Synthesis of fluoroalkyl-containing 1,2,3-triketone 2-hetarylhydrazones and their reactions with hydrazines

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Fluoroalkyl-containing 1,2,3-triketone 2-(2,3-dimethyl-5-oxo-1-phenyl-1,2-dihydropyrazol-4-yl)-, 2-(4-ethoxycarbonylpyrazol-3-yl)-, and 2-(1,2,4-triazol-3-yl)hydrazones were synthesized by the azo coupling reactions of fluorinated 1,3-diketones with the corresponding hetaryldiazonium chlorides. The hetarylhydrazones thus synthesized were subjected to cyclocondensation with hydrazines at the 1,3-dicarbonyl fragment to give 3-fluoroalkyl-4-hetarylazopyrazoles.

Key words: fluoroalkyl-containing 1,3-diketones, hetaryldiazonium salts, 1,2,3-triketone 2-hetarylhydrazones, hydrazines, pyrazoles.

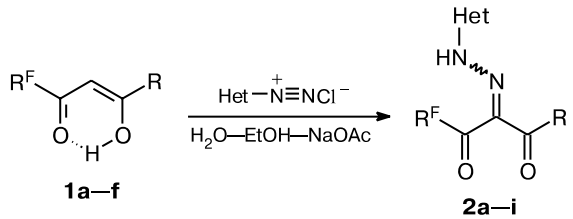
Nonfluorinated 1,3-diketones are involved in azo coupling reactions with diazolyl-[1—3] and triazolyldiazonium[4,5] salts in an aqueous-alcoholic medium in the presence of sodium acetate to form 1,2,3-triketone 2-hetarylhydrazones. The construction of new heterocyclic 1,2,3-triketone hydrazones and investigation of their properties are of interest because of the complex-forming ability of these compounds,[1] their tendency to undergo intramolecular cyclization,[2,4,5] and the possibility of condensation with nucleophilic reagents at the 1,3-dicarbonyl fragment. For fluorine-containing representatives of this class of compounds, only the synthesis of trifluoromethyl- and pentafluoroethyl-substituted 1,2,3-triketone 2-(4-phenyl-1*H*-pyrazol-5-yl)hydrazones was described.[6]

The present study was aimed at synthesizing fluoroalkyl-containing 1,2,3-triketone 2-(2,3-dimethyl-5-oxo-1-phenyl-1,2-dihydropyrazol-4-yl)-, 2-(4-ethoxycarbonylpyrazol-3-yl)-, and 2-(1,2,4-triazol-3-yl)hydrazones and investigating their heterocyclization with hydrazines.

It was found that fluoroalkyl-containing 1,3-diketones **1a—f** are coupled with (2,3-dimethyl-5-oxo-1-phenyl-1,2-dihydropyrazol-4-yl)-, (4-ethoxycarbonylpyrazol-3-yl)-, and (1,2,4-triazolyl-3-yl)diazonium chlorides in the presence of sodium acetate to give 1,2,3-triketone 2-hetarylhydrazones **2a—i** in 38—70% yields (Scheme 1).

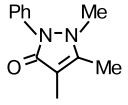
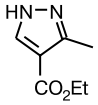
Moderate yields of hetarylhydrazones **2a—i** are attributable to various side reactions with Japp—Klingemann hydrolysis predominating. In the azo coupling reaction of 1,3-diketone **1g** containing the bulky *tert*-butyl substituent, the Japp—Klingemann cleavage becomes the major process, because compound **3** was isolated as the main reaction product. According to the ^{1}H NMR spectroscopic data, the latter exists in a $CDCl_3$ solution as a mixture of hydrazone-ketone (**A**) and azo-enol (**B**) tautomers (Scheme 2).

Scheme 1



1a—f **2a—i**

1: R = Bu, R^F = $H(CF_2)_2$ (**a**);
R = Me, R^F = HCF_2 (**b**), CF_3 (**c**);
R = Ph, R^F = C_3F_7 (**d**), CF_3 (**e**), $H(CF_2)_2$ (**f**)

Compound	Het	R	R^F
2a		Bu	$H(CF_2)_2$
2b		Me	HCF_2
2c		Me	CF_3
2d		Ph	C_3F_7
2e		Me	CF_3
2f		Ph	CF_3
2g		Ph	CF_3
2h		Ph	$H(CF_2)_2$
2i		Ph	C_3F_7

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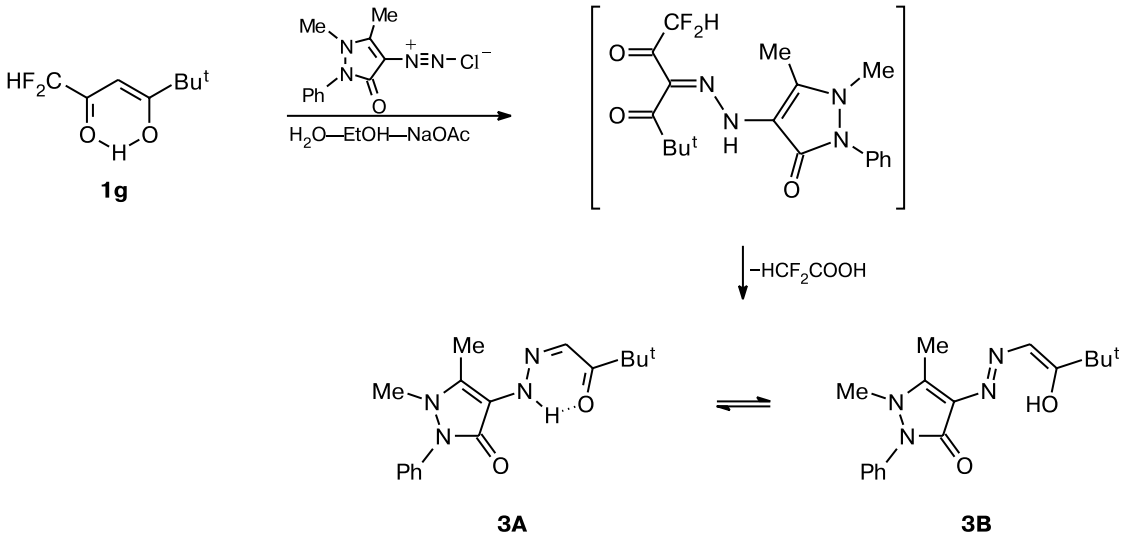
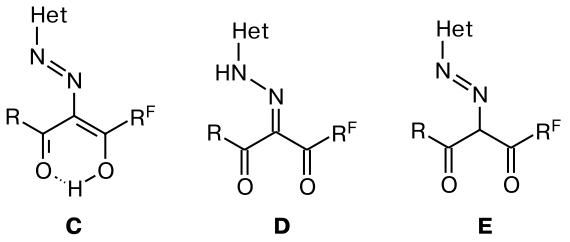
Scheme 2

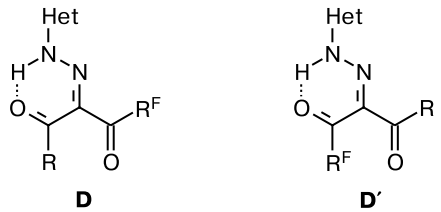


Since both azo-hydrazone and keto-enol tautomerisms are possible for compounds **2a—i**, they can exist as three tautomers (**C**, **D**, and **E**).



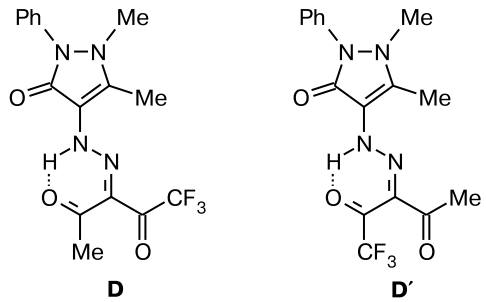
Taking into account that the IR spectra of these compounds show characteristic absorption bands of carbonyl groups at 1650—1700 cm^{-1} and the fact that a signal for the methine proton is absent in the ^1H NMR spectra (see the Experimental section), the hydrazone-diketo form **D** seems to be preferable for these products.

In addition, 1,2,3-triketone 2-hetarylhydrazones **2** are characterized by isomerism associated with the different positions of the hetarylhydrazone substituent with respect to the C=N bond (structures **D** and **D′**).



These isomers are stabilized through an intramolecular hydrogen bond, resulting in a low-frequency shift of absorption bands of the carbonyl groups in the IR spectra and a downfield shift of the signal for the proton of the hydrazone group in the ^1H NMR spectra (see the Experimental section). The presence of one set of signals in the ^1H and ^{19}F NMR spectra of hetarylhydrazones **2a,c,e—i** indicates that these compounds exist as one isomer. The exceptions are hetarylhydrazones **2b,d**, whose NMR spectra have two sets of identical signals.

In our opinion, the structures of isomers cannot unambiguously be judged from the available data. However, we succeeded in establishing the structure of an isomer for one compound. In the ^{13}C NMR spectrum of compound **2c**, the signal of the methyl group at the C=C bond of the antipyrine fragment appears as a quartet (δ_C of C(9) 11.27) with a coupling constant of 1.5 Hz due to spin-spin coupling between the carbon nucleus of this methyl group and the fluorine nuclei of the trifluoromethyl substituent. This is possible only in the case of the isomer **D** (see the Experimental section).



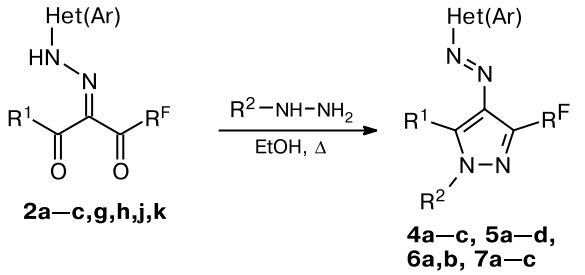
2c

Most likely, other 1,2,3-triketone 2-hetarylhydrazones **2a,e—i** also exist in $CDCl_3$ and DMSO-d_6 solutions as the isomer **D**, whereas 1,2,3-triketone 2-(2,3-dimethyl-5-oxo-1-phenyl-1,2-dihydropyrazol-4-yl)hydrazones

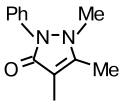
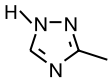
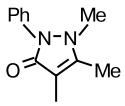
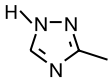
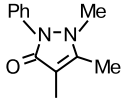
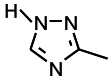
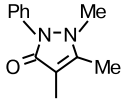
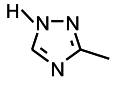
2b,d exist as mixtures of the isomers **D** and **D´**, with the former essentially predominating.

We demonstrated that the above-described 1,2,3-triketone 2-hetarylhydrazones can be used for the construction of new heterocyclic systems. These compounds react with hydrazine hydrate, methylhydrazine, (2-hydroxyethyl)hydrazine, and phenylhydrazine at the 1,3-dicarbonyl fragment to give pyrazole derivatives **4a—c**, **5a,b**, **6a,b**, and **7a—c** in 58—77% yields (Scheme 3). In some cases (see the Experimental section), $BF_3 \cdot Et_2O$ was added as a catalyst.

Scheme 3



2a—c,g,h,j,k → **4a—c, 5a—d, 6a,b, 7a—c**

Compound	Het (Ar)	R^1	R^2	R^F
2j	Ph	Me	—	CF_3
2k	4-MeC_6H_4	Ph	—	CF_3
4a		Me	H	HCF_2
4b		Bu	H	$H(CF_2)_2$
4c		Ph	H	CF_3
5a		Me	Me	CF_3
5b		Ph	Me	CF_3
5c	Ph	Me	Me	CF_3
5d	4-MeC_6H_4	Ph	Me	CF_3
6a		Me	$(CH_2)_2OH$	CF_3
6b		Ph	$(CH_2)_2OH$	$H(CF_2)_2$
7a		Me	Ph	HCF_2
7b		Ph	Ph	CF_3
7c		Ph	Ph	$H(CF_2)_2$

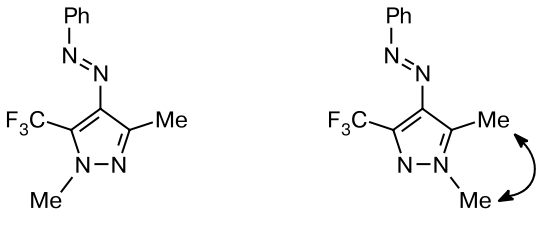
For compounds **4a—c**, azo-hydrazone tautomerism can occur, as opposed to *N*-substituted pyrazoles **5—7** existing in the azo form. However, the same character of absorption bands in the UV spectra of pyrazoles **4c** and **7b** provides evidence in favor of the 4-triazolylazo form of pyrazole **4c** (see the Experimental section). A comparative analysis of the IR and NMR spectroscopic characteristics of pyrazoles **4a—c** led us to the conclusion that these compounds exist in the azo form.

Cyclocondensation of 1,2,3-triketone 2-hetarylhydrazones with substituted hydrazines can afford 3-R^F and 5-R^F regioisomers or their mixtures.

Earlier,[7] we have synthesized pyrazoles from the corresponding fluoroalkyl-containing 1,2,3-triketone 2-arylhydrazones by the reaction with phenylhydrazine. However, the position of the *N*-phenyl substituent in these heterocycles was not determined. To establish the regioisomeric structures of the pyrazoles, we synthesized *N*-methyl-substituted pyrazoles by condensation of trifluoromethyl-containing 1,2,3-triketone 2-arylhydrazones with methylhydrazine (see Scheme 3).

It is known that the ^1H NMR spectrum of 1-methyl-5-trifluoromethylpyrazole derived from 5-trifluoroacetyladamantan-4-one has signals for the protons of the methyl group as a quartet with a coupling constant of 1.2 Hz due to spin-spin coupling with the vicinal trifluoromethyl group,[8] whereas the spin-spin coupling constant in the spectra of 1-methyl-3-trifluoromethylpyrazoles prepared from 2-trifluoroacetylcyclohexanone and 5-trifluoroacetyladamantan-4-one is either equal to 0.6 Hz or is not observed at all.[8,9]

In the ^1H and ^{19}F NMR spectra of trifluoromethyl- and *N*-methyl-substituted pyrazoles **5a,b,d**, the signals of the methyl and trifluoromethyl groups appear as singlets. Only the ^{19}F NMR spectrum of pyrazole **5c** shows a quartet of the trifluoromethyl group with a spin-spin coupling constant of 0.5 Hz (see the Experimental section). In addition, the 2D NOESY spectrum of pyrazole **5c** has a cross-peak between the protons of the *N*-methyl group



5c

and the *C*-methyl protons, which can occur in the 3-R^F isomer.

The results of NMR spectroscopy indicate that pyrazoles **5a—c** have 3-R^F-regioisomeric structures. Heterocycles **6a,b** containing the *N*-(2-hydroxyethyl) substituent exist as 3-R^F regioisomers, because the ^{1}H NMR spectra of these compounds do not show an additional coupling between the methylene protons and the fluorine nuclei.

In the study,[10] the authors reasoned that the regioisomeric structures of pyrazoles can be judged from the chemical shifts of the protons of the *C*-methyl groups in the ^{1}H NMR spectra recorded in $CDCl_3$, because these signals in the spectra of 3-methyl- and 5-methylpyrazoles are observed at δ 2.3 and 2.7, respectively. The ^{1}H NMR spectra of all *C*-methyl-containing pyrazoles synthesized in the present study, which were recorded both in $CDCl_3$ and DMSO-d_6, show signals of the methyl group at δ 2.58—2.63, which indicates that these compounds have 5-Me-regioisomeric structures.

In addition, the regioisomeric structures of these compounds are also evidenced by the position of the signal of the trifluoromethyl group in the ^{19}F NMR spectra. The signal of the trifluoromethyl substituent in the ^{19}F NMR spectra of 4-fluorine-substituted[11] and 4-unsubstituted pyrazoles[12] is observed at δ ~101 (C_6F_6 as the internal standard) and ~105 for the 3-CF_3 and 5-CF_3 isomers, respectively. Pyrazoles **4c**, **5a—d**, **6a**, and **7b** containing the trifluoromethyl substituent are characterized by the chemical shift at δ 99.76—100.27 in $CDCl_3$ and at δ 100.32—102.33 in DMSO-d_6, which corresponds to the 3-CF_3 isomer.

Earlier,[13] it has been found that the signals of the α-CF_2-group in the 3-fluoroalkyl substituent of pyrazoles have a diamagnetic shift relative to 54 ppm (C_6F_6 as the internal standard). Since the chemical shifts of the α-CF_2 group of the polyfluoroalkyl substituents in the spectra of pyrazoles **4a,b**, **6b**, and **7a,c** are 48.02—53.10 ppm (in DMSO-d_6), we studied the structures of the 3-fluoroalkyl derivatives of pyrazoles containing the HCF_2 and $H(CF_2)_2$ substituents.

It is known that the reactions of fluorine-containing enolized 1,3-diketones with hydrazines can afford two regioisomers, whereas 1,3-diketones, which exist predominantly in the diketo form (for example, 1,1,1,3-tetrafluoromethylpentane-2,4-dione), form the 3-CF_3 regioisomer[11] due to the attack of the primary amino group of hydrazine on the more electrophilic carbonyl group, *i.e.*, on the trifluoroacetyl group. 1,2,3-Triketone 2-(het)arylhydrazones **2a—i** synthesized in the present study exist exclusively in the hydrazone-diketo form **D** and, apparently, that is why they react with hydrazines to form exclusively the 3-R^F regioisomers.

Therefore, we established that fluoroalkyl-containing 1,2,3-triketone 2-(het)arylhydrazones undergo regioselective cyclocondensation with hydrazines to give 3-R^F-pyrazoles.

Experimental

The IR spectra were measured on a Perkin Elmer Spectrum One Fourier-transform IR spectrometer in a 4000—400-cm^{-1} region. The NMR spectra were recorded on a Bruker DRX-400 spectrometer (400 MHz for ^{1}H and 100.6 MHz for ^{13}C, relative to $SiMe_4$; 75 MHz for ^{19}F, relative to C_6F_6). The UV spectra were measured on a Shimadzu UV-2401 PC spectrophotometer. Elemental analysis was carried out on a Carlo Erba CHNS-O EA 1108 elemental analyzer.

Synthesis of 1,2,3-triketone 2-hetarylhydrazones (general procedure). Hetaryldiazonium salts were prepared as follows. Hetarylamine (10 mmol) was placed in a two-neck flask equipped with a stirrer and a dropping funnel. Then a dilute hydrochloric acid solution, which was prepared from concentrated HCl (3 mL) and water (10 mL), was added, and a solution of sodium nitrite (0.70 g) in water (3 mL) was slowly added dropwise with vigorous stirring and cooling to 0 °C. In another flask, a solution of sodium acetate (4.55 g) in water (8 mL) was mixed with a solution of 1,3-diketone **1a—g** (10 mmol) in ethanol (31 mL). A solution of the hetaryldiazonium salt was slowly added dropwise to the resulting mixture at 10 °C. At the end of the addition of the salt, precipitation of crystals of hydrazone started. The precipitate was filtered off, recrystallized from ethanol, and dried *in vacuo*.

1,1,2,2-Tetrafluorononane-3,4,5-trione 4-(2,3-dimethyl-5-oxo-1-phenyl-1,2-dihydropyrazol-4-yl)hydrazone (2a). The yield was 50%, m.p. 124—126 °C. IR ($CHCl_3$), ν/cm^{-1}: 3310, 1590 (NH); 1680, 1670 (C=O); 1615, 1520, 1500 (C=N, C=C); 1070—1140 (C—F). ^{1}H NMR ($CDCl_3$), δ: 0.93 (t, 3 H, $(CH_2)_3\underline{Me}$, $^3J_{H,H}$ = 7.5 Hz); 1.38, 1.61, and 2.97 (all m, 2 H each, $(C\underline{H}_2)_3Me$); 2.49 (s, 3 H, Me); 3.19 (s, 3 H, NMe); 6.77 (tt, 1 H, $H(CF_2)_2$, $^2J_{H,F}$ = 53.0 Hz, $^3J_{H,F}$ = 5.8 Hz); 7.36—7.52 (m, 5 H, Ph); 15.44 (s, 1 H, NH). ^{19}F NMR ($CDCl_3$), δ: 24.16 (dt, 2 F, HCF_2, $^2J_{F,H}$ = 53.0 Hz, $^3J_{F,F}$ = 8.0 Hz); 41.42 (m, 2 F, CF_2). Found (%): C, 54.13; H, 5.16; F, 17.17; N, 12.77. $C_{20}H_{22}F_4N_4O_3$. Calculated (%): C, 54.30; H, 5.01; F, 17.18; N, 12.66.

1,1-Difluoropentane-2,3,4-trione 3-(2,3-dimethyl-5-oxo-1-phenyl-1,2-dihydropyrazol-4-yl)hydrazone (2b). The yield was 45%, m.p. 158—160 °C. IR ($CHCl_3$), ν/cm^{-1}: 3445, 1595 (NH); 1700, 1665, 1660 sh (C=O); 1615, 1525, 1490 (C=N, C=C); 1050—1180 (C—F). ^{1}H NMR ($CDCl_3$, δ) of a mixture of isomers **D—D´** (85 : 15); isomer **D**, 2.52 and 2.62 (both s, 3 H each, Me); 3.19 (s, 3 H, NMe); 6.57 (t, 1 H, HCF_2, $^2J_{H,F}$ = 53.0 Hz); 7.27—7.52 (m, 5 H, Ph); 15.05 (s, 1 H, NH); isomer **D´**, 2.43 and 2.59 (both s, 3 H each, Me); 3.20 (s, 3 H, NMe); 6.83 (t, 1 H, HCF_2, $^2J_{H,F}$ = 53.0 Hz); 7.27—7.52 (m, 5 H, Ph); 14.38 (s, 1 H, NH). ^{19}F NMR ($CDCl_3$), δ: isomer **D**, 34.45 (d, HCF_2, $^2J_{F,H}$ = 53.0 Hz); isomer **D´**, 33.21 (d, HCF_2, $^2J_{F,H}$ = 53.0 Hz). Found (%): C, 53.47; H, 4.46; F, 11.14; N, 16.23. $C_{15}H_{16}F_2N_4O_3$. Calculated (%): C, 53.25; H, 4.74; F, 11.23; N, 16.56.

1,1,1-Trifluoropentane-2,3,4-trione 3-(2,3-dimethyl-5-oxo-1-phenyl-1,2-dihydropyrazol-4-yl)hydrazone (2c). The yield was 43%, m.p. 173—175 °C. IR ($CHCl_3$), ν/cm^{-1}: 3450, 1595 (NH); 1695, 1685, 1670 (C=O); 1610, 1525, 1490 (C=N, C=C);

1120—1230 (C—F). ^{1}H NMR ($CDCl_3$), δ: 2.56 and 2.59 (both s, 3 H each, Me); 3.21 (s, 3 H, NMe); 7.35—7.52 (m, 5 H, Ph); 15.34 (s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 11.27 (q, C(9), $J_{C,F}$ = 1.5 Hz); 30.99 (C(1)); 35.60 (C(10)); 113.29—129.53 (C(11), C(12), C(13), C(14), C(15), C(16)); 117.52 (q, C(5), $J_{C,F}$ = 292.4 Hz); 133.79 (C(3)); 144.22 (C(8)); 158.50 (C(7)); 176.45 (q, C(4), $J_{C,F}$ = 32.2 Hz); 196.94 (C(2)); 196.95 (C(6)). ^{19}F NMR ($CDCl_3$), δ: 91.06 (d, CF_3, $^2J_{F,H}$ = 0.7 Hz). Found (%): C, 52.19; H, 3.93; F, 15.51; N, 15.37. $C_{16}H_{15}F_3N_4O_3$. Calculated (%): C, 52.18; H, 4.11; F, 15.47; N, 15.21.

4,4,4,5,5,6,6-Heptafluoro-1-phenylhexane-1,2,3-trione 2-(2,3-dimethyl-5-oxo-1-phenyl-1,2-dihydropyrazol-4-yl)hydrazone (2d). The yield was 38%, m.p. 119—120 °C. IR ($CHCl_3$), ν/cm^{-1}: 3445, 1600 (NH); 1690, 1680 (C=O); 1630, 1610, 1530, 1500 (C=N, C=C); 1125—1240 (C—F). ^{1}H NMR ($CDCl_3$, δ) of a mixture of isomers **D—D´** (90 : 10), isomer **D**, 2.56 (s, 3 H, Me); 3.19 (s, 3 H, NMe); 7.35—7.57 (m, 10 H, 2Ph); 13.87 (s, 1 H, NH); isomer **D´**, 2.59 (s, 3 H, Me); 3.09 (s, 3 H, NMe); 7.35—7.57 (m, 10 H, 2 Ph); 13.94 (s, 1 H, NH). ^{19}F NMR ($CDCl_3$), δ: isomer **D**, 37.37 and 48.88 (both m, 2 F each, CF_2); 81.76 (m, 3 F, CF_3); isomer **D´**, 35.15 and 48.32 (both m, 2 F each, $(CF_2)_2$); 81.32 (m, 3 F, CF_3). Found (%): C, 51.91; H, 3.34; F, 24.84; N, 10.50. $C_{23}H_{17}F_7N_4O_3$. Calculated (%): C, 52.08; H, 3.23; F, 25.07; N, 10.56.

1,1,1-Trifluoropentane-2,3,4-trione 3-(1*H*-4-ethoxycarbonylpyrazol-3-yl)hydrazone (2e). The yield was 66%, m.p. 152—154 °C. IR ($CHCl_3$), ν/cm^{-1}: 3270, 3210 (NH); 1700, 1680 (C=O); 1610, 1560 (C=N, C=C); 1100—1235 (C—F). ^{1}H NMR (DMSO-d_6), δ: 1.30 (t, 3 H, $CO_2CH_2C\underline{H}_3$, J = 7.1 Hz); 2.44 (s, 3 H, MeCO); 4.29 (q, 3 H, $CO_2C\underline{H}_2CH_3$, J = 7.1 Hz); 8.03 (s, 1 H, CH=); 8.94 and 12.74 (both s, 1 H each, 2 NH). ^{19}F NMR (DMSO-d_6), δ: 85.71 (t, CF_3, J = 0.8 Hz). Found (%): C, 41.29; H, 3.53; F, 17.53; N, 17.33. $C_{11}H_{11}F_3N_4O_4$. Calculated (%): C, 41.26; H, 3.46; F, 17.80; N, 17.50.

4,4,4-Trifluoro-1-phenylbutane-1,2,3-trione 2-(1*H*-4-ethoxycarbonylpyrazol-3-yl)hydrazone (2f). The yield was 62%, m.p. 183—185 °C. IR ($CHCl_3$), ν/cm^{-1}: 3250, 3205, 1600 (NH); 1690 (C=O); 1635, 1610 (C=N, C=C); 1145—1245 (C—F). ^{1}H NMR (DMSO-d_6), δ: 1.99 (t, 3 H, $CO_2CH_2C\underline{H}_3$, J = 7.1 Hz); 4.28 (m, 2 H, $CO_2C\underline{H}_2CH_3$, J = 7.1 Hz); 7.53—7.80 (m, 5 H, Ph); 8.07 (s, 1 H, CH=); 9.32 and 12.65 (both s, 1 H each, 2 NH). ^{19}F NMR (DMSO-d_6), δ: 85.84 (s, CF_3). Found (%): C, 50.00; H, 3.38; F, 14.89; N, 14.57. $C_{16}H_{13}F_3N_4O_4$. Calculated (%): C, 49.62; H, 3.38; F, 14.91; N, 14.66.

4,4,4-Trifluoro-1-phenylbutane-1,2,3-trione 2-(1*H*-1,2,4-triazol-3-yl)hydrazone (2g). The yield was 58%, m.p. 225—227 °C. IR (Nujol mulls), ν/cm^{-1}: 3270, 3205, 1590 (NH); 1655 sh, 1650 (C=O); 1600, 1550, 1530 (C=N, C=C); 1100—1200 (C—F). ^{1}H NMR (DMSO-d_6/CCl_4), δ: 7.46—7.82 (m, 5 H, Ph); 7.86 (s, 1 H, CH=); 9.04 and 13.09 (both s, 1 H each, 2 NH). ^{19}F NMR (DMSO-d_6/CCl_4), δ: 84.26 (s, CF_3). Found (%): C, 46.48; H, 2.64; F, 18.04; N, 22.49. $C_{12}H_8F_3N_5O_2$. Calculated (%): C, 46.31; H, 2.59; F, 18.31; N, 22.50.

4,4,5,5-Tetrafluoro-1-phenylpentane-1,2,3-trione 2-(1*H*-1,2,4-triazol-3-yl)hydrazone (2h). The yield was 70%, m.p. 205—206 °C. IR (Nujol mulls), ν/cm^{-1}: 3290, 3190, 1580 (NH); 1650 (C=O); 1600, 1540 (C=N, C=C); 1110—1210 (C—F). ^{1}H NMR (DMSO-d_6/CCl_4), δ: 6.75 (tdd, 1 H, $H(CF_2)_2$, $^2J_{H,F}$ = 53.0 Hz, $^3J_{H,F}$ = 10.0 Hz, $^3J_{H,F}$ = 3.1 Hz); 7.48—7.91 (m, 5 H, Ph); 7.91 (s, 1 H, CH=), 8.97 (d, 1 H, NH, J = 3.1 Hz); 13.09 (s, 1 H, NH). ^{19}F NMR (DMSO-d_6/CCl_4), δ: 27.66 (m, 2 F, CF_2, AB system, Δν = 268.9, $^2J_{F,F}$ = 296.6 Hz); 38.08 (m, 2 F, HCF_2, AB system, Δν = 557.7, $^2J_{F,F}$ = 266.1 Hz, $^2J_{F,H}$ = 53.0 Hz). Found (%): C, 45.41; H, 2.51; F, 22.25; N, 20.33. $C_{13}H_9F_4N_5O_2$. Calculated (%): C, 45.49; H, 2.64; F, 22.14; N, 20.40.

4,4,5,5,6,6,6-Heptafluoro-1-phenylhexane-1,2,3-trione 2-(1*H*-1,2,4-triazol-3-yl)hydrazone (2i). The yield was 61%, m.p. 181—183 °C. IR (Nujol mulls), ν/cm^{-1}: 3250, 3210, 1590 (NH); 1655 sh, 1650 (C=O), 1610, 1550, 1500 (C=N, C=C); 1100—1200 (C—F). ^{1}H NMR (DMSO-d_6/CCl_4), δ: 7.30—7.80 (m, 5 H, Ph); 7.93 (s, 1 H, CH=); 9.20 and 13.23 (both s, 1 H each, 2 NH). Found (%): C, 40.80; H, 1.83; F, 32.18; N, 16.76. $C_{14}H_8F_7N_5O_2$. Calculated (%): C, 40.89; H, 1.96; F, 32.34; N, 17.03.

3,3-Dimethylbutane-1,2-dione 1-(2,3-dimethyl-5-oxo-1-phenyl-3-pyrazolin-4-yl)hydrazone (3). The yield was, 35%, m.p. 164—165 °C. IR ($CHCl_3$), ν/cm^{-1}: 3440, 1590 (NH); 1680 (C=O); 1610, 1550, 1500 (C=N, C=C). ^{1}H NMR ($CDCl_3$, δ) of a mixture of tautomers **A—B** (85 : 15), tautomer **A**, 1.22 (s, 9 H, CMe_3); 2.43 and 2.99 (both s, 3 H each, NMe); 7.19 (s, 1 H, CH=); 7.26—7.47 (m, 5 H, Ph); 13.96 (s, 1 H, NH); tautomer **B**, 1.30 (s, 9 H, CMe_3); 2.44 (s, 3 H, Me); 3.01 (s, 3 H, NMe); 7.19 (s, 1 H, CH=); 7.26—7.47 (m, 5 H, Ph); 7.87 (s, 1 H, OH). Found (%): C, 64.74; H, 7.27; N, 18.30. $C_{17}H_{22}N_4O_2$. Calculated (%): C, 64.95; H, 7.05; N, 17.82.

Reaction of 1,2,3-triketone 2-hydrazones with hydrazines (general procedure). 1,2,3-Triketone hydrazone (3 mmol) was dissolved in ethanol (in isobutanol for **5d**) (30 mL). Then hydrazine (3 mmol) was added, and boron trifluoride etherate (0.5 mL) (for compounds **4b,c**, **5a,c,d,** and **6a**) was added dropwise. The reaction mixture was refluxed for 4 h. The precipitate that formed was filtered off and dried *in vacuo*.

4-(3-Difluoromethyl-5-methyl-1*H*-pyrazol-4-ylazo)-2,3-dimethyl-1-phenyl-1,2-dihydropyrazol-5-one (4a). The yield was 62%, m.p. 219—221 °C (from ethanol). IR (Nujol mulls), ν/cm^{-1}: 3200, 1580 (NH); 1660 (C=O); 1600, 1545, 1490 (C=N, C=C, N=N); 1020—1100 (C—F). ^{1}H NMR (DMSO-d_6), δ: 2.45 and 2.58 (both s, 3 H each, 2 Me); 3.33 (s, 3 H, NMe); 7.10 (t, 1 H, HCF_2, $^2J_{H,F}$ = 53.0 Hz); 7.24—7.57 (m, 5 H, Ph); 13.24 (s, 1 H, NH). ^{19}F NMR (DMSO-d_6), δ: 48.31 (d, HCF_2, $^2J_{F,H}$ = 53.0 Hz). Found (%): C, 55.20; H, 4.56; F, 10.77; N, 24.28. $C_{16}H_{16}F_2N_6O$. Calculated (%): C, 55.49; H, 4.66; F, 10.97; N, 24.27.

4-(5-Butyl-3-tetrafluoroethyl-1*H*-pyrazol-4-ylazo)-2,3-dimethyl-1-phenyl-1,2-dihydropyrazol-5-one (4b). The yield was 69%, m.p. 215—216 °C (reprecipitated from chloroform with hexane). IR (Nujol mulls), ν/cm^{-1}: 3100, 1550 (NH); 1635 (C=O); 1600, 1490 (C=N, C=C, N=N); 1100—1220 (C—F). ^{1}H NMR (DMSO-d_6), δ: 0.93 (t, 3 H, Me, $^3J_{H,H}$ = 7.5 Hz); 1.40, 1.69, and 2.97 (all m, 2 H each, 3 CH_2, $^3J_{H,H}$ = 7.5 Hz); 2.61 (s, 3 H, Me); 3.33 (s, 3 H, NMe); 6.93 (tt, 1 H, $H(CF_2)_2$, $^2J_{H,F}$ = 53.0 Hz, $^3J_{H,F}$ = 5.7 Hz); 7.35—7.52 (m, 5 H, Ph); 10.11 (s, 1 H, NH). ^{19}F NMR (DMSO-d_6), δ: 23.58 (dt, 2 F, HCF_2, $^2J_{F,H}$ = 53.0 Hz, $^3J_{F,F}$ = 9.5 Hz); 48.54 (m, 2 F, CF_2). Found (%): C, 54.51; H, 4.97; F, 17.15; N, 19.29. $C_{20}H_{22}F_4N_6O$. Calculated (%): C, 54.79; H, 5.06; F, 17.33; N, 19.17.

3-(5-Phenyl-3-trifluoromethyl-1*H*-pyrazol-4-ylazo)-1*H*-1,2,4-triazole (4c). The yield was 68%, m.p. 167—168 °C. The product was purified by column chromatography (chloroform as the eluent). IR (Nujol mulls), ν/cm^{-1}: 3110, 1580 (NH); 1480 (C=C, C=N); 1080—1220 (C—F). UV (MeOH), λ_{max}/nm (ε): 206 (10560), 248 (10980), 335 (11980), 436 sh (720). ^{1}H NMR (DMSO-d$_6$/CCl$_4$), δ: 7.47—8.06 (m, 5 H, Ph); 8.52 (s, 1 H, CH=); 14.40 (s, 2 H, 2 NH). ^{19}F NMR (DMSO-d$_6$/CCl$_4$), δ: 100.32 (s, CF_3). Found (%): C, 46.95; H, 3.10; F, 18.36; N, 29.75. $C_{12}H_8F_3N_7$. Calculated (%): C, 46.91; H, 2.62; F, 18.52; N, 31.91.

4-(1,5-Dimethyl-3-trifluoromethylpyrazol-4-ylazo)-2,3-dimethyl-1-phenyl-1,2-dihydropyrazol-5-one (5a). The yield was 67%, m.p. 222—223 °C. The product was purified by column chromatography (chloroform as the eluent). IR (Nujol mulls), ν/cm^{-1}: 1660 (C=O); 1590, 1490 (C=C, C=N, N=N); 1130—1190 (C—F). ^{1}H NMR ($CDCl_3$), δ: 2.57 and 2.62 (both s, 3 H each, 2 Me); 3.32 and 3.84 (both s, 3 H each, 2 NMe); 7.34—7.50 (m, 5 H, Ph). ^{19}F NMR ($CDCl_3$), δ: 99.76 (s, CF_3). Found (%): C, 53.88; H, 4.65; F, 14.52; N, 22.32. $C_{17}H_{17}F_3N_6O$. Calculated (%): C, 53.97; H, 4.53; F, 15.06; N, 22.21.

3-(1-Methyl-5-phenyl-3-trifluoromethylpyrazol-4-ylazo)-1*H*-1,2,4-triazole (5b). The yield was 75%, m.p. 235—236 °C (washed with chloroform). IR (Nujol mulls), ν/cm^{-1}: 3110, 1540 (NH); 1490, 1470 (C=N, C=C, N=N); 1080—1220 (C—F). ^{1}H NMR (DMSO-d$_6$), δ: 3.93 (s, 3 H, NMe); 7.58—7.68 (m, 5 H, Ph); 8.58 (s, 1 H, CH=); 14.57 (br.s, 1 H, NH). ^{19}F NMR (DMSO-d$_6$), δ: 101.53 (s, CF_3). Found (%): C, 48.49; H, 3.42; F, 17.51; N, 30.58. $C_{13}H_{10}F_3N_7$. Calculated (%): C, 48.60; H, 3.14; F, 17.74; N, 30.52.

1,5-Dimethyl-4-phenyl-3-trifluoromethylazopyrazole (5c). The yield was 65%, m.p. 93—95 °C (from ethanol). IR (Nujol mulls), ν/cm^{-1}: 1550, 1500, 1480 (C=N, C=C, N=N); 1120—1200 (C—F). ^{1}H NMR ($CDCl_3$), δ: 2.63 (s, 3 H, Me); 3.89 (s, 3 H, NMe); 7.41—7.85 (m, 5 H, Ph). ^{19}F NMR ($CDCl_3$), δ: 100.27 (q, CF_3, J = 0.5 Hz). Found (%): C, 53.50; H, 4.17; F, 21.00; N, 20.72. $C_{12}H_{11}F_3N_4$. Calculated (%): C, 53.73; H, 4.13; F, 21.25; N, 20.89.

1-Methyl-4-(4-methylphenyl)-5-phenyl-3-trifluoromethylazopyrazole (5d). The yield was 68%, m.p. 89—91 °C (from ethanol). IR (Nujol mulls), ν/cm^{-1}: 1600, 1490, 1475 (C=N, C=C, N=N); 1090—1160 (C—F). ^{1}H NMR ($CDCl_3$), δ: 2.42 (s, 3 H, Me); 3.96 (s, 3 H, NMe); 7.24—7.65 (m, 4 H, C_6H_4); 7.53—7.59 (m, 5 H, Ph). ^{19}F NMR ($CDCl_3$), δ: 99.81 (s, CF_3). Found (%): C, 62.50; H, 4.36; F, 16.50; N, 16.15. $C_{18}H_{15}F_3N_4$. Calculated (%): C, 62.79; H, 4.39; F, 16.27; N, 16.55.

4-[1-(2-Hydroxyethyl)-5-methyl-3-trifluoromethylpyrazol-4-ylazo]-2,3-dimethyl-1-phenyl-1,2-dihydropyrazol-5-one (6a). The yield was 77%, m.p. 218—219 °C (washed with chloroform). IR (Nujol mulls), ν/cm^{-1}: 3330, 3290 (OH); 1640 (C=O); 1540, 1510, 1490 (C=N, C=C, N=N); 1120—1210 (C—F). ^{1}H NMR (DMSO-d$_6$), δ: 2.52 and 2.58 (both s, 3 H each, 2 Me); 3.34 (s, 3 H, NMe); 3.75 (q, 2 H, CH_2, $^3J_{H,H}$ = 5.5 Hz); 4.20 (t, 2 H, CH_2, $^3J_{H,H}$ = 5.5 Hz); 5.00 (t, 1 H, OH, $^3J_{H,H}$ = 5.5 Hz); 7.36—7.57 (m, 5 H, Ph). ^{19}F NMR (DMSO-d$_6$), δ: 102.33 (s, CF_3). Found (%): C, 52.60; H, 4.83; F, 13.98; N, 20.54. $C_{18}H_{19}F_3N_6O_2$. Calculated (%): C, 52.94; H, 4.69; F, 13.96; N, 20.58.

3-[1-(2-Hydroxyethyl)-5-phenyl-3-tetrafluoroethylpyrazol-4-ylazo]-1*H*-1,2,4-triazole (6b). The yield was 58%, m.p. 168—170 °C. The product was purified by column chromatography (chloroform—ethanol, 1 : 50, as the eluent). IR (Nujol mulls), ν/cm^{-1}: 3100, 1550 (NH); 1500, 1480 (C=N, C=C, N=N); 1080—1190 (C—F). ^{1}H NMR (DMSO-d$_6$), δ: 3.82 (q, 2 H, CH_2; $^3J_{H,H}$ = 5.4 Hz); 4.21 (t, 2 H, CH_2; $^3J_{H,H}$ = 5.4 Hz); 5.07 (t, 1 H, OH; $^3J_{H,H}$ = 5.4 Hz); 6.95 (tt, 1 H, H(CF$_2$)$_2$; $^2J_{H,F}$ = 53.0 Hz; $^3J_{H,F}$ = 5.0 Hz); 7.45—7.69 (m, 5 H, Ph); 8.62 (s, 1 H, CH=); 14.53 (s, 1 H, NH). ^{19}F NMR (DMSO-d$_6$), δ: 25.73 (dt, 2 F, HCF_2, $^2J_{F,H}$ = 53.0 Hz, $^3J_{F,F}$ = 10.0 Hz); 48.02 (m, 2 F, CF_2). Found (%): C, 46.76; H, 3.19; F, 19.85; N, 25.22. $C_{15}H_{13}F_4N_7O$. Calculated (%): C, 47.00; H, 3.42; F, 19.83; N, 25.58.

4-(3-Difluoromethyl-5-methyl-1-phenylpyrazol-4-ylazo)-2,3-dimethyl-1-phenyl-1,2-dihydropyrazol-5-one (7a). The yield was 63%, m.p. 225—227 °C (from a 10 : 1 chloroform—hexane mixture). IR (Nujol mulls), ν/cm^{-1}: 1670 (C=O); 1600, 1540, 1500 (C=N, C=C, N=N); 1100—1170 (C—F). ^{1}H NMR (DMSO-d$_6$), δ: 2.45 and 2.63 (both s, 3 H each, 2 Me); 3.39 (s, 3 H, NMe); 7.28 (t, 1 H, HCF_2, $^2J_{H,F}$ = 53.0 Hz); 7.38—7.58 (m, 10 H, 2 Ph). ^{19}F NMR (DMSO-d$_6$), δ: 51.52 (d, HCF_2, $^2J_{F,H}$ = 53.0 Hz). Found (%): C, 61.37; H, 4.90; F, 9.46; N, 20.31. $C_{21}H_{20}F_2N_6O$. Calculated (%): C, 61.46; H, 4.91; F, 9.26; N, 20.48.

3-(1,5-Diphenyl-3-trifluoromethylpyrazol-4-ylazo)-1*H*-1,2,4-triazole (7b). The yield was 71%, m.p. >250 °C (washed with chloroform). IR (Nujol mulls), ν/cm^{-1}: 3100, 1540 (NH); 1585, 1490 (C=N, C=C, N=N); 1120—1180 (C—F). UV (MeOH), λ_{max}/nm (ε): 205 (22600), 255 (10460), 310 (8640), 436 sh (800). ^{1}H NMR (DMSO-d$_6$—CCl$_4$), δ: 7.36—7.46 (m, 10 H, 2 Ph); 8.49 (s, 1 H, CH=); 14.46 (s, 1 H, NH). ^{19}F NMR (DMSO-d$_6$—CCl$_4$), δ: 100.57 (s, CF_3). Found (%): C, 56.44; H, 3.12; F, 14.68; N, 25.77. $C_{18}H_{12}F_3N_7$. Calculated (%): C, 56.40; H, 3.16; F, 14.87; N, 25.58.

3-(1,5-Diphenyl-3-tetrafluoroethylpyrazol-4-ylazo)-1*H*-1,2,4-triazole (7c). The yield was 74%, m.p. 215—217 °C (washed with chloroform). IR (Nujol mulls), ν/cm^{-1}: 3120, 1540 (NH); 1590, 1500 (C=N, C=C, N=N); 1100—1220 (C—F). ^{1}H NMR (DMSO-d$_6$), δ: 7.05 (tt, 1 H, H(CF$_2$)$_2$, $^2J_{H,F}$ = 53.0 Hz, $^3J_{H,F}$ = 5.5 Hz); 7.43—7.90 (m, 10 H, 2 Ph); 8.72 (s, 1 H, CH=); 14.72 (s, 1 H, NH). ^{19}F NMR (DMSO-d$_6$), δ: 26.52 (dt, 2 F, HCF_2, $^2J_{F,H}$ = 53.0 Hz, $^3J_{F,F}$ = 10.0 Hz); 53.10 (m, 2 F, CF_2, $^3J_{F,H}$ = 5.5 Hz, $^3J_{F,F}$ = 10.0 Hz). Found (%): C, 54.79; H, 3.31; F, 18.80; N, 24.40. $C_{19}H_{13}F_4N_7$. Calculated (%): C, 54.94; H, 3.15; F, 18.30; N, 23.61.

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