Reactions of trifluoro- and hexafluoroacetylacetones with thiobenzoylhydrazine

V. V. Alekseyev,[a] V. V. Pakal´nis,[b] I. V. Zerova,[b] and S. I. Yakimovich[b]*

[a]S. M. Kirov Military Medical Academy,
6 ul. Akad. Lebedeva, 194044 Saint Petersburg, Russian Federation.
Fax: +7 (812) 329 7118. E-mail: alekseyevv.v@mail.ru
[b]Saint Petersburg State University,
26 Universitetsky prosp., 198504 Saint Petersburg, Russian Federation.
Fax: +7 (812) 428 6939. E-mail: viktoriapakalnis@mail.ru

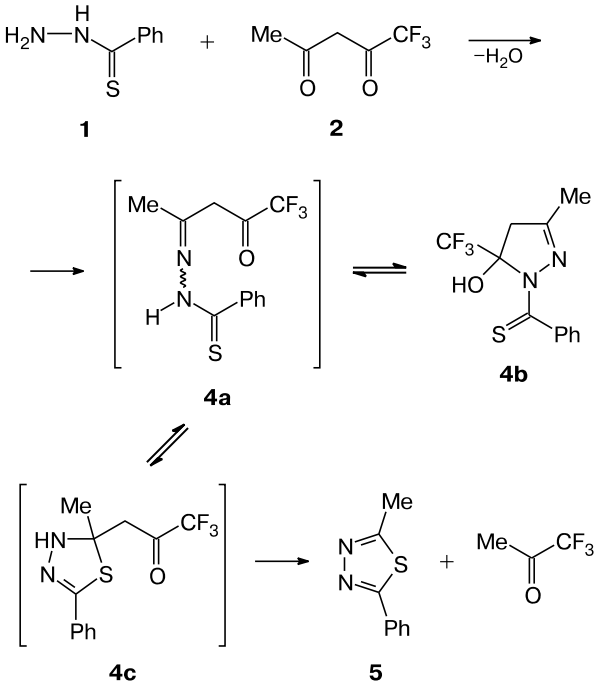
The reaction of thiobenzoylhydrazine with trifluoroacetylacetone leads to the product of condensation at the $CH_3C{=}O$ bond with the 5-hydroxy-2-pyrazoline structure. The tautomeric transition to the 2,3-dihydro-1,3,4-thiadiazole isomer occurs in solution. This isomer undergoes the cleavage to 2-methyl-5-phenyl-1,3,4-thiadiazole and trifluoroacetone. The reaction of thiobenzoylhydrazine with hexafluoroacetylacetone affords one of diastereomers of [3,5-dihydroxy-3,5-bis(trifluoromethyl)pyrazolidin-1-yl](phenyl)thioketone, which at equilibrium is transformed in solution into the second diastereomer of the 3,5-dihydroxypyrazolidine form followed by the elimination of water elements and formation of a tautomeric 5-hydroxy-2-pyrazoline—2,3-dihydro-1,3,4-thiadiazole mixture.

Key words: trifluoroacetylacetone, hexafluoroacetylacetone, thiobenzoylhydrazine, 3,5-dihydroxypyrazolidine, 2-pyrazoline, 2,3-dihydro-1,3,4-thiadiazole, ring-ring tautomerism.

The products of the reactions of acetylacetone and its 3-alkyl-substituted analogs with thiobenzoylhydrazine show in solutions a unique equilibrium involving two heterocyclic forms: of the 5-hydroxy-2-pyrazoline and 2,3-dihydro-1,3,4-thiadiazole structures.[1] There are few examples for similar ring-ring equilibria, where heterocycles of different nature compete.[2—4] In this work we studied the reactions of thiobenzoylhydrazine **1** with fluorinated analogs of acetylacetone, trifluoro- and hexafluoroacetylacetones **2** and **3**.

The reaction of thiobenzoylhydrazine **1** with trifluoroacetylacetone **2** occurs with 100% regioselectivity at the MeC=O bond. Due to the intramolecular cyclization of intermediate hydrazone structure **4a**, the condensation product has 5-hydroxy-2-pyrazoline structure **4b** (Scheme 1).

Scheme 1



The ^1H NMR spectrum of derivative **4b** in $CDCl_3$ detected immediately after dissolution contain two signals as nonsymmetrical doublets at δ_H 3.25 and 3.41. Their intensity is one proton each, and they form a typical AB system (J_{AB} = 18.9 Hz). The spectrum also contains a broadened signal at δ_H 8.23. These signals should be ascribed to the diastereotopic protons at the carbon atom in position 4 of the pyrazoline cycle and to the proton of the hydroxyl group. The downfield position of the latter is due to the influence of the adjacent electron-acceptor trifluoromethyl group. The data of ^{13}C NMR spectroscopy is completely consistent with the structure proposed for **4b** (see Experimental). The quartet signal at δ_C 93.35 ($^2J_{C,F}$ = 33.9 Hz) can be mentioned as the most characteristic one. This signal should be attributed to the quaternary carbon atom in position 5 of the heterocycle. The

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quartet shape of the signal indicates the bond with the trifluoromethyl group. The spectral characteristics of the discussed compound **4b** are close, to a considerable extent, to the results of the spectral study of the condensation product of trifluoroacetylacetone with benzoylhydrazine.[5,6] The X-ray structure of study of the latter showed that this product is formed by the condensation at the MeC=O bond and is 5-hydroxy-2-pyrazoline bearing the methyl group in position 3 and the trifluoromethyl group in position 5.

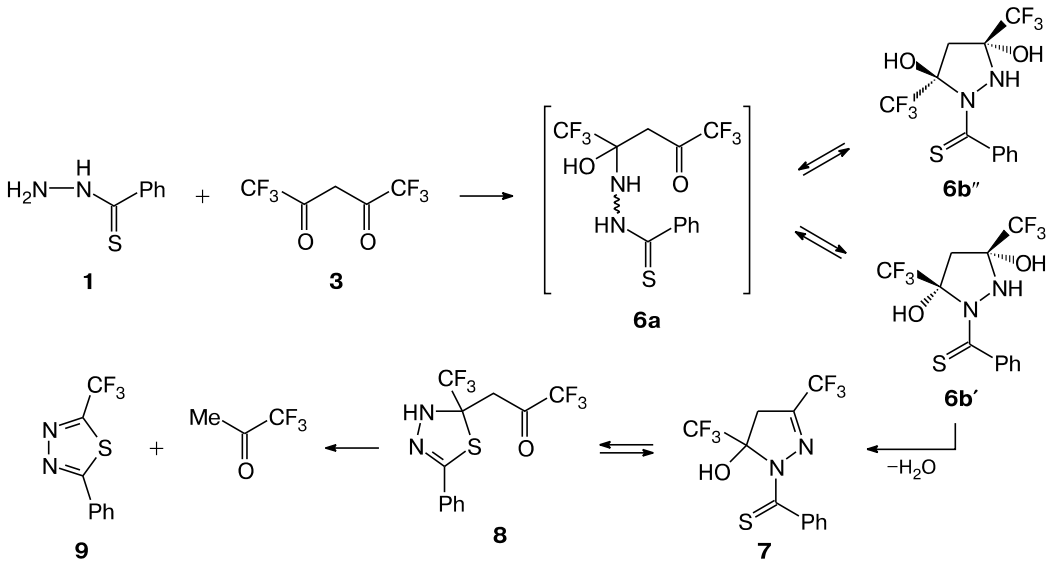
The shape of the ^{1}H NMR spectrum of a solution of derivative **4b** changes on storage. The second set of resonance signals appears in the spectrum. It turned out that this set does not correspond to possible tautomeric forms, *viz.*, linear hydrazone (**4a**) or cyclic 1,3,4-thiadiazoline (**4c**), but is due to the formation of the structure of the 1,3,4-thiadiazole type: 2-methyl-5-phenyl-1,3,4-thiadiazole (**5**). The initial 5-hydroxy-2-pyrazoline **4b** completely disappears with time. Derivative **4b** is also transformed into thiadiazole **5** on its keeping in methanol.

This can be explained as follows. A very insignificant equilibrium transition to the 2,3-dihydro-1,3,4-thiadiazole form **4c** occurs in solutions of the condensation product of trifluoroacetylacetone with thiobenzoylhydrazine **4b**. The heterocycle formed undergoes conversion to 2-methyl-5-phenyl-1,3,4-thiadiazole upon the elimination of trifluoroacetone. The driving force of the process is the aromatic character o the formed 1,3,4-thiadiazole cycle. The cleavage of the carbon—carbon bond with the substituent in position 2 of the heterocycle is favored by the fact that the trifluoroacetone anion is eliminated in which the negative charge is stabilized by strong electron-acceptor properties of the trifluoromethyl group. The tautomeric transition recovers the current concentration of 1,3,4-thiadiazoline **4c**, and the cleavage process continues to the complete disappearance of the primary condensation product, 5-hydroxy-2-pyrazoline **4b**.

The results of the interaction of thiobenzoylhydrazine **1** with hexafluoroacetylacetone **3** in dioxane (Scheme 2) are worth detailed discussion. According to the mass spectrometric and elemental analysis data, the isolated derivative corresponded to hydroxyhydrazine **6a**, formed due to the initial addition of polynucleophile **1** to the C=O bond of one of the trifluoroacetyl groups, or to the product of subsequent cyclization at the second carbonyl group, *viz.*, to the corresponding 3,5-dihydroxypyrazolidine **6b**. A certain argument against the hydroxyhydrazine structure is the fact that the IR spectrum of the discussed compound in KBr exhibits no absorption band in the region of stretching vibrations of the C=O bond (1700—1750 cm^{-1}). The NMR spectral data certainly show that the reaction affords one of the diastereomers of compound **6b**.

The ^{1}H NMR spectrum of derivative **6** in $CDCl_3$ recorded immediately after dissolution exhibits two nonsymmetrical doublet signals forming the AB system at δ_H 2.61 and 2.63 (J_{AB} = 16.0 Hz) and three broadened one-proton singlet signals at δ_H 4.11, 5.82, and 6.78, whose position and broadened shape indicate that they belong to the protons bound to the heteroatoms. In principle, this does not contradict to linear (**6a**) or cyclic structure (**6b**) of compound **6**. Structure **6a** has a chirality center, and dihydroxypyrazolidine **6b** has two such centers. This results in diastereotopicity of the protons of their methylene groups and, correspondingly, the appearance of the AB system in the ^{1}H NMR spectrum. However, linear structure **6a** contains the NH bond of the thioamide type. In

Scheme 2



the spectrum the signal of the corresponding proton should lie in rather downfield region. Thus, the shape of the ^{1}H NMR spectrum of derivative **6** indicates in favor of cyclic structure **6b**.

The final choice between the presented structures can be made on the basis of ^{13}C NMR spectroscopic data. A distinctive feature of hydroxyhydrazine structure **6a** should be the presence of the quartet signal from the carbon atom of the C=O bond in the trifluoroacetyl group at δ_C 190 of the carbon spectrum. The experimental ^{13}C NMR spectrum of compound **6** in $CDCl_3$ contains no similar signal but has two quartet signals at δ_C 81.76 ($^2J_{C,F}$ = 29.9 Hz) and 92.50 ($^2J_{C,F}$ = 30.9 Hz). They are assigned to the carbon atoms in positions 3 and 5 of pyrazolidine structure **6b**.

The shape of the ^{1}H NMR spectrum changes in time on storage of a solution of isolated derivative **6**. First, two signals as nonsymmetrical doublets at δ_H 2.64 and 2.67 forming the AB system (J_{AB} = 16.0 Hz) appear. The very close position of the already present and newly appeared signals of two AB systems indicates the formation of the second diastereomer of 3,5-dihydroxypyrazolidine structure **6**. In several hours, the intensity ratio of the signals of two AB systems stop changing. Evidently, two diastereomeric 3,5-dihydroxypyrazolidines **6b´** and **6b″** are equilibrated. Judging from the intensity of their signals, the ratio between these isomers is 4 : 1 in favor of the initial form. The predominant configurational isomer should rather contain *cis*-arranged bulky trifluoromethyl groups (**6b´**), where they can take the equatorial orientation for the heterocycle as an envelop or a half-chair.

The mutual transformation of diastereomers **6b´** and **6b″** can occur only through linear hydroxyhydrazine structure **6a**, which is not detected by NMR spectroscopy.

The ^{1}H NMR spectrum of compound **6** detected 1 day after the preparation of the solution shows the formation of two new exceptionally different structures.

In the ^{1}H NMR spectrum one of them gives nonsymmetrical doublet signals at δ_H 3.51 and 3.71 (AB system, J_{AB} = 19.6 Hz) and somewhat broadened singlet signal at δ_H 7.83. Another compound give signals at δ_H 3.58 and 3.69 in the form of nonsymmetrical doublets (AB system, J_{AB} = 17.4 Hz) and a broadening signal at δ_H 6.86. It can be assumed that water elements are eliminated from diastereomeric 3,5-dihydroxypyrazolidines **6b´** and **6b″** to form 5-hydroxy-2-pyrazoline **7**, which further undergoes the equilibrium transition to 1,3,4-thidiazoline tautomer **8** through the intermediate linear structure of the hydrazone form. Compounds **7** and **8** have chirality centers, and the hydrogen atoms of their methylene groups are diastereotopic, due to which we observed two AB systems in the ^{1}H NMR spectrum.

The signals forming the first AB system (δ_H 3.51 and 3.71) belonging to 5-hydroxy-2-pyrazoline **7**. This follows from a comparison with the spectral characteristics obtained for the reaction product of hexafluoroacetylacetone and benzoylhydrazine having the 5-hydroxy-2-pyrazoline structure.[7]

The position of signals forming the second AB system (δ_H 3.58 and 3.69) corresponds to 1,3,4-thiadiazoline heterocycle **8**. This is confirmed by a comparison with the spectral data for the reaction products of thiobenzoylhydrazine with a series of aroyltrifluoroacetones formed by the condensation at the CF_3C=O bond and having the 1,3,4-thiadiazoline structure.[8] A comparison of the intensity of the signals corresponding to 5-hydroxy-2-pyrazoline **7** and 1,3,4-thiadiazoline **8** is 1 : 3 in favor of the latter form.

The intensity of the ^{1}H NMR signals belonging to diastereomeric 3,5-dihydroxypyrazolidines **6b´** and **6b″** decrease in time and that of the signals from 5-hydroxy-2-pyrazoline **7** and 1,3,4-thiadiazoline **8** increases. This process is related to the elimination of water elements and is very slow. The signals from 3,5-dihydroxypyrazolidine **6b´** prevailing in the configurational equilibrium are retained in the ^{1}H NMR spectrum even in three months. At this moment, its fraction in a mixture with derivatives **7** and **8** is about 15%. Note that the ratio of cyclic tautomers **7** and **8** remains almost unchanged in time. This means that the equilibrium between them is established rather rapidly.

The ^{13}C NMR spectrum was recorded for a mixture obtained after the three-month keeping of the initial derivative **6b´**. Taking into account that thiadiazoline **8** is the major component in this mixture, we could rather reliably reveal the signals belonging to this heterocycle (see Experimental). The most characteristic ones are the quartet signals at δ_C 81.23 ($^2J_{C,F}$ = 30.9 Hz) and 186.10 ($^2J_{C,F}$ = 37.9 Hz) corresponding to the carbon atoms in position 2 of the heterocycle and the C=O bond of the trifluoroacetyl group.

The sequence of transformations that occur on storage in a solution of the isolated product of the reaction of hexafluoroacetylacetone with thiobenzoylhydrazine of the dihydroxypyrazolidine structure **6b´** are presented above. Several processes occur simultaneously.

The primary diastereomer of the dihydroxypyrazolidine structure **6b´** is rather rapidly transformed into alternative configurational isomer **6b″**, and these structures are equilibrated. Water elements are simultaneously eliminated from these structures to form 5-hydroxy-2-pyrazoline **7**. In turn, 1,3,4-thiadiazoline heterocycle **8** is formed through the intermediate undetected hydrazone structure. As a result, the ring-ring tautomeric equilibrium involving heterocycles **7** and **8** is established.

After the dihydroxypyrazolidine derivative is kept in boiling toluene for 4 h, 5-trifluoromethyl-2-phenyl-1,3,4-thiadiazole (**9**) was isolated. All processes of transformation of the heterocycles to other heterocycles are accelerated on reflux in toluene. The high temperature favors the irreversible cleavage of 1,3,4-thiadiazoline structure **8** with

the formation of 1,3,4-thiadiazole **9** and trifluoroacetone. As mentioned above, similar cleavage also takes place also for the condensation product of trifluoroacetylacetone with thiobenzoylhydrazine but at ambient temperature.

A comparison of the results obtained by the study of the reaction products of thiobenzoylhydrazine with acetylacetone[5,6,9] and its fluorinated analogs (trifluoro- and hexafluoroacetylacetones) suggests the following.

As mentioned above, the ring-ring equilibrium of two heterocycles is observed for acetylacetone in solutions. The storage of solutions for a sufficiently prolonged time is not accompanied by irreversible changes.

For the trifluoroacetylacetone, the 5-hydroxy-2-pyrazoline structure is considerably more favorable than the 1,3,4-thiadiazoline structure; however, the smallest amounts of this tautomer, which cannot be detected by NMR spectroscopy, result on storage in the decomposition of the condensation product to form 1,3,4-thiadiazole and trifluoroacetone.

Diastereomeric dihydroxypyrazolidine structures are possible for the product with hexafluoroacetylacetone. This is due to an increase in the lifetime of the primary reaction product of 1,3-diketone with polynucleophile (hydroxyhydrazine), where the strong electron-withdrawing trifluoromethyl group prevents the elimination of water elements and allows the intramolecular addition to the second $CF_3C{=}O$ bond to occur. The diastereomeric dihydroxypyrazolidines that formed eliminate water very slowly due to the same electron-acceptor properties of the trifluoromethyl groups. 5-Hydroxy-2-pyrazoline formed experiences, in turn, the reversible tautomeric transition to 2,3-dihydro-1,3,4-thiadiazole, and the ring-ring equilibrium with comparable amounts of two heterocycles is established. This resembles the situation with the acetylacetone derivative.

Thus, the replacement of one methyl group in the 1,3-diketone component for the reaction product with thiobenzoylhydrazine results in the almost complete disappearance of the 5-hydroxy-2-pyrazoline—2,3-dihydro-1,3,4-thiadiazole equilibrium, and the replacement of the second methyl group by the trifluoromethyl group successfully recovers this equilibrium.

Experimental

NMR spectra were recorded on a Bruker DX-300 spectrometer at 300 (^{1}H) and 75 MHz (^{13}C) under the conditions of complete spin-spin proton decoupling. An internal standard was HMDS. The spectra were recorded in DMSO-d_6 and $CDCl_3$. IR spectra were recorded on a Perkin Elmer FT-IR System Spectrum spectrometer (KBr) at 400—4000 cm^{-1}. Mass spectra were measured on an MX 1321 instrument (EI, 70 eV). The reaction course and purity of the synthesized compounds were monitored by TLC on Silufol UV-254 plates (eluent $CHCl_3$). Melting points were determined in a glass capillary. The starting thiobenzoylhydrazine **1** was synthesized using a known procedure.[10] Trifluoroacetylacetone **2** and hexafluoroacetylacetone **3** (Aldrich) were used without additional purification.

[5-Hydroxy-3-methyl-5-(trifluoromethyl)-4,5-dihydro-1*H*-pyrazol-1-yl](phenyl)thioketone (4b). Trifluoroacetylacetone **2** (0.462 g, 3 mmol) was added with stirring to a solution of thiobenzoylhydrazine (0.456 g, 3 mmol) in methylene chloride (5 mL) at 20 °C. The reaction mixture was kept for 20 min, the solvent was evaporated under reduced pressure without heating, and the crystalline residue was washed with cooled methanol and dried *in vacuo*. The yield was 0.58 g (67%), m.p. 41 °C. Found (%): C, 49.84; H, 3.76; N, 9.60. $C_{12}H_{11}F_3N_2OS$. Calculated (%): C, 50.00; H, 3.85; N, 9.72. ^{1}H NMR ($CDCl_3$), δ: 2.86 (s, 3 H, Me); 3.25, 3.41 (both d, 1 H each, H(4), J_{AB} = 18.9 Hz); 7.27—7.50 (m, 5 H, Ar); 8.23 (s, 1 H, OH). ^{13}C NMR ($CDCl_3$), δ: 15.46 (Me); 43.34 (C(4)); 93.35 (q, C(5), $^2J_{C,F}$ = 33.9 Hz); 122.55 (q, CF_3, $^1J_{C,F}$ = 285.2 Hz); 127.72—129.49 (Ar); 157.68 (C(3)); 200.72 (C=S).

2-Methyl-5-phenyl-1,3,4-thiadiazole (5). A solution of 5-hydroxy-3-methyl-1-thiobenzoyl-4,5-dihydro-1*H*-pyrazole **4b** (0.288 g, 1 mmol) in methanol (3 mL) was kept at 20 °C for 1 day, the solvent was evaporated under reduced pressure, and the residue was recrystallized from benzene and dried *in vacuo*. The yield was 0.161 g (67%), m.p. 108 °C (Ref. 11: 108 °C). ^{1}H NMR ($CDCl_3$), δ: 2.82 (s, 3 H, Me); 7.52 (m, 3 H, Ar); 8.02 (m, 2 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 16.16 (Me); 128.25—131.32 (Ar); 165.18 (C(2)); 169.30 (C(5)).

[(3*RS*,5*SR*)-3,5-Dihydroxy-3,5-di(trifluoromethyl)pyrazolidin-1-yl](phenyl)thioketone (6b´). A solution of thiobenzoylhydrazine (0.228 g, 1.5 mmol) in anhydrous dioxane (3 mL) was added dropwise with stirring to a solution of hexafluoroacetylacetone **3** (0.312 g, 1.5 mmol) in anhydrous dioxane (5 mL) at 20 °C. The reaction mixture was kept until the reaction ceased, the solvent was evaporated under reduced pressure without heating, and the crystalline residue was washed with cooled chloroform and dried *in vacuo*. The yield was 0.47 g (87%), m.p. 125—127 °C. Found (%): C, 39.80; H, 2.79; N, 7.54. $C_{12}H_{10}F_6N_2O_2S$. Calculated (%): C, 40.01; H, 2.80; N, 7.78. MS (EI, 70 eV), *m/z* (I_{rel} (%)): 360 $[M]^+$ (3), 342 $[M - H_2O]^+$ (19), 290 (19), 273 $[M - H_2O - CF_3]^+$ (100), 231 $[M - H_2O - CH_2COCF_3]^+$ (53), 177 (50), 136 (16), 121 $[CSPh]^+$ (72), 104 (47), 77 $[Ph]^+$ (69). ^{1}H NMR ($CDCl_3$), δ: 2.61, 2.63 (both d, 1 H each, H(4), J_{AB} = 16.0 Hz); 4.11 (br.s, 1 H, NH); 5.82 (br.s, 1 H, OH); 6.78 (br.s, 1 H, OH); 7.46 (m, 3 H, Ar); 7.65 (m, 2 H, Ar). ^{13}C NMR (DMSO-d_6), δ: 37.87 (C(4)); 81.76 (q, C(3), $^2J_{C,F}$ = 29.9 Hz); 92.50 (q, C(5), $^2J_{C,F}$ = 30.9 Hz); 124.25 (q, CF_3, $^1J_{C,F}$ = 290.2 Hz); 125.55 (q, CF_3, $^1J_{C,F}$ = 285.2 Hz); 127.17—131.32 (Ar); 200.22 (C=S).

[5-Hydroxy-3,5-di(trifluoromethyl)-4,5-dihydro-1*H*-pyrazol-1-yl](phenyl)thioketone (7) was synthesized in a mixture with compounds **6b** and **8** on keeping for 1 day of a solution of the reaction mixture of hexafluoroacetylacetone and thiobenzoylhydrazine in $CDCl_3$. ^{1}H NMR ($CDCl_3$), δ: 3.51, 3.71 (both d, 1 H each, H(4), J_{AB} = 19.6 Hz); 7.37—7.55 (m, 5 H, Ar); 7.83 (s, 1H, OH).

1,1,1-Trifluoro-3-(2-trifluoromethyl-5-phenyl-2,3-dihydro-1,3,4-thiadiazol-2-yl)propan-2-one (8) was synthesized in a mixture of compounds **6b** and **7** on keeping for 1 day of a solution of the reaction mixture of hexafluoroacetylacetone and thiobenzoylhydrazine in $CDCl_3$. ^{1}H NMR ($CDCl_3$), δ: 3.58, 3.69 (both d, 1 H each, CH_2, J_{AB} = 17.4 Hz); 6.86 (br.s, 1 H, NH); 7.42 (m, 3 H, Ar); 7.56 (m, 2 H, Ar). ^{13}C NMR ($CDCl_3$), δ:

41.17 (CH_2); 81.23 (q, C(2), $^2J_{C,F}$ = 30.9 Hz); 115.31 (q, CF_3, $^1J_{C,F}$ = 291.2 Hz); 124.56 (q, CF_3, $^1J_{C,F}$ = 286.2 Hz); 127.41—130.88 (Ar); 160.65 (C(5)); 186.10 (q, $\underline{C}OCF_3$, $^2J_{C,F}$ = = 37.9 Hz).

5-Trifluoromethyl-2-phenyl-1,3,4-thiadiazole (9). A solution of [3,5-dihydroxy-3,5-di(trifluoromethyl)tetrahydro-1*H*-pyrazol-1-yl](phenyl)thioketone **6b** (0.360 g, 1 mmol) in anhydrous toluene (5 mL) was refluxed for 40 h, the solvent was evaporated under reduced pressure, and the residue was recrystallized from hexane and dried *in vacuo*. The yield was 0.191 g (53%), m.p. 92—93 °C. Found (%): C, 46.90; H, 2.09; N, 12.25. $C_9H_5N_2F_3S$. Calculated (%): C, 46.96; H, 2.19; N, 12.17. ^{1}H NMR ($CDCl_3$), δ: 7.52—7.63 (m, 3 H, Ar), 8.03 (d, 2 H, Ar, *J* = 6.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 119.79 (q, CF_3, $^1J_{C,F}$ = 273.2 Hz); 128.75—132.81 (Ar); 157.02 (q, C(5), $^2J_{C,F}$ = 38.9 Hz); 172.28 (C(2)).

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