml). ^{1}H NMR ($(CD_3)_2SO$ coumarin, chromone isomers (see text) ratio 1:2)δ: 2.57, 2.67 (1H, s, CH_3); 2.96–3.26 (6H, m, SCH_2); 3.47–3.60 (6H, m, OCH_2); 4.7 (3H, br.s, 3OH); 9.9, 11.6 (2H, br.s, 2OH) ppm. ^{19}F NMR ($(CD_3)_2SO$) δ: −99.7, −101.6 (1F, s) ppm. IR: 3250, 2700 (OH); 1700, 1680 (C=O); 1600, 1550 (C=C); 1030–1000 (CF) cm^{-1}. Analysis: Found: C, 45.75; H, 4.35; F, 4.13; S, 21.23. Calc. for $C_{17}H_{19}FO_7S_3$: C, 45.32; H, 4.25; F, 4.22; S, 21.35%.

*2.3.3. 4-Hydroxy-3-iminoacetyl-5,7,8-tri-(2-hydroxyethylthio)-6-fluorocoumarin (**18**) (nc)*

(a) To a solution of coumarin **3** (5.7 g, 20.7 mmol) in 80 ml of DMSO, 2-mercaptoethanol (18 g, 231 mmol) and triethylamine (18 ml) were added. The reaction mixture was heated at 80°C for 3 h, cooled to 20°C and poured into a solution of conc. HCl (50 ml) in 300 ml of water. The solution was stored at 20°C for 24 h. The resulting precipitate was filtered off, dried and recrystallized from acetonitrile to give compound **18** (8.0 g, 86%) as white crystals (m.p. 186–190°C). ^{1}H NMR ($(CD_3)_2SO$) δ: 2.55 (3H, s, CH_3); 3.03–3.16 (6H, m, SCH_2); 3.4–3.6 (6H, m, OCH_2); 4.4 (3H, br.s, OH); 9.98 (1H, br.s, NH); 11.8 (1H, br.s, OH) ppm. ^{19}F NMR ($(CD_3)_2SO$) δ: −101.5 (1F, s) ppm. IR: 3500–3000 (OH, NH); 1680 (C=O); 1600, 1550, 1510 (C=C, C=N); 990 (CF) cm^{-1}. Analysis: Found: C, 45.05; H, 4.63; F, 3.97; N, 2.85. Calc. for $C_{17}H_{20}FNO_6S_3$: C, 45.42; H, 4.48; F, 4.23; N, 3.11%.

(b) A solution of compound **20** (0.45 g, 0.94 mmol) in 30 ml of 25% aqueous NH_4OH was stirred for 48 h at 18°C. The resulting precipitate was collected by filtration and dried to give compound **18** (0.3 g, 71%). The physicochemical data were identical to those listed above.

*2.3.4. 3-Ethoxycarbonyl-7-(2-hydroxyethylthio)-2-methyl-5,6,8-trifluorochromone (**19**) (nc)*

2-Mercaptoethanol (3.8 g, 48.7 mmol) was added to a solution of chromone **10** (3.8 g, 12.5 mmol) in 70 ml of DMSO. The reaction mixture was cooled to 20°C, 2 ml of triethylamine added and stored at 20°C for 2 min. The reaction mixture was poured into a solution of conc. HCl (120 ml) in 130 ml of water. The resulting precipitate was collected by filtration, dried and recrystallized form CCl_4 to give compound **19** (3.7 g, 82%) as white crystals (m.p. 121–123°C). ^{1}H NMR ($(CD_3)_2SO$) δ: 1.29 (3H, t, OCH_2CH_3), 2.46 (3H, s, CH_3); 3.18 (2H, s, SCH_2); 3.59 (2H, m, OCH_2); 4.31 (2H, q, OCH_2CH_3); 4.96 (1H, br.s, OH) ppm. ^{19}F NMR ($(CD_3)_2SO$) δ: −146.22 (1F, d-d, F-5, $J_{(5\text{-}6)} = 22.4$, $J_{(5\text{-}8)} = 15.5$ Hz); −135.75 (1F, d-d, F-6, $J_{(6\text{-}5)} = 22.4$, $J_{(6\text{-}8)} = 0$ Hz); −129.78 (1F, d-d, F-8, $J_{(8\text{-}5)} = 15.5$, $J_{(8\text{-}6)} = 0$ Hz) ppm. IR: 3510, 3450 (OH); 1720, 1710 (CO_2Et); 1640 (C=O); 1540 (C=C); 990 (CF) cm^{-1}. Analysis: Found: C, 49.73; H, 3.71; F, 15.74. Calc. for $C_{15}H_{13}F_3O_5S$: C, 49.73; H, 3.62; F, 15.73%.

*2.3.5. 3-Ethoxycarbonyl-5,7,8-tri(2-hydroxyethylthio)-2-methyl-6-fluorochromone (**20**) (nc)*

(a) To a solution of chromone **10** (8.4 g, 27.6 mmol) in 150 ml of DMSO, 2-mercaptoethanol (16 g, 205 mmol) and triethylamine (16 ml) were added. The reaction mixture was heated at 80°C for 3 h, cooled and poured into a solution of conc. HCl (50 ml) in 300 ml of water. The resulting precipitate was filtered off, dried and recrystallized from acetonitrile to give compound **20** (7.0 g, 53%) as white crystals (m.p. 133–137°C). ^{1}H NMR ($(CD_3)_2SO$) δ: 1.30 (3H, t, OCH_2CH_3), 2.46 (3H, s, CH_3); 3.0–3.2 (6H, m, SCH_2); 3.5–3.62 (6H, m, OCH_2); 4.30 (2H, q, OCH_2CH_3); 4.6 (3H, br.s, OH) ppm. ^{19}F NMR ($(CD_3)_2SO$) δ: −107.9 (1F, s) ppm. IR: 3500–3200 (OH); 1730 (CO_2Et); 1620 (C=O); 1540, 1500 (C=C); 990 (CF) cm^{-1}. Analysis: Found: C, 47.90; H, 4.76; F, 3.84. Calc. for $C_{19}H_{23}FO_7S_3$: C, 47.69; H, 4.84; F, 3.97%.

(b) By analogy, compound **20** (3.8 g, 80%) was obtained from chromone **19** (3.62 g, 10 mmol), 2-mercaptoethanol (7.8 g, 100 mmol) and triethylamine (5 ml). The physicochemical data were identical to those listed above.

*2.3.6. 4-Hydroxy-7-(2-hydroxyethylthio)-3-iminoacetyl-5,6,8-trifluorocoumarin (**21**) (nc)*

A solution of compound **19** (10 g, 27.6 mmol) in 200 ml of 25% aqueous NH_4OH was stirred at 20°C for 48 h. The resulting precipitate was filtered off and dried to give compound **21** (7.0 g, 76%) as white crystals (m.p. 186–191°C). ^{1}H NMR ($(CD_3)_2SO$) δ: 2.55 (3H, s, CH_3); 3.12 (2H, s, SCH_2); 3.55 (2H, m, OCH_2); 4.93 (1H, br.s, OH); 10.15 (1H, br.s, NH); 11.74 (1H, br.s, OH) ppm. ^{19}F NMR ($(CD_3)_2SO$) δ: −147.36 (1F, d-d, F-5, $J_{(5\text{-}6)} = 23.5$, $J_{(5\text{-}8)} = 15.0$ Hz); −138.91 (1F, d-d, F-6, $J_{(6\text{-}5)} = 23.5$, $J_{(6\text{-}8)} = 0$ Hz); −131.94 (1F, d-d, F-8, $J_{(8\text{-}5)} = 15.0$, $J_{(8\text{-}6)} = 0$ Hz) ppm. IR: 3340, 3180 (OH); 1680 (C=O); 1610, 1550 (C=C, C=N); 980 (CF) cm^{-1}. Analysis: Found: C, 46.73; H, 3.12; F, 17.06; N, 4.28. Calc. for $C_{13}H_{10}F_3NO_4S$: C, 46.85; H, 3.02; F, 15.73; N, 4.20%.

*2.3.7. 3-Ethoxycarbonyl-7-carboxymethylthio-2-methyl-5,6,8-trifluorochromone (**22**) (nc)*

To a solution of chromone **10** (2 g, 6.58 mmol) in 30 ml of DMSO, mercaptoacetic acid (3.8 g, 41.3 mmol) and triethylamine (0.3 ml) were added. The mixture was stored at 18°C for 20 min and then poured into a mixture of 150 ml of water and 10 ml of conc. HCl. The resulting precipitate was filtered off, washed with water and recrystallized from toluene to give compound **22** (1.3 g, 53%) as white crystals (m.p. 161–163°C). ^{1}H NMR ($(CD_3)_2SO$) δ: 1.29 (3H, t, OCH_2CH_3); 2.46 (3H, s, CH_3); 3.95 (2H, s, SCH_2); 4.31 (2H, q, OCH_2CH_3); 13.0 (1H, br.s, COOH) ppm. ^{19}F NMR ($(CD_3)_2SO$) δ: −146.18 (1F, d-d, F-5, $J_{(5\text{-}6)} = 22.0$, $J_{(5\text{-}8)} = 15.6$ Hz); −136.07 (1F, d-d, F-6, $J_{(6\text{-}5)} = 22.0$, $J_{(6\text{-}8)} = 0$ Hz); −130.13 (1F, d-d, F-8, $J_{(8\text{-}5)} = 15.6$, $J_{(8\text{-}6)} = 0$ Hz) ppm. IR: 3300–3000 (OH); 1720 (CO_2Et); 1670 (CO_2H); 1630 (C=O); 1550 (C=C); 990 (CF) cm^{-1}. Analysis: Found: C, 48.04; H, 2.83; F, 15.01. Calc. for $C_{15}H_{11}F_3O_6S$: C, 47.88; H, 2.95; F, 15.15%

*2.3.8. 1,2-Bis((3-ethoxycarbonyl-2-methyl-5,6,8-trifluorochromone-7-yl)thio)ethane (**23**) (nc)*

To a solution of chromone **10** (3 g, 9.87 mmol) in 60 ml of DMSO, 1,2-ethanedithiol (0.5 g, 5.32 mmol) and triethylamine (0.3 ml) were added. The reaction mixture was stored at 18°C for 10 min. The resulting precipitate was filtered off, washed with water and recrystallized from CCl_4 to give compound **23** (2.5 g, 76%) as white crystals (m.p.

204–206°C). ^{1}H NMR ($(CD_3)_2SO$) δ: 1.39 (3H, t, OCH_2CH_3); 2.51 (3H, s, CH_3); 3.27 (2H, s, SCH_2); 4.31 (2H, q, OCH_2CH_3) ppm. ^{19}F NMR ($(CD_3)_2SO$) δ: −143.73 (1F, d-d, F-5, $J_{(5\text{-}6)} = 22.0$, $J_{(5\text{-}8)} = 16.6$ Hz); −134.75 (1F, d-d, F-6, $J_{(6\text{-}5)} = 22.0$, $J_{(6\text{-}8)} = 0$ Hz); −130.16 (1F, d-d, F-8, $J_{(8\text{-}5)} = 16.6$, $J_{(8\text{-}6)} = 0$ Hz) ppm. IR: 1730 (CO_2Et); 1645 (C = O); 1560 (C = C); 990 (CF) cm^{-1}. Analysis: Found: C, 50.74; H, 3.06; F, 17.17. Calc. for $C_{28}H_{20}F_6O_8S_2$: C, 50.76; H, 3.04; F, 17.21%.

2.3.9. 7-(2-Hydroxyethylthio)-2-methyl-5,6,8-trifluorochromone-3-carboxylic acid (**24**) (nc)

a. A solution of compound **21** (0.45 g, 1.24 mmol) in 40 ml of 25% aqueous NH_4OH was refluxed for 2 h, then treated with conc. HCl to pH = 1–2. The resulting precipitate was collected by filtration, dried and recrystallized from a mixture of heptane and CCl_4 (1:1) to give compound **24** (0.1 g, 24%) as white crystals (m.p. 135°C decomp.). ^{1}H NMR ($(CD_3)_2SO$) δ: 2.68 (3H, s, CH_3); 3.22 (2H, s, SCH_2); 3.61 (2H, s, OCH_2), 6.6 (1H, br.s, OH) ppm. ^{19}F NMR ($(CD_3)_2SO$) δ: −142.40 (1F, d-d, F-5, $J_{(5\text{-}6)} = 23.0$, $J_{(5\text{-}8)} = 15.0$ Hz); −137.55 (1F, d-d, F-6, $J_{(6\text{-}5)} = 23.0$, $J_{(6\text{-}8)} = 0$ Hz); −131.48 (1F, d-d, F-8, $J_{(8\text{-}5)} = 15.0$, $J_{(8\text{-}6)} = 0$ Hz) ppm. IR: 3300 (OH); 1730 (CO_2H); 1630 (C=O); 1600, 1535 (C=C); 1010–990 (CF) cm^{-1}. Analysis: Found: C, 46.74; H, 2.89; F, 17.16. Calc. for $C_{13}H_9F_3O_5S$: C, 46.71; H, 2.71; F, 17.05%.

(b) A solution of compound **19** (6 g, 18 mmol) and NaOH (7 g, 175 mmol) in 200 ml of water was stirred at 20°C for 2 h and treated with conc. HCl to pH = 2–3. The resulting precipitate was filtered off, washed with water, dried and recrystallized from CCl_4 to give compound **24** (2.5 g, 86%). The physicochemical data were identical to those listed above.

2.3.10. 7-(2-Acetoxyethylthio)-2-methyl-5,6,7-trifluorochromone (**25**) (nc)

(a) A solution of compound **19** (0.65 g, 1.79 mmol) in a mixture of conc. acetic acid (15 ml) and conc. HCl (3 ml) was refluxed for 15 h, then poured into 100 ml of water. The resulting precipitate was collected by filtration, washed with water, dried and then dissolved in 10 ml of heptane. The resulting solution was filtered from small amounts of insoluble material. The solvent was removed in vacuum to give compound **25** (0.4 g, 67%) as white crystals (m.p. 87–90°C). ^{1}H NMR ($(CD_3)_2SO$) δ: 2.03 (3H, s, CH_3CO); 2.40 (3H, s, CH_3); 3.28 (2H, s, SCH_2); 4.24 (2H, s, OCH_2), 6.1 (1H, br.s, OH) ppm. ^{19}F NMR ($(CD_3)_2SO$) δ: −143.73 (1F, d-d, F-5, $J_{(5\text{-}6)} = 22.0$, $J_{(5\text{-}8)} = 16.6$ Hz); −134.75 (1F, d-d, F-6, $J_{(6\text{-}5)} = 22.0$, $J_{(6\text{-}8)} = 0$ Hz); −130.16 (1F, d-d, F-8, $J_{(8\text{-}5)} = 16.6$, $J_{(8\text{-}6)} = 0$ Hz) ppm. IR: 1730 (CO_2Et); 1630 (C=O); 1600, 1530 (C=C); 1000 (CF) cm^{-1}. Analysis: Found: C, 50.41; H, 3.26; F, 17.26. Calc. for $C_{14}H_{11}F_3O_4S$: C, 50.60; H, 3.34; F, 17.15%.

(b) By analogy, product **25** (0.28 g, 80%) was obtained from compound **24** (0.40 g, 1.2 mmol). The physicochemical data were identical to those listed above.

3. Results and discussion

3.1. Reaction of 4-hydroxy-5,6,7,8-tetrafluorocoumarin derivatives with o-aminothiophenol

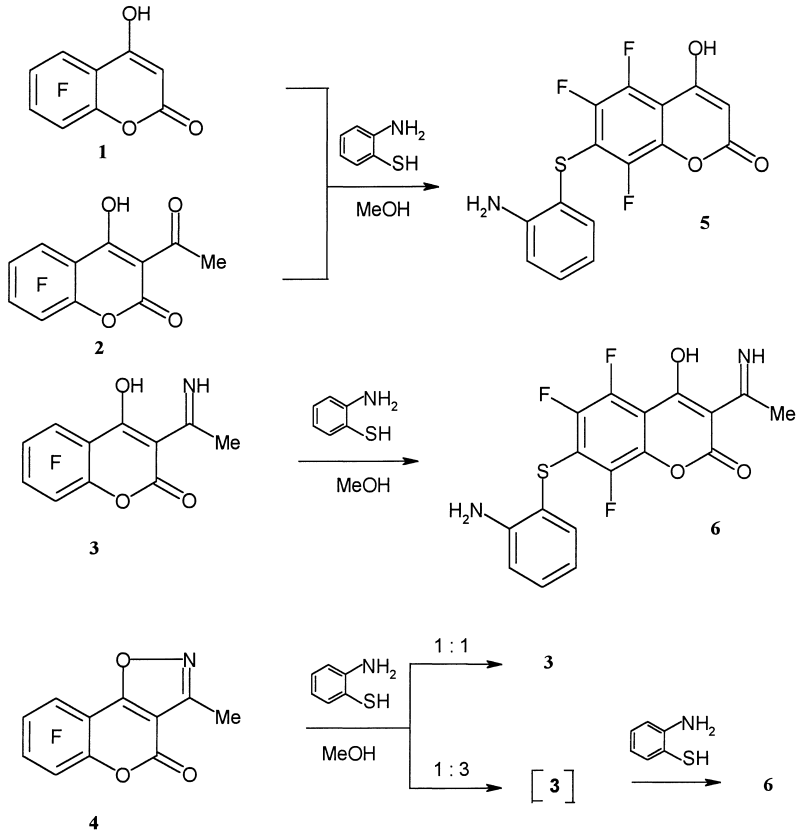
In the present work, it has been found that coumarin **1** reacts with *o*-aminothiophenol in refluxing methanol to form product **5**. The structure of the compound results from nucleophilic displacement of the C-7 fluorine atom in the heterocycle. Under analogous conditions, 3-acetyl-substituted coumarin **2** with *o*-aminothophenol also affords compound **5**. Probably, in this case the displacement is accompanied by deacylation. Coumarin **3** with an iminoacetyl group at the C-3 position on reaction with *o*-aminothiophenol gives the corresponding 7-substituted product **6** (Scheme 1). It should be noted that the reactions described do not require the addition of base as catalyst and are carried out in methanol rather than DMSO unlike the interaction of fluoroquinolone-carboxylic acid derivatives with *o*-aminothiophenol [4]. The use of DMSO as a solvent in the reactions of coumarins **1–3** with *o*-aminothiophenol decreases the selectivity of these transformations and leads to a mixture of products that is difficult to separate.

Interaction of benzopyranoisoxazole **4** with an equimolar amount of *o*-aminothiophenol leads to coumarin **3** as a result of the reductive splitting of the isoxazole ring (Scheme 1). The lability of isoxazoles under treatment with such bases as hydrazine, phenylhydrazine is known [12]. However, such a result in the reaction with *o*-aminothiophenol was obtained for the first time. Benzopyranoisoxazole **4** with an excess of *o*-aminothiophenol forms compound **6** which was obtained from coumarin **3**.

In contrast to the above-mentioned transformations, interaction of compound **4** with ammonia and morpholine (which do not possess reducing properties) leads to the splitting of pyrone ring with retention of the isoxazole ring [3].

Coumarins **5**, **7** with substituents at the C-7 atom inert to nucleophilic displacement do not react with *o*-aminothiophenol on refluxing in methanol. Under more severe conditions on refluxing in toluene, coumarins **5**, **7** with *o*-aminothiophenol form benzothiazole derivatives **8**, **9** (Scheme 2) as a result of the reaction of the nucleophile at the lactone ring followed by cleavage of the C–O bond.

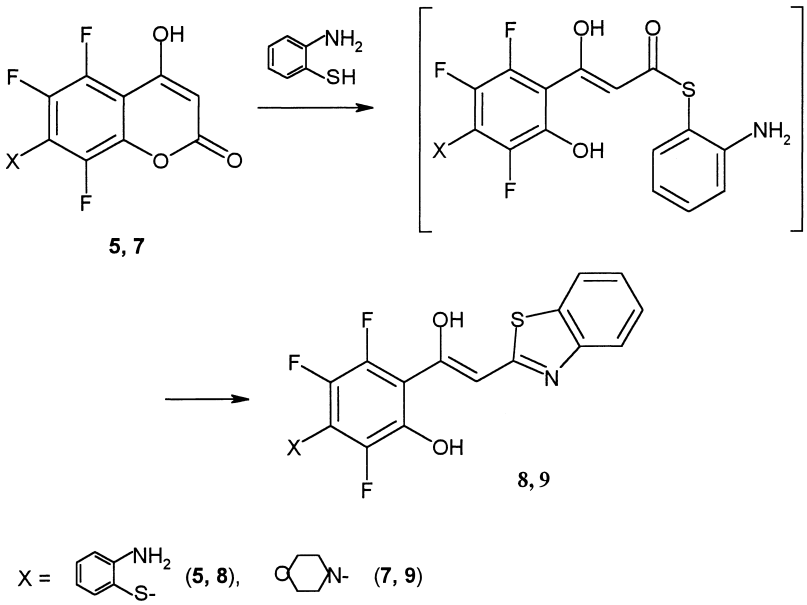
Interaction of 3-ethoxycarbonyl-2-methyl-5,6,7,8-tetrafluorochromone **10** (that is the precursor of coumarin **3** in an acyl-lactone rearrangement [2]) with *o*-aminothiophenol results in the formation of benzothiazole **11** on refluxing in toluene (Scheme 3). A similar benzimidazole was obtained in the reaction of the chromone **10** with *o*-phenylenediamine [2]. Obviously, cleavage of the pyrone ring proceeds as the



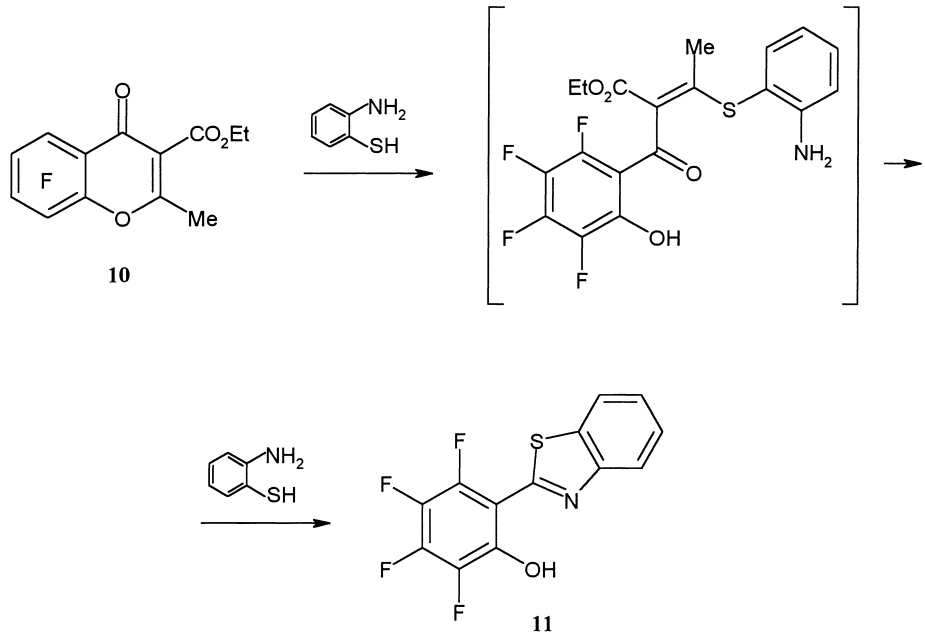
Scheme 1.

first step of these transformations to form a 2-acylsubstituted 3-oxoester as an intermediate. Under reaction conditions, the latter undergo acid splitting to give the corresponding heterocycles. It is known that acid splitting is typical for the interaction of fluorine-containing 2-acyl-3-oxoesters with amines to form derivatives of fluorine-containing carboxylic acid — amides and 2-fluoroalkylbenzimidazole [13,14].

The behavior of S-substituted coumarins **5, 6** have been studied in various mediums. It has been found that heterocycle of compounds **5**, **6** is destroyed to acetophenone **12** on refluxing in aqueous solution of NaOH (Scheme 4). Similar



Scheme 2.



Scheme 3.

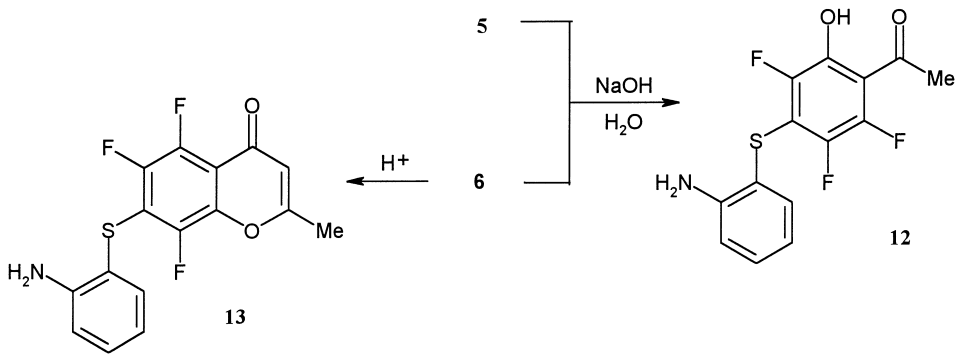
splitting was observed for 7-amino-4-hydroxy-3-iminoacetyl-5,6,8-trifluorocoumarin [3].

In an acid medium, compound **6** gives chromone **12** as a result of a process that is inverse to a coumarin rearrangement followed by decarboxylation (Scheme 4). Analogous transformations were described for the reaction of non-substituted coumarin **3** [2].

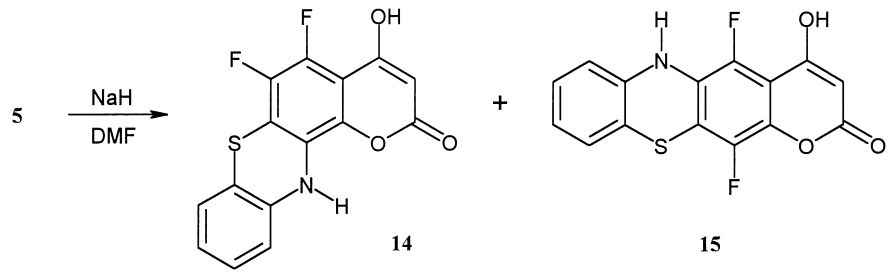
Intramolecular heterocyclization is possible for coumarin **5** due to the nucleophilic displacement of a fluorine atom by an aminogroup of 2-aminophenylthio-substituent. The attack of nucleophile may occur either at atom C-8 to form phenothiazine **14** or at atom C-6 to give phenothiazine **15**. Intramolecular displacement at both positions is known for quinolones [4,15]. The reaction is carried out in the presence of NaH or NaOH as condensing reagents in anhydrous DMF under argon. The product isolated in the reaction has a microanalysis that corresponded to both phenothiazine **14** and its isomer **15**. ^{1}H- and ^{19}F NMR-spectra indicate that the product is a mixture of phenothiazines **14** and **15** (Scheme 5) in the ratio 3:1. The ^{1}H NMR spectrum of the mixture in DMF-d_7 showed aromatic protons as a multiplet between δ 6.8 and 7.4 ppm; protons of amino- and hydroxygroups as a broad signal at δ 8.7 ppm. Two singlet signals at δ 5.66 and 5.62 ppm were assigned to methine protons of phenothiazines **14** and **15**. In the ^{19}F NMR spectrum of the mixture, two doublet signals at δ −150.07 and −145.46 ppm with coupling constant of 22 Hz between *ortho*-atoms of fluorine were assigned to phenothiazine **15**; the doublet at δ –139.88 ppm, doublet of doublets δ –138.77 ppm with coupling constants of 14 and 3 Hz between *para*-atoms of fluorine and the F-5 atom and NH-group, respectively, were assigned to phenothiazine **14**. Only product **14** was isolated by recrystallization from *o*-xylene as a pure substance.

3.2. Reaction of 4-hydroxy-5,6,7,8-tetrafluorocoumarin derivatives with 2-mercaptoethanol

Interaction of coumarin **1** with 2-mercaptoethanol in DMSO in the presence of an excess of Et_3N at 80°C for



Scheme 4.



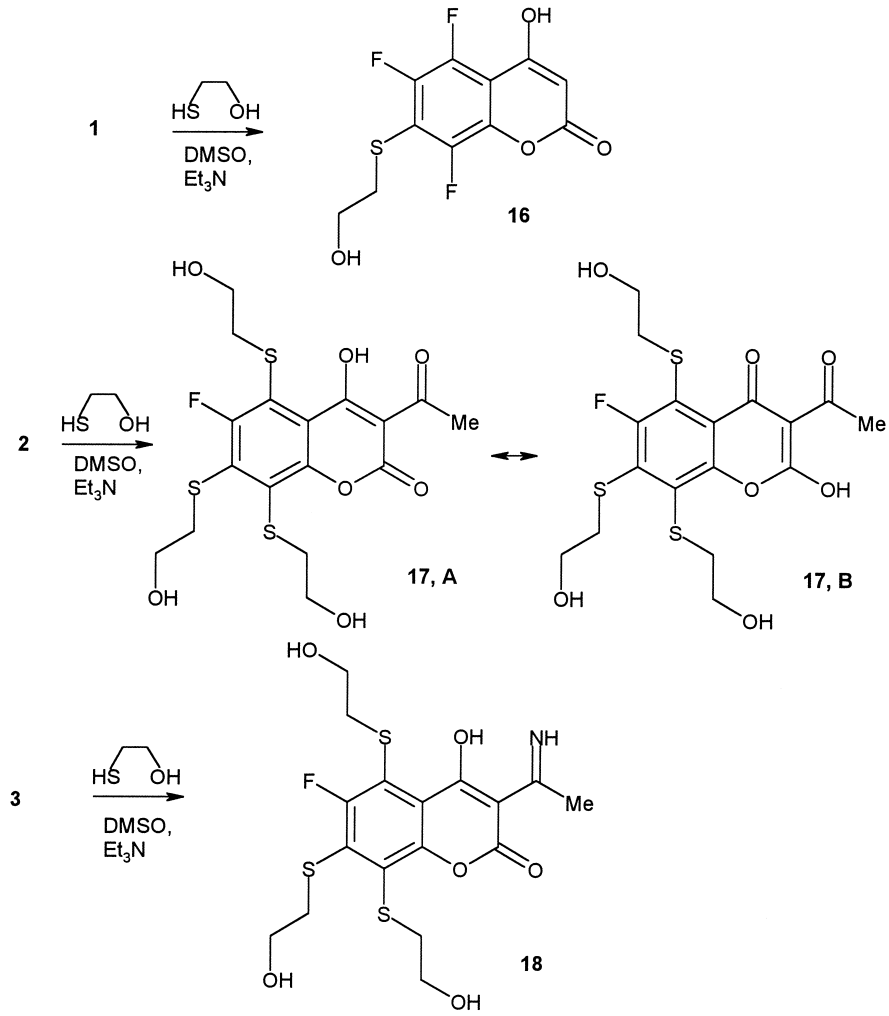
Scheme 5.

3 h results in product **16**. The structure of the compound results from displacement of fluoride by an S-nucleophile. Under similar conditions, coumarins **2**, **3** in the reaction with 2-mercaptoethanol afford the tri-substituted products **17**, **19** (Scheme 6). IR and NMR spectra of compound **17** indicate that the product exists as a mixture of two tautomers (coumarin **A** and chromone **B**) unlike coumarins **16**, **19**.

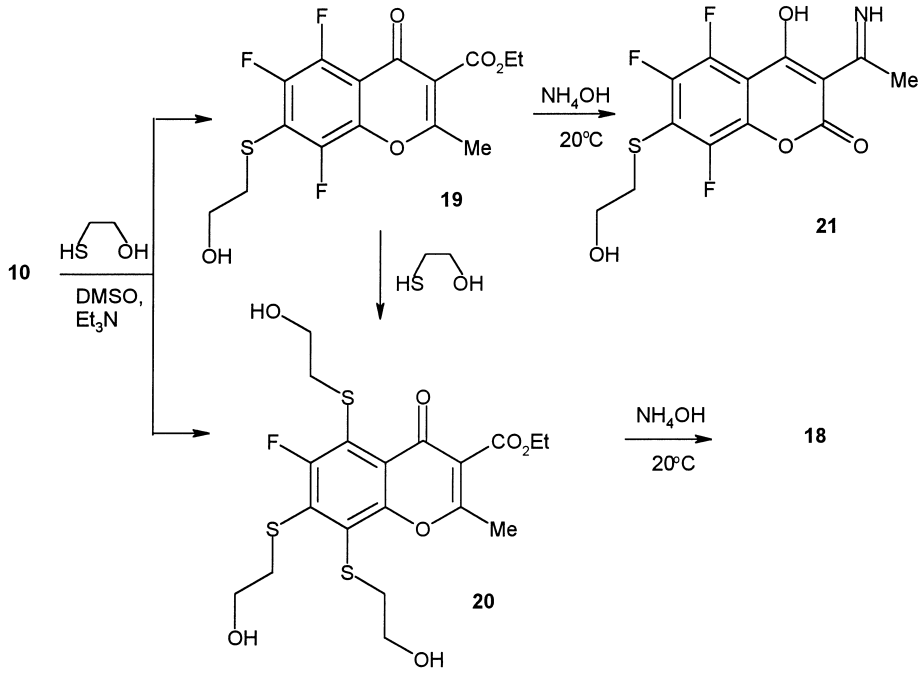
Under analogous conditions, interaction of chromone **10** with 2-mercaptoethanol, leads to the formation of the tri-substituted compound **19** (Scheme 7). When the reaction is carried out at room temperature for a shorter period (3 min), product of mono-displacement **20** can be obtained (Scheme 8). Chromone **20** reacts with 2-mercaptoethanol to afford compound **19**.

The above-mentioned reactions require the presence of Et_3N as a catalyst. Thus, heating chromone **10** with an excess of 2-mercaptoethanol for 10 h without a basic catalyst does not give any products.

Treatment of chromones **19**, **20** with aqueous ammonia at room temperature affords coumarins **21**, **18**, respectively (Scheme 7). These compounds may result from the addition of amine at the C-2 atom with opening of pyrone ring



Scheme 6.



Scheme 7.

followed by intramolecular cyclization. Thus, acyl-lactone rearrangement in basic medium is typical for mono- and tri-substituted chromones **19**, **20** like starting non-substituted chromones [2].

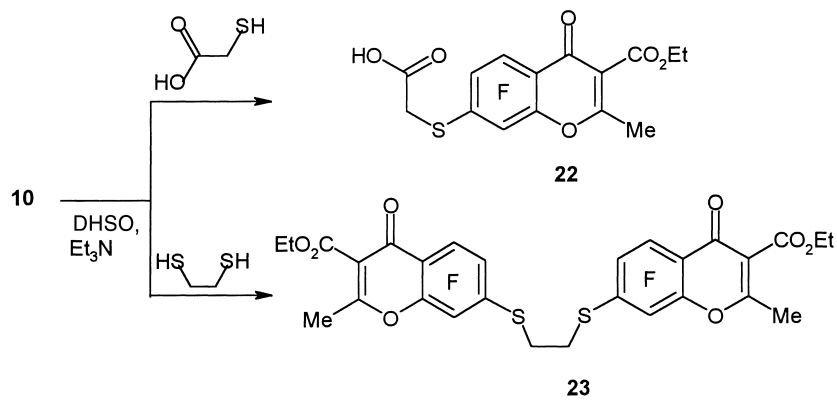
In contrast to the reaction of chromone **10** with *o*-phenylenediamine (Scheme 8), interaction of compound **10** with 2-mercaptoethanol affords the products of fluorine atom displacement rather than product of pyrone ring opening followed by splitting.

For comparison the reactions of chromone **10** with other S-nucleophiles have been studied. Thus, chromone **10** reacts with mercaptoacetic acid in DMSO in the presence of a catalytic amount of Et_3N at 18°C for 20 min to form the substituted product **22**. Under analogous conditions, the interaction of chromone **10** with 1,2-ethanedithiol also yields the substituted compound **23**. The latter results from displacement of a fluorine atom of two-chromone molecule at the C-7 position by one S-dinucleophile. A similar product was obtained by the reaction of 2-etoxycarbonyl-5,6,7,8-tetrafluorochromone with ethylenediamine in DMSO [16].

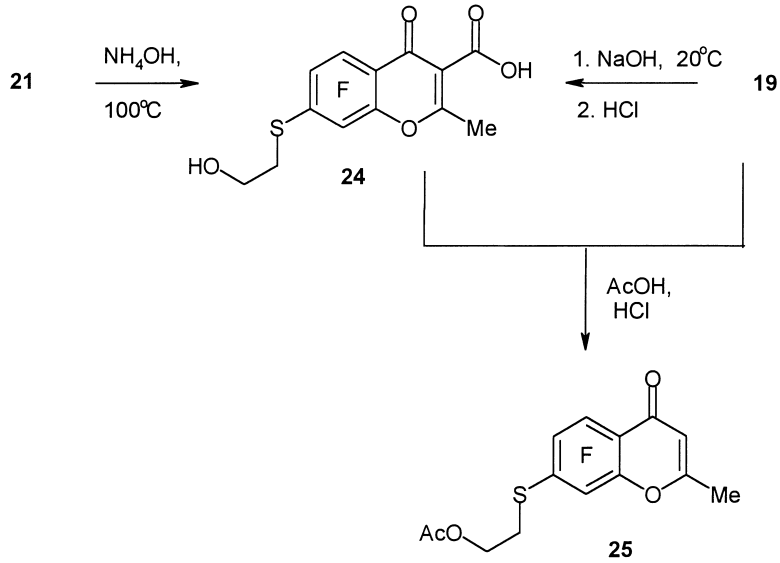
Displacement of a fluorine atom by an S-nucleophile (2-mercaptoethanol) in coumarin **21** changes the chemical properties of the heterocycle. Thus, compound **21** on boiling in aqueous ammonia is converted into chromone-carboxylic acid **24** (Scheme 9) that does not occur in case of non-substituted coumarin **3** [3]. It is known that 2-methyl-5,6,7,8-tetrafluorochromone-3-carboxylic acid readily undergoes heterocyclic opening and decarboxylation when treated with aqueous ammonia [2]. Under similar conditions, acid **24** is stable.

IR and NMR spectroscopies and microanalysis of compound **24** makes it possible to consider alternative structure for 3-acetylcoumarin **C**.

The structure of compound **24** was proved by the chemical transformations. Thus, hydrolysis of ester of chro-



Scheme 8.



Scheme 9.

mone **19** results in acid **24**. Both acid **24** and its ester **19** give the same product **25** when treated with a mixture of acetic and hydrochloric acids. Compound **25** results from decarboxylation and acylation of the hydroxyl group of the mercaptoethanol fragment (Scheme 9). This product cannot be obtained from coumarin **C**.

In general, interaction of coumarins **1–3** and chromone **10** with S-nucleophiles leads to displacement of fluorine atoms but not the opening of sensitive heterocycle rings that occur in reactions with N-nucleophiles [2]. Similar reactions of fluorine-containing quinoline-3-carboxylic acids with 2-mercaptoethanol are known to result in 7-monosubstituted quinolinones [4–6]. Displacement of the fluorine atom at the position 5 or 8 in quinolones is possible when the heterocycle already has the substituent at the C-7 atom [8–10].

The formation of tri-substituted products in the reaction of fluorinated coumarins **2**, **3** and chromone **10** with S-nucleophiles was found for the first time. The attempts to obtain mono-substituted products in the reactions of coumarins **2**, **3** with 2-mercaptoethanol were unsuccessful. Such an activating effect of the thioalkyl group on displacement of fluorine atoms may compare to that of electron-withdrawing groups (CF_3, NO_2) [17,18]. This is due to high polarizability of the S–Ar_F bond unlike other donating substituents X–Ar_F (X = OAlk, OH, NH_2, CH_3 et al.).

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