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TRANSFORMATIONS OF 3-(1-AMINOETHYLIDENE)-5,6,7,8-TETRAFLUOROBENZOPYRAN-2,4-DIONE WITH HYDRAZINES

Konstantin V. Shcherbakov, Yanina V. Burgart, and Victor I. Saloutin*

I. Ya. Postovski Institute of Organic Synthesis of Urals Division of Russian Academy of Sciences, 22/20, S. Kovalevskoi / Akademicheskaya Str., Ekaterinburg, GSP-147, Russia, 620041, fax (+7343) 374 5954; e-mail: saloutin@ios.uran.ru, specialk@mail.ru

Abstract – 3-(1-Aminoethylidene)-5,6,7,8-tetrafluorobenzopyran-2,4-dione reacts with the substituted hydrazines depending on hydrazine nucleophilicity and the reaction conditions. 3-R-hydrazinoethylidene-5,6,7,8-tetrafluorobenzo-pyrandiones are formed as a result of the transamination at aminoethylidene fragment by hydrazine NH_2-group. In the case of methylhydrazine and hydrazine the transamination can be accompanied by the substitution of fluorine atom at the atom C-7. Benzopyrano[2,3-*c*]pyrazolone derivatives are produced due to the intramolecular addition of the RNH-group at the C-2 atom followed by the intramolecular substitution of fluorine atom by hydroxyl group.

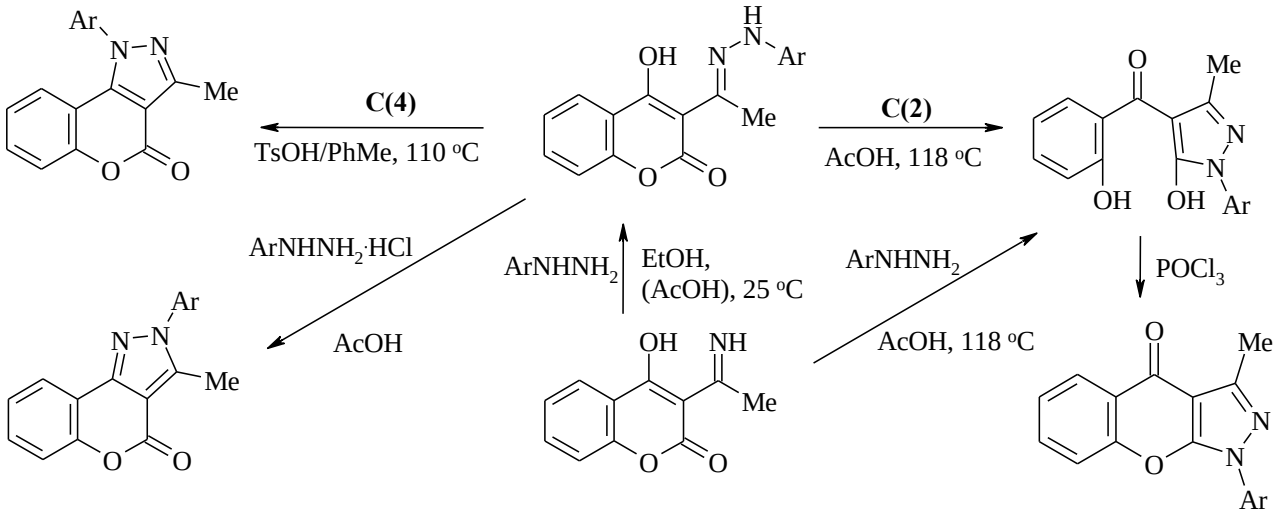
INTRODUCTION

Coumarins are well-known for their biological activity and high-reaction ability and widely used in organic synthesis.[1,2] We have developed the effective methods for the synthesis of the fluorinated 4-hydroxycoumarin derivatives.[3] Reactions of these compounds with primary and secondary monoamines and with *o*-phenylenediamine have been studied in our previous investigations.[4,5,6] It was found that condensation at the acyl group and the substitution of the fluorine atom at the C(7) position (or substitution of the fluorine atom at the C(5) position in some cases) are the competitive reactions in the transformations of the 3-acyl-5,6,7,8-tetrafluoro-4-hydroxycoumarins with primary amines. This is depended on the solvent used and the amine nucleophilicity.[4] Whereas, substitution of the fluorine atom is the initial process in the reactions of coumarins with secondary amines. α-Pyrone ring was found to be stable to attack of the nucleophiles in comparison with the non-fluorinated analogues.

Herein, we report the transformations of 3-(1-aminoethylidene)-5,6,7,8-tetrafluorobenzopyran-2,4-dione

(**1**) with hydrazines under the different reaction conditions to show the utility of the fluorinated coumarins as block-synthons in organic synthesis.

It is widely known that the non-fluorinated 3-acetyl-4-hydroxycoumarins react with arylhydrazines to give 3-arylhydrazinoethylidene-4-hydroxycoumarins which can undergo further cyclizations depending on the reaction conditions (Scheme 1). There are two ways for cyclization: firstly, at the C(2) position with formation of 1-aryl-5-hydroxy-4-(2-hydroxybenzoyl)-3-methyl-1*H*-pyrazole which can be transformed into 1-aryl-3-methylbenzopyrano[2,3-*c*]pyrazol-4-ones, and secondly, at the C(4) position with formation of 1-aryl-3-methylbenzopyrano[4,3-*c*]pyrazol-4-ones. The last-ones can lead to the isomeric 2-aryl-3-methylbenzopyrano[4,3-*c*]pyrazol-4-ones in the reaction with arylhydrazine hydrochloride.[7,8,9,10,11,12,13]



Scheme 1

We selected hydrazines having the different nucleophilicity for our investigation. Nucleophilicity are known to correlate with basicity in the series of the related nucleophiles. Therefore, we can set our hydrazines in order to their basicity: phenylhydrazine (pK_a = 5.27), hydrazine hydrate (pK_a = 6.50), and methylhydrazine (pK_a = 7.87).[14]

RESULTS AND DISCUSSION

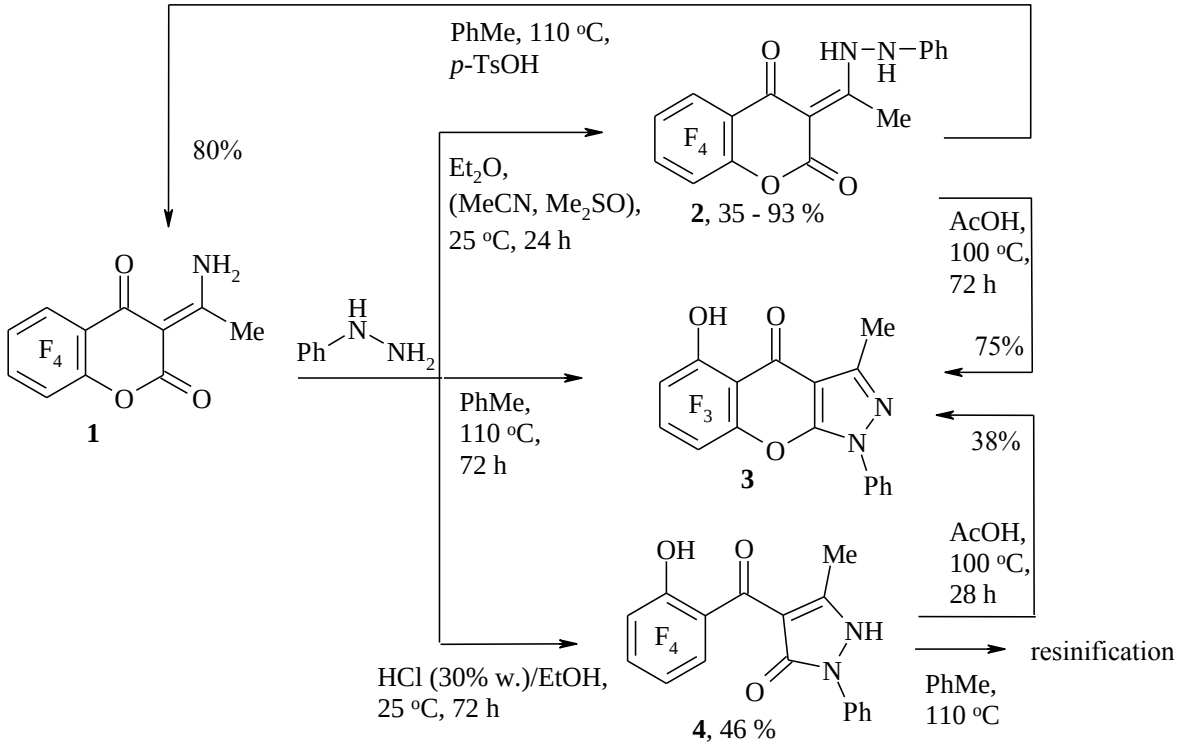
2.1. Reactions of 3-(1-aminoethylidene)-5,6,7,8-tetrafluorobenzopyran-2,4-dione (1) with phenylhydrazine.

It was found that coumarin (**1**) reacts with phenylhydrazine at room temperature to result in the formation of 5,6,7,8-tetrafluoro-3-[1-(2-phenylhydrazino)ethylidene]benzopyran-2,4-dione (**2**), similarly to the non-fluorinated analogues (Scheme 2). The way of reaction does not depend on type of solvent used.

Our attempts to convert benzopyrandione (**2**) into benzopyrano[4,3-*c*]pyrazolone under reaction conditions of the non-fluorinated analogues (in refluxing toluene with a catalytic quantity of *p*-toluene sulfonic acid) have led to coumarin (**1**), which are formed as a result of the hydrazine fragment *N*-*N* bond

cleavage (Scheme 2). Hydrazone derivatives can be undergone to such cleavage in the reactions with the bases.[15] The mass spectrum of compound (**2**) has the peak *m/z* 274 (23.23 %) corresponding to the fragment [M-NH_2Ph]. This fact confirms the *N*-*N* bond instability under the influence of high-temperature. Nevertheless 6,7,8-trifluoro-5-hydroxy-3-methyl-1-phenylbenzopyrano[2,3-*c*]pyrazol-4(1*H*)-one (**3**) was obtained from benzopyrandione (**2**) upon heating in acetic acid (Scheme 2). It is significant that the transformations of the non-fluorinated analogues under the similar reaction conditions have resulted in 1-aryl-5-hydroxy-4-(2-hydroxybenzoyl)-3-methylpyrazols,[9,10,12] which were undergone intramolecular condensation by heating with $POCl_3$ only to give benzopyrano[2,3-*c*]pyrazolones (Scheme 1).

Obviously compound (**3**) is generated by the attack of the phenyl substituent *NH*-group of benzopyrandione (**2**) at the C(2) atom to form 4-(2,3,4,5-tetrafluoro-6-hydroxybenzoyl)-1,2-dihydro-5-methyl-2-phenyl-3*H*-pyrazol-3-one intermediate (**4**). Easy cyclization of pyrazolone (**4**) into benzopyranopyrazolone (**3**) could be explained by the presence of the fluorine atoms at the benzoyl substituent. Pyrone ring formation is occurred *via* intramolecular substitution of the fluorine atom to hydroxyl group of the pyrazole fragment. The non-fluorinated analogues can be converted into the benzopyranopyrazolones due to H_2O elimination by heating with dehydrating agents only.



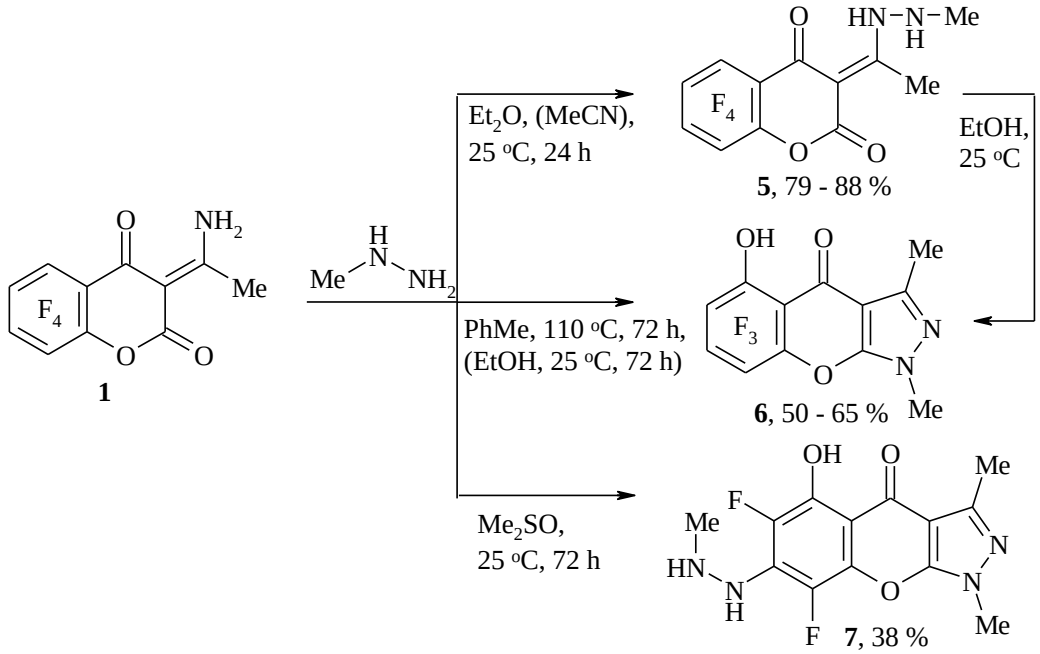
Scheme 2

Coumarin (**1**) reacted with phenylhydrazine in water-ethanol solution of hydrochloric acid at the room temperature to result in pyrazolone (**4**) (Scheme 2). Attempt to convert pyrazolone (**4**) to compound (**3**) in refluxing toluene led to resinification of the reaction mixture. However, this conversion was realized in acetic acid (Scheme 2). According to our researches in the field of transformations of 3-acyl-4-

hydroxycoumarins with *o*-phenylenediamine,[6] we proved the formation of the new heterocyclic systems by heating in high-boiling solvents. Thus, coumarin (**1**) with phenylhydrazine formed benzopyranopyrazolone (**3**) in refluxing toluene.

2.2. Reactions of 3-(1-aminoethylidene)-5,6,7,8-tetrafluorobenzopyran-2,4-dione (1) with methylhydrazine.

The reaction of coumarin (**1**) with methylhydrazine was found to depend on the solvent even at room temperature. Methylhydrazine reacted with coumarin (**1**) in diethyl ether or acetonitrile to give 5,6,7,8-tetrafluoro-3-[1-(2-methylhydrazino)ethylidene]benzopyran-2,4-dione (**5**) (Scheme 3).



Scheme 3

However 6,7,8-trifluoro-5-hydroxy-1,3-dimethylbenzopyrano[2,3-*c*]pyrazol-4(1*H*)-one (**6**) was obtained from the same reaction in ethanol at the room temperature. Benzopyrandione (**5**) was converted into compound (**6**) by the stirring in ethanol.

The reaction of coumarin (**1**) with methylhydrazine in boiling toluene resulted in benzopyranopyrazolone (**6**) similarly to transformations with phenylhydrazine.

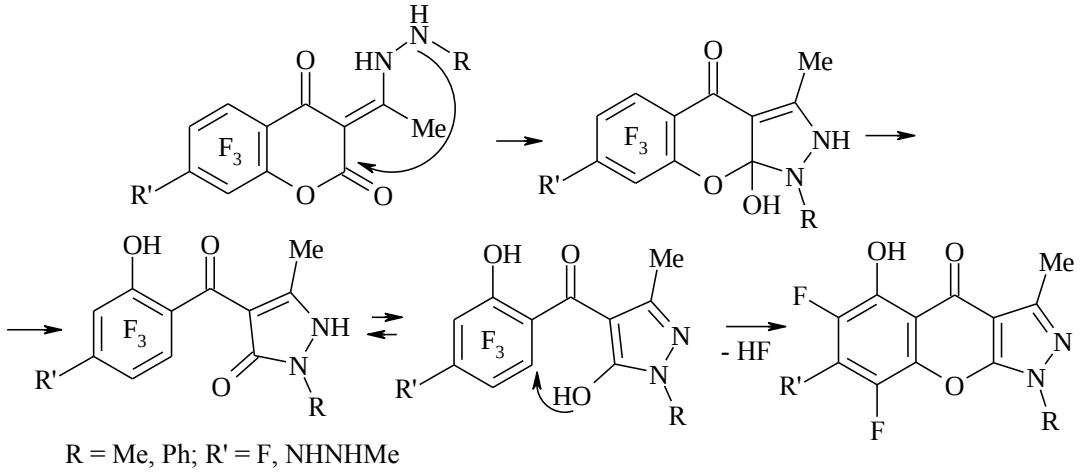
Coumarin (**1**) with methylhydrazine in DMSO at the room temperature gave 6,8-difluoro-5-hydroxy-1,3-dimethyl-7-(2-methylhydrazino)benzopyrano[2,3-*c*]pyrazol-4(1*H*)-one (**7**) (Scheme 3). According to our research on the transformations of 3-acetyl- and 3-acetimidoyl-5,6,7,8-tetrafluoro-4-hydroxycoumarins with monoamines, we have shown that the condensation at the acyl fragment of coumarins was accompanied by the substitution of the fluorine atom at the C(7) position in high-polar DMSO.

It is significant that the peak at δ 3.18 ppm corresponding to signal of *Me*-NHNH-group methyl protons in ^{1}H NMR spectrum of compound (**7**) is coupled in triplet with the coupling constant $^6J_{H\text{-}F}$ = 2.5 Hz due

to the interaction with fluorine atoms. An alternative structure attached Me(NH_2)N-group at C-7 atom must be assumed for compound (**7**), however the IR spectrum excepts such structure because it does not contain doublet absorption bands corresponding to asymmetrical and symmetrical vibrations of NH_2-group.

The comparative analysis of the mass spectra of the 3-(1-methyl(phenyl)hydrazinoethylidene)-substituted benzopyrandiones (**2,5**) was evidence of this fact also More nucleophilic methylhydrazine showed high ability to the cyclization.. The mass spectrum of the methyl-substituted benzopyrandione (**5**) has peak *m/z* 284 (25.57%), corresponding to [M-HF] fragment, while the similar peak in mass spectrum of the phenyl-substituted benzopyrandione (**2**) has lesser intensity - *m/z* 346 (1.57%) [M-HF], *m/z* 345 (7.33%) [M-H-HF].

We can propose the general scheme of the benzopyranopyrazolones (**3,6,7**) formation in the reactions of coumarin (**1**) and the substituted hydrazines based on the experimental data (Scheme 4).



Scheme 4

Change of the recyclization way on the stage of pyrazole intermediates conversion is the distinguishing feature of reactions of the fluorinated coumarin (**1**) with the substituted hydrazines in contrast to the non-fluorinated analogues. In the case of coumarin (**1**), the formation of the new heterocycle is a result of the intramolecular nucleophilic substitution of the fluorine atom accompanied by HF elimination. It must be noted that transformations of the fluorinated coumarin (**1**) are more selective in contrast to the non-fluorinated analogues. The preferable attack of the *NH*-group at the C(2) atom in the fluorinated 3-(1-methyl(phenyl)hydrazinoethylidene)-substituted benzopyrandiones (**2**,**5**) is determined by easiness and irreversibility of the recyclization due to the substitution of the fluorine atom.

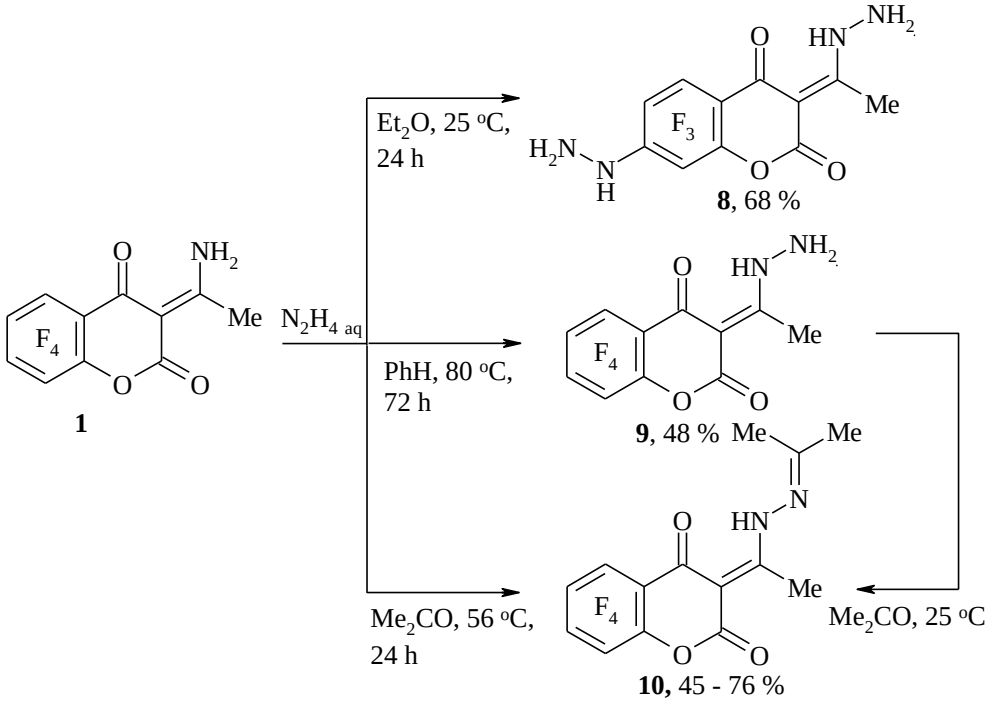
2.3. Reactions of 3-(1-aminoethylidene)-5,6,7,8-tetrafluorobenzopyran-2,4-dione (1) with hydrazine hydrate.

The reactions of coumarin (**1**) with hydrazine hydrate were found to pass unequally under the similar reaction conditions to the transformations with methyl- and phenylhydrazines. Thus, the reaction of

coumarin (**1**) with excess of hydrazine hydrate in diethyl ether at the room temperature gave 5,6,8-trifluoro-7-hydrazino-3-(1-hydrazinoethylidene)benzopyran-2,4-dione (**8**) (Scheme 5).

Then we made an attempt to obtain benzopyranopyrazolone system by heating in high-boiling solvents similarly to the reactions with methyl- and phenylhydrazines. 5,6,7,8-Tetrafluoro-3-(1-hydrazinoethylidene)benzopyran-2,4-dione (**9**) was formed from coumarin (**1**) and hydrazine hydrate in refluxing benzene (Scheme 5). Refluxing of coumarin (**1**) and hydrazine hydrate in toluene resulted in the inseparable mixture of products. The conversion of coumarin (**1**) was not achieved by heating in acetic acid.

It was shown that benzopyrandione (**9**) easily reacted with some electrophilic agents. Thus, compound (**9**) converted rapidly into 5,6,7,8-tetrafluoro-3-{1-[2-(1-methylethylidene)hydrazino]ethylidene}benzopyran-2,4-dione (**10**) by standing in acetone at room temperature. Product (**10**) was obtained by refluxing of coumarin (**1**) with hydrazine hydrate in acetone as well (Scheme 5). These transformations are acid- or base catalytic reactions usually. Compound (**9**) probably serves as a base catalyst in this case.



Scheme 5

CONCLUSION

So, we have found that the transformations of coumarin (**1**) with hydrazines depended on hydrazine nucleophilicity and the solvent nature. The initial act in these reactions is the transamination of coumarin (**1**) at aminoethylidene fragment by hydrazine NH_2-group. In the case of more nucleophilic methylhydrazine and hydrazine the transamination can be accompanied by the substitution of fluorine atom at the atom C-7. Further the intramolecular attack of the RNH-group at the C-2 atom can lead to opening α-pyrone ring and the intermediate formation of pyrazole derivative such as (**4**). The latter is

turned readily into benzopyrano[2,3-*c*]pyrazolone in a result of the intramolecular substitution of fluorine atom by hydroxyl group. The derivative of more nucleophilic methylhydrazine reveals the most tendency to recyclization. Thus, we can mark more regioselectivity of the reactions of coumarin (**1**) with hydrazines as compared with the similar conversions of non-fluorinated analogs. We can offer also to use the reactions of 3-(1-aminoethylidene)-5,6,7,8-tetrafluorobenzopyran-2,4-dione (**1**) with substituted hydrazines as a method for annelations of pyrazole ring to the benzopyranone ring.

EXPERIMENTAL

The melting points were measured on «Stuart SMP3» in open capillaries and are uncorrected. The infrared spectra were recorded on Perkin Elmer Spectrum One FT-IR spectrometer at 4000 – 400 cm^{-1} in the nujol mulls. The ^{1}H and ^{19}F NMR spectra were measured on Bruker DRX-400 spectrometer (^{1}H, 400, relative to Me_4Si, ^{19}F, 376 MHz relative to C_6F_6). The mass spectra were recorded on «Shimadzu LCMS-2010» (APC-ionization, mobile phase – acetonitrile). The microanalyses were carried out on Perkin-Elmer PE 2400 series II elemental analyzer.

The starting coumarin (**1**) was obtained by a known method.[16]

4.1. The general procedure of the reactions of the coumarin (**1**) with hydrazines.

Method A. Hydrazine (0.5 mmol) was added to a solution of the coumarin (**1**) (0.5 mmol) in suitable solvent (30 mL). The reaction mixture was stirred at rt. The reaction control was monitored by TLC method. The solvent was removed and the residue was recrystallized from the corresponding solvent.

Method B. Hydrazine (0.5 mmol) was added to a solution of the coumarin (**1**) (0.5 mmol) in suitable solvent (60 mL). The reaction mixture was refluxed. The reaction control was monitored by TLC method. The solvent was removed and the residue was recrystallized from the corresponding solvent.

4.2.1. 3-(1-Aminoethylidene)-5,6,7,8-tetrafluorobenzopyran-2,4-dione (**1**).

Compound (**1**) was obtained from benzopyrandione (**2**) in refluxing toluene in the presence of *p*-TsOH as catalyst for 72 h according to method *B*. Yield after recrystallization from hexane, 80 % (110 mg); mp 165 ^{o}C.[16]

4.2.2. 5,6,7,8-Tetrafluoro-3-[1-(2-phenylhydrazino)ethylidene]benzopyran-2,4-dione (**2**).

Compound (**2**) was obtained from coumarin (**1**) and phenylhydrazine according to method *A*. Yield after recrystallization from Et_2O, 93 % (170 mg) in Et_2O, 62 % (114 mg) in MeCN, 35 % (64 mg) in DMSO; mp 221-224 ^{o}C. ^{1}H NMR [$(CD_3)_2CO$] δ: 2.85 (3H, s, CH_3); 3.77 (2H, s, 2 NH); 7.18 (5H, d.m, C_6H_5). ^{19}F NMR [$(CD_3)_2CO$] δ: -2.54, 2.55, 12.04, 18.96 (all m, in 1F). MS, *m/z* (rel. int): 366 [M] (14.06); 365 [M-H] (70.80); 274 [M-$C_6H_5NH_2$] (23.23); 233 [$C_9HF_4O_3$] (11.41); 216 [$C_9F_4O_2$] (51.38). IR, ν: 3312 (NH); 1690 (OC=O); 1650 (C=O); 1602, 1523 (NH, C=C); 1015 (CF) cm^{-1}. Anal. Calcd for $C_{17}H_{10}F_4N_2O_3$: C, 55.75; H, 2.75; F, 20.75; N, 7.65. Found: C, 55.64; H, 2.54; F, 20.87; N, 7.62.

4.2.3. 6,7,8-Trifluoro-5-hydroxy-3-methyl-1-phenylbenzopyrano[2,3-*c*]pyrazol-4(1*H*)-one (**3**).

Compound (**3**) was obtained from coumarin (**1**) and phenylhydrazine in refluxing toluene for 72 h according to method *B*. Yield after recrystallization from ethanol, 75 % (130 mg). Compound (**3**) was obtained from benzopyrandione (**2**) by heating in acetic acid at 100 ^{o}C for 72 h according to method *B*. Yield after recrystallization from EtOH, 42 % (73 mg). Compound (**3**) was obtained from pyrazolone (**4**) by heating in acetic acid at 100 ^{o}C for 28 h according to method *B*. Yield after recrystallization from EtOH, 38 % (23 mg); mp 215 ^{o}C. ^{1}H NMR [DMSO-d_6] δ: 2.58 (3H, s, CH_3); 7.49 – 7.87 (5H, m, C_6H_5); 12.80 (1H, s, OH). ^{19}F NMR [DMSO-d_6] δ: -5.36 (1F, d.d, ^{4}J = 4.9, ^{3}J = 21.9 Hz); -1.93 (1F, d.d, ^{4}J = 4.9, ^{3}J = 21.9 Hz); 13.79 (1F, t.m, ^{3}J = 21.9 Hz). IR, ν: 3100 (OH); 1671 (C=O); 1623, 1596, 1541 (C=C); 1020 (CF) cm^{-1}. Anal. Calcd for $C_{17}H_9F_3N_2O_3$: C, 58.97; H, 2.62; F, 16.46; N, 8.09. Found: C, 58.50; H, 2.63; F, 16.55; N, 8.03.

4.2.4. 4-(2,3,4,5-Tetrafluoro-6-hydroxybenzoyl)-1,2-dihydro-5-methyl-2-phenyl-3*H*-pyrazol-3-one (**4**).

Compound (**4**) was obtained from coumarin (**1**) and phenylhydrazine by stirring in EtOH solution of hydrochloric acid (30 % w.) according to method *A*. Yield after recrystallization from EtOH, 46 % (84 mg); mp 205 ^{o}C. ^{1}H NMR [DMSO-d_6] δ: 2.31 (3H, s, CH_3); 6.43 (1H, s, NH); 7.22 – 7.39 (5H, m, C_6H_5); 10.95 (1H, s, OH). ^{19}F NMR [DMSO-d_6] δ: -8.14, 1.94, 6.49, 21.80 (all m, in 1F). IR, ν: 3062 (NH); 3020 (OH); 1691, 1655 (C=O); 1596, 1520 (C=C); 992 (CF) cm^{-1}. Anal. Calcd for $C_{17}H_{10}F_4N_2O_3$: C, 55.75; H, 2.75; F, 20.75; N, 7.65. Found: C, 55.33; H, 2.82; F, 20.92; N, 7.49.

4.2.5. 5,6,7,8-Tetrafluoro-3-[1-(2-methylhydrazino)ethylidene]benzopyran-2,4-dione (**5**).

Compound (**5**) was obtained from coumarin (**1**) and methylhydrazine according to method *A*. Yield after recrystallization from Et_2O, 88 % (134 mg) in Et_2O, 79 % (120 mg) in MeCN; mp 164-166 ^{o}C. ^{1}H NMR [$(CD_3)_2CO$] δ: 2.77, 2.87 (6H, both s, 2 CH_3); 5.64, 14.79 (2H, both s, 2 NH). ^{19}F NMR [$(CD_3)_2CO$] δ: -2.94, 2.33, 11.27, 18.31 (all m, in 1F). IR, ν: 3306 (NH); 1718 (OC=O); 1648 (C=O); 1591, 1525 (NH, C=C); 1032 (CF) cm^{-1}. MS, *m/z* (rel. int): 304 [M] (14.56); 303 [M-H] (100); 284 [M-HF] (25.57). Anal. Calcd for $C_{12}H_8F_4N_2O_3$.: C, 47.38; H, 2.65; F, 24.98; N, 9.21. Found: C, 47.12; H, 2.45; F, 24.67; N, 9.11.

4.2.6. 6,7,8-Trifluoro-5-hydroxy-1,3-dimethylbenzopyrano[2,3-*c*]pyrazol-4(1*H*)-one (**6**).

Compound (**6**) was obtained from coumarin (**1**) and methylhydrazine in refluxing toluene for 72 h according to method *B*. Yield after recrystallization from hexane, 50 % (71 mg). Compound (**6**) was obtained from benzopyrandione (**5**) by stirring in EtOH for 24 h according to method *A*. Yield after recrystallization from hexane, 65 % (46 mg). mp 137-139 ^{o}C. ^{1}H NMR [DMSO-d_6] δ: 2.47 (3H, s, C-CH_3), 3.85 (3H, s, N-CH_3); 12.99 (1H, s, OH). ^{19}F NMR [DMSO-d_6] δ: -5.58 (1F, d.d, ^{4}J = 5.3, ^{3}J = 22.2 Hz); -2,46 (1F, d.d, ^{4}J = 5.3, ^{3}J = 22.2 Hz); 13,38 (1F, t.m, ^{3}J = 22.2 Hz). IR, ν: 3060 (OH); 1641 (C=O); 1581, 1517 (C=C); 1001 (CF) cm^{-1}. Anal. Calcd for $C_{12}H_7F_3N_2O_3$: C, 50.72; H, 2.48; F, 20.05; N, 9.86. Found: C, 50.47; H, 2.30; F, 19.75; N, 9.71.

4.2.7. 6,8-Difluoro-5-hydroxy-1,3-dimethyl-7-(2-methylhydrazino)benzopyrano[2,3-*c*]pyrazol-4(1*H*)-one (**7**).

Compound (**7**) was obtained from coumarin (**1**) and methylhydrazine by stirring in DMSO for 72 h according to method *A*. Yield after recrystallization from EtOH, 38 % (59 mg); mp 190 °C. ^{1}H NMR [DMSO-d_6] δ: 2.41 (3H, s, C-CH_3), 3.79 (3H, s, N-CH_3); 3.18 (3H, t, N-CH_3, $^6J_{H\text{-}F}$ = 2.5 Hz); 4.89 (2H, s, 2 NH); 12.54 (1H, s, OH). ^{19}F NMR [DMSO-d_6] δ: 7.27 (1F, dq, $^4J_{F\text{-}F}$ = 1.2 Hz, $^6J_{F\text{-}H}$ = 2.5 Hz), 10.32 (1F, dq, $^4J_{F\text{-}F}$ = 1.2 Hz, $^6J_{F\text{-}H}$ = 2.5 Hz). IR, ν: 3354 (NH); 3050 (OH); 1660 (C=O); 1626, 1584 (NH, C=C); 1000 (CF) cm^{-1}. Anal. Calcd for $C_{13}H_{12}F_2N_4O_3$: C, 50.33; H, 3.90; F, 12.25; N, 18.06. Found: C, 50.04; H, 3.78; F, 12.01; N, 17.97.

4.2.8. 5,6,8-Trifluoro-7-hydrazino-3-(1-hydrazinoethylidene)benzopyran-2,4-dione (**8**).

Compound (**8**) was obtained from coumarin (**1**) and hydrazine hydrate by stirring in Et_2O for 24 h according to method *A*. Yield after recrystallization from Et_2O, 68 % (103 mg); mp 226-227 °C. ^{1}H NMR [DMSO-d_6] δ: 2.57 (3H, s, CH_3); 4.60 (2H, s, NH_2); 6.05 (2H, s, NH_2); 7.50 (1H, s, NH); 12.20 (1H, s, NH). ^{19}F NMR [DMSO-d_6] δ: 1.00 (1F, d.m, ^3J = 19.9 Hz); 4.01(1F, m), 13.57 (1F, d.d, ^4J = 10.6, ^3J = 19.9 Hz). IR, ν: 3346 (NH); 1719 (OC=O); 1651 (C=O); 1574, 1505 (NH, C=C); 997 (CF) cm^{-1}. Anal. Calcd for $C_{11}H_9F_3N_4O_3$: C, 43.72; H, 3.00; F, 18.86; N, 18.54. Found: C, 43.80; H, 2.92; F, 19.01; N, 18.24.

4.2.9. 5,6,7,8-Tetrafluoro-3-(1-hydrazinoethylidene)benzopyran-2,4-dione (**9**).

Compound (**9**) was obtained from coumarin (**1**) and hydrazine hydrate in refluxing benzene during 72 h according to method *B*. Yield after recrystallization from EtOH-water solution, 48 % (70 mg); mp 169 °C. ^{1}H NMR [DMSO-d_6] δ: 2.58 (3H, s, CH_3); 6.24 (2H, s, NH_2); 14.73 (1H, s, NH). ^{19}F NMR DMSO-d_6] δ: -3.12, 1.73, 10.56, 16.46 (all m, in 1F). IR, ν: 3328 (NH); 1709 (OC=O); 1649 (C=O); 1576, 1525 (NH, C=C); 996 (CF) cm^{-1}. Anal. Calcd for $C_{11}H_6F_4N_2O_3$: C, 45.53; H, 2.08; F, 26.19; N, 9.65. Found: C, 45.72; H, 2.22; F, 25.94; N, 9.82.

4.2.10. 5,6,7,8-Tetrafluoro-3-{1-[2-(1-methylethylidene)hydrazino]ethylidene}benzopyran-2,4-dione (**10**).

Compound (**10**) was obtained from benzopyrandione (**9**) by stirring in acetone for 2 h according to method *A*. Yield after recrystallization from EtOH, 76 % (125 mg). Compound (**10**) was obtained from coumarin (**1**) and hydrazine hydrate by refluxing in acetone for 24 h according to method *B*. Yield after recrystallization from EtOH, 45 % (74 mg); mp 192-195 °C. ^{1}H NMR [DMSO-d_6] δ: 2.16, 2.18, 2.82 (9H, all s, 3 CH_3); 15.72 (1H, s, NH). ^{19}F NMR [DMSO-d_6]: -2.36, 2.26, 12.60, 17.74 (all m, in 1F). IR, ν: 3371, 3349 (NH); 1725 (OC=O); 1650 (C=O); 1589, 1579, 1525 (NH, C=C); 1001 (CF) cm^{-1}. MS, *m/z* (rel. int): 329 [M-H] (100); 310 [M-HF], (14.67). Anal. Calcd for $C_{14}H_{10}F_4N_2O_3$: C, 50.92; H, 3.05; F, 23.01; N, 8.48. Found: C, 50.96; H, 2.73; F, 23.25; N, 8.68.

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