Reaction of 2-polyfluoroacylcyclohexanones with semicarbazides

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2-Polyfluoroacylcyclohexanones react with semicarbazide and thiosemicarbazide to give 2-(thio)carbamoyl-3-hydroxy-3-polyfluoroalkyl-3,3a,4,5,6,7-hexahydro-2*H*-indazoles, one of which was studied by X-ray diffraction.

Key words: polyfluoroalkyl-containing 1,3-diketones, semicarbazide, thiosemicarbazide, polyfluoroalkyl-containing indazoles.

Reactions of fluorinated 1,3-diketones containing cyclic fragments with polynucleophilic reagents are of considerable interest both from the theoretical point of view and for the synthesis of new heterocyclic compounds endowed with useful properties.[1,2] So far, semicarbazide and its derivatives have not been involved in this reaction; therefore, we studied reactions of diketones (**1a—f**) with thiosemicarbazide (**2a**) and semicarbazide (**2b**) in the framework of systematic investigations of the properties of 2-polyfluoroacylcyclohexanones.[3,4] The reactions of semicarbazide and its derivatives with nonfluorinated 1,3-diketones (including symmetrical ones) are of rather complicated character[5,6] and yield mono- and bis-semicarbazones, 5-hydroxy-2-pyrazolines, 5-semicarbazido-2-pyrazolines, and pyrazoles. The direction of the reactions depends in a complex manner on the nature of diketone and semicarbazide, the reagent ratio, and the reaction conditions.

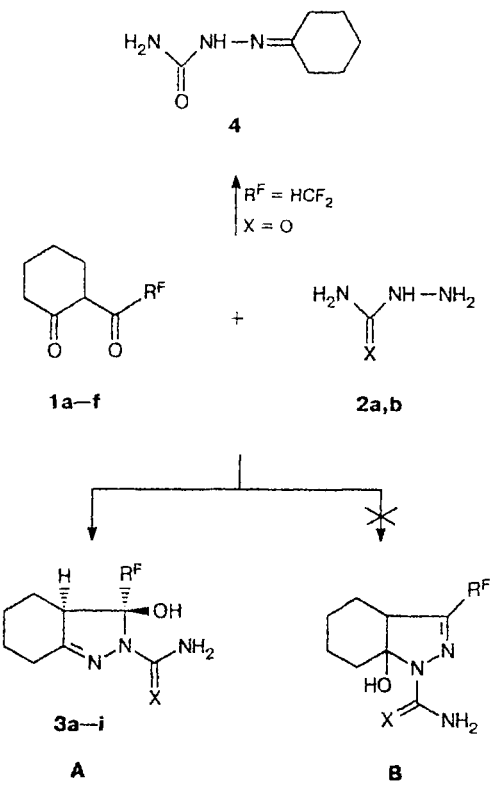
We found that the reactions of 2-polyfluoroacylcyclohexanones **1a—f** with compounds **2a** and **2b** yield hydroxypyrazolines (**3a—i**) as the sole reaction products (Tables 1 and 2). Depending on the site of the initial attack, isomeric structures **A** and **B** can be ascribed to the products (Scheme 1).

The X-ray diffraction data obtained for compound **3e** (Fig. 1, Tables 3—5) allowed us to choose between the alternative structures **A** and **B**.

The cyclohexane ring has the chair conformation with the C(2) and C(5) atoms deviating by 0.62 and −0.65 Å, respectively, from the plane of the other ring atoms. The conformation of the pyrazoline ring is a strongly flattened envelope with the C(1) atom deviating by 0.08 Å out of the plane of the other ring atoms.

The hydroxy group at C(1) occupies a pseudoequatorial position (the torsion angle O(1)—C(1)—C(2)—C(7) −127.9(2)°). The perfluorohexyl substituent at C(1) is

Scheme 1



	1a, 3a	**1b, 3b, 3g**	**1c, 3c**
R^F	HCF_2	CF_3	$H(CF_2)_2$
	1d, 3d	**1e, 3e, 3h**	**1f, 3f, 3i**
R^F	n-C_4F_9	n-C_6F_{13}	n-C_8F_{17}
	2a, 3a—f	**2b, 3g—i**	
X	S	O	

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Table 1. Properties of 3(*R**),3a(*S**),4,5,6,7-hexahydro-2*H*-indazoles (**3a—i**)

Compound	R^F	X	M.p./°C (solvent)	Found / Calculated (%)					Molecular formula	Yield (%)
				C	H	F	N	S		
3a	HCF_2	S	77—78 (*n*-hexane)	43.31 / 43.36	5.18 / 5.27	15.00 / 15.24	16.71 / 16.86	12.65 / 12.86	$C_9H_{13}F_2N_3OS$	51
3b	CF_3	S	95—96 (*n*-hexane—$CHCl_3$, 5 : 1)	40.76 / 40.44	4.72 / 4.53	20.72 / 21.32	15.58 / 15.72	11.67 / 12.00	$C_9H_{12}F_3N_3OS$	50
3c	$H(CF_2)_2$	S	92—93 (*n*-heptane)	40.24 / 40.13	4.65 / 4.38	25.93 / 25.39	13.89 / 14.04	10.58 / 10.71	$C_{10}H_{13}F_4N_3OS$	68
3d	*n*-C_4F_9	S	127—128 (light petroleum—*o*-xylene, 2 : 1)	34.30 / 34.54	2.85 / 2.90	40.76 / 40.98	10.01 / 10.07	7.73 / 7.68	$C_{12}H_{12}F_9N_3OS$	75
3e	*n*-C_6F_{13}	S	124 (*n*-hexane—*o*-xylene, 1 : 1)	32.59 / 32.51	2.16 / 2.34	47.85 / 47.74	8.04 / 8.12	—	$C_{14}H_{12}F_{13}N_3OS$	76
3f	*n*-C_8F_{17}	S	135—136 (*n*-hexane—toluene, 1 : 1)	31.31 / 31.13	1.70 / 1.96	52.47 / 52.32	6.96 / 6.81	5.01 / 5.19	$C_{16}H_{12}F_{17}N_3OS$	54
3g	CF_3	O	187—188 (benzene)	42.98 / 43.03	4.79 / 4.82	22.69 / 22.69	16.64 / 16.73	—	$C_9H_{12}F_3N_3O_2$	40
3h	*n*-C_6F_{13}	O	142—143 (*n*-hexane—$CHCl_3$, 1 : 1)	33.48 / 33.55	2.61 / 2.41	49.45 / 49.27	8.34 / 8.38	—	$C_{14}H_{12}F_{13}N_3O_2$	44
3i	*n*-C_8F_{17}	O	134—135 (*n*-heptane)	31.96 / 31.96	2.14 / 2.01	53.69 / 53.71	6.68 / 6.99	—	$C_{16}H_{12}F_{17}N_3O_2$	30

Table 2. Spectral characteristics of 3(*R**),3a(*S**),4,5,6,7-hexahydro-2*H*-indazoles (**3a—i**)

Compound	R^F	X	IR (Vaseline oil), ν/cm^{-1}			^{1}H NMR ($CDCl_3$), δ (*J*/Hz)				
			«Amide II»	«Amide I»	NH, OH	$(CH_2)_4$ (m, 8 H)	CH (m, 1 H)	NH_2 (2 H)	R^F	OH (s, 1 H)
3a	HCF_2	S	—	—	3140, 3270, 3430	1.26—2.73	3.19—3.35	6.54—6.84 (m)	7.02 (dd, 1 H, J_{H,CF_a} = 57.51, J_{H,CF_b} = 56.34)	7.1 (br.s.)
3b	CF_3	S	—	—	3180, 3270, 3430	1.39—2.73	3.08—3.25	6.7, 7.2 (both br.s.)	—	7.93
3c	$H(CF_2)_2$	S	—	—	3195, 3310, 3445	1.49—2.60	3.11—3.45	8.07, 8.62 (both br.s.)	6.81 (tt, 1 H, $^2J_{H,F}$ = 51.65, $^3J_{H,F}$ = 6.81)	8.42
3d	*n*-C_4F_9	S	—	—	3150, 3300, 3405	1.26—2.73	3.12—3.28	6.4, 7.2 (both br.s.)	—	8.22
3e[a]	*n*-C_6F_{13}	S	—	—	3290, 3450	1.47—2.65	3.30—3.48	8.16, 8.72 (both br.s.)	—	8.89
3f	*n*-C_8F_{17}	S	—	—	3290, 3450	1.27—2.60	3.11—3.28	6.2, 7.2 (both br.s.)	—	8.22
3g	CF_3	O	1630	1670	3340, 3470	1.42—2.59	2.98—3.15	5.6 (br.s.)	—	6.22
3h	*n*-C_6F_{13}	O	1635	1655	3200, 3270, 3330, 3465	1.26—2.58	3.05—3.20	5.5 (br.s.)	—	6.55
3i[b]	*n*-C_8F_{17}	O	1635	1660	3200, 3265, 3330, 3460	1.24—2.98	3.15—3.39	6.39 (br.s.)	—	7.25 (br.s.)

[a] The ^{1}H NMR spectrum was recorded in DMSO-d_6. [b] The ^{1}H NMR spectrum was recorded in acetone-d_6 with HMDS as the internal standard.

pseudoaxial (the torsion angle C(9)—C(1)—C(2)—C(7) 108.1(2)°) and has the transoid conformation (the torsion angles are as follows: C(1)—C(9)—C(10)—C(11) 157.6(2)°, C(9)—C(10)—C(11)—C(12) 162.7(2)°, C(10)—C(11)—C(12)—C(13) 162.6(2)°, and C(11)—C(12)—C(13)—C(14) 170.5(2)°). The bond angles C(2)—C(1)—C(9) 111.3(2)° and F(9a)—C(9)—C(1) 111.5(2)° are larger than the angles N(2)—C(1)—C(9) 106.7(2)° and F(9b)—C(9)—C(1) 108.0(2)°, which is probably due to the shortened intramolecular contacts H(2)...F(9b) 2.42 Å (the sum of the van der Waals radii is 2.56 Å [7]) and C(8)...F(9a) 3.00 Å (3.11 Å).

The thiocarbamoyl substituent is rotated relative to the plane of the pyrazoline ring (the torsion angle

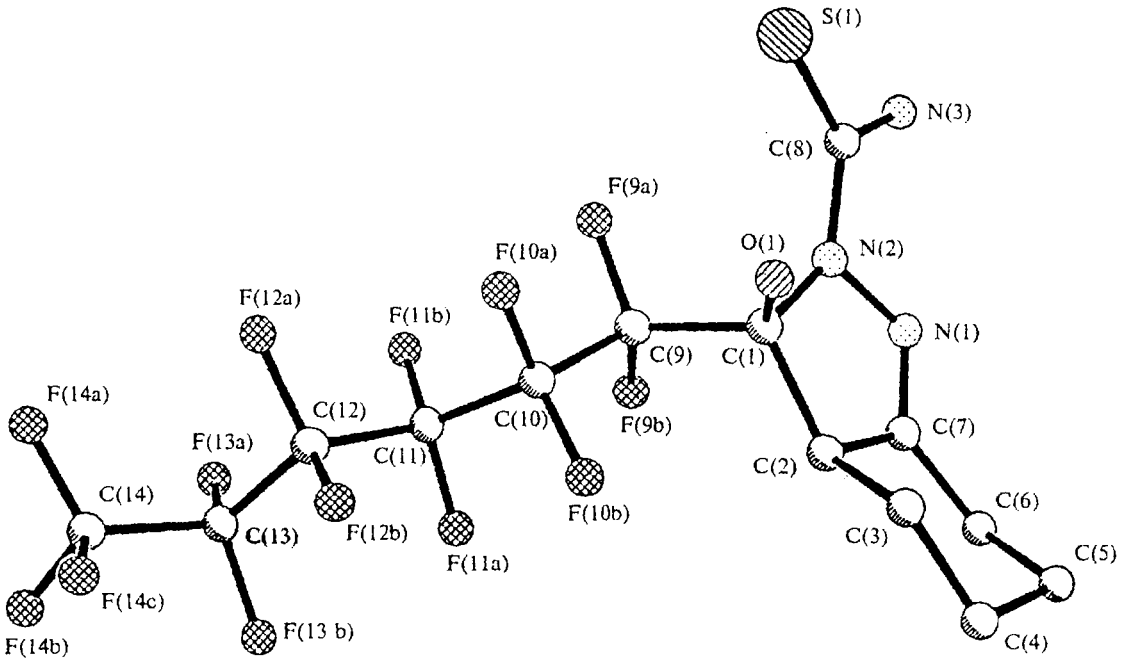

Fig. 1. The general view of molecule **3e**.

N(3)—C(8)—N(2)—N(1) 16.9(2)°) and forms weak intramolecular hydrogen bonds S(1)...H(10) (S...H 2.30 Å (3.00 Å), S...H—O 139(1)°) and N(1)...H(3Nb) (N...H 2.27 Å (2.66 Å), N...H—N 104(1)°).

The crystalline molecules form dimers owing to shortened intermolecular contacts S(1)...H(3Na) ($-x$, $1-y$, $-z$), 2.65 Å.

Taking into account the X-ray diffraction data, which prove structure **A** for compound **3e**, and the fact that the spectral characteristics of all compounds **3a—i** are virtually identical (see Table 2), one may conclude that these compounds exist in the form of regioisomer **A**.

The reaction of 1,3-diketone **1a** with semicarbazide **2b** proceeds abnormally to give cyclohexanone semicarbazone (**4**), which may be a result of ketonic splitting of **1a**.

In contrast to the products of the reaction of 2-polyfluoroacylcycloalkanones with 4-chlorophenylhydrazine,[2] which undergo *in situ* dehydration to give the corresponding pyrazoles, the 2-(thio)carbamoyl-3-hydroxy-3-polyfluoroalkyl-3,3a,4,5,6,7-hexahydro-2*H*-indazoles **3** obtained are resistant to dehydration under treatment with conc. H_2SO_4 or P_2O_5.

In addition, 2*H*-indazoles **3a—i**, unlike 5-hydroxy-2-pyrazolines obtained by the reaction of monoacylhydrazines with acyclic (including polyfluoroalkyl-containing) 1,3-diketones,[8—10] do not undergo ring-chain tautomeric transformation into acyclic oxo(thio)semicarbazones. This conclusion is confirmed by the IR spectra of compounds **3a—f** (no absorption band characteristic of the keto group at 1600—1750 cm^{-1}) and by the ^1H NMR spectra of compounds **3a—i** recorded in $CDCl_3$, DMSO-d_6, and acetone-d_6 (only one set of signals) (see Table 2).

This reaction is not only regiospecific; it also proceeds stereoselectively, which results in predominant formation of only one pair of enantiomers (of two possible pairs). X-ray diffraction data showed that the configurations of the chiral centers of the molecules of this pair are *R,S* and *S,R*. The presence of only one set of signals in the ^1H NMR spectra of compounds **3a—i** suggests that the content of the other pair of enantiomers (*R,R* and *S,S*) in the reaction products is low and, for example, does not exceed 3% for **3b**, which is evidenced by the ratio of the integral intensity of ^{19}F signals for the fluorine atoms of two different

Table 3. Bond lengths (*d*) in structure **3e**

Bond	*d*/Å	Bond	*d*/Å
S(1)—C(8)	1.696(3)	C(9)—C(10)	1.547(3)
O(1)—C(1)	1.381(3)	C(10)—F(10a)	1.341(3)
C(1)—N(2)	1.484(3)	C(10)—F(10b)	1.344(3)
C(1)—C(2)	1.543(3)	C(10)—C(11)	1.557(3)
C(1)—C(9)	1.568(3)	C(11)—F(11b)	1.328(3)
N(1)—C(7)	1.275(3)	C(11)—F(11a)	1.353(3)
N(1)—N(2)	1.418(3)	C(11)—C(12)	1.549(3)
N(2)—C(8)	1.361(3)	C(12)—F(12b)	1.333(3)
C(2)—C(7)	1.500(3)	C(12)—F(12a)	1.339(3)
C(2)—C(3)	1.526(4)	C(12)—C(13)	1.549(4)
N(3)—C(8)	1.309(3)	C(13)—F(13b)	1.338(3)
C(3)—C(4)	1.534(4)	C(13)—F(13a)	1.334(3)
C(4)—C(5)	1.509(5)	C(13)—C(14)	1.544(4)
C(5)—C(6)	1.526(5)	C(14)—F(14a)	1.298(4)
C(6)—C(7)	1.496(4)	C(14)—F(14c)	1.305(4)
C(9)—F(9a)	1.337(3)	C(14)—F(14b)	1.320(4)
C(9)—F(9b)	1.360(3)		

Table 4. Bond angles (ω) in structure **3e**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
O(1)—C(1)—N(2)	114.5(2)	N(3)—C(8)—N(2)	115.8(2)	C(12)—C(11)—C(10)	115.2(2)
O(1)—C(1)—C(2)	112.0(2)	N(3)—C(8)—S(1)	121.4(2)	F(12b)—C(12)—F(12a)	108.4(2)
N(2)—C(1)—C(2)	101.7(2)	N(2)—C(8)—S(1)	122.8(2)	F(12b)—C(12)—C(13)	108.4(2)
O(1)—C(1)—C(9)	110.3(2)	F(9a)—C(9)—F(9b)	106.5(2)	F(12a)—C(12)—C(13)	108.3(2)
N(2)—C(1)—C(9)	106.7(2)	F(9a)—C(9)—C(10)	107.0(2)	F(12b)—C(12)—C(11)	109.8(2)
C(2)—C(1)—C(9)	111.3(2)	F(9b)—C(9)—C(10)	108.5(2)	F(12a)—C(12)—C(11)	107.9(2)
C(7)—N(1)—N(2)	107.4(2)	F(9a)—C(9)—C(1)	111.5(2)	C(13)—C(12)—C(11)	113.9(2)
C(8)—N(2)—N(1)	117.2(2)	F(9b)—C(9)—C(1)	108.0(2)	F(13b)—C(13)—F(13a)	108.9(2)
C(8)—N(2)—C(1)	128.4(2)	C(10)—C(9)—C(1)	115.0(2)	F(13b)—C(13)—C(14)	106.4(2)
N(1)—N(2)—C(1)	112.6(2)	F(10a)—C(10)—F(10b)	107.9(2)	F(13a)—C(13)—C(14)	107.7(2)
C(7)—C(2)—C(3)	109.4(2)	F(10a)—C(10)—C(9)	108.9(2)	F(13b)—C(13)—C(12)	109.2(2)
C(7)—C(2)—C(1)	102.5(2)	F(10b)—C(10)—C(9)	110.3(2)	F(13a)—C(13)—C(12)	108.9(2)
C(3)—C(2)—C(1)	116.8(2)	F(10a)—C(10)—C(11)	107.9(2)	C(14)—C(13)—C(12)	115.6(2)
C(2)—C(3)—C(4)	109.3(3)	F(10b)—C(10)—C(11)	107.8(2)	F(14a)—C(14)—F(14c)	109.4(3)
C(5)—C(4)—C(3)	112.3(3)	C(9)—C(10)—C(11)	113.9(2)	F(14a)—C(14)—F(14b)	108.2(2)
C(4)—C(5)—C(6)	111.4(3)	F(11b)—C(11)—F(11a)	108.4(2)	F(14c)—C(14)—F(14b)	107.6(3)
C(7)—C(6)—C(5)	108.4(3)	F(11b)—C(11)—C(12)	108.5(2)	F(14a)—C(14)—C(13)	112.1(3)
N(1)—C(7)—C(6)	124.0(2)	F(11a)—C(11)—C(12)	108.0(2)	F(14c)—C(14)—C(13)	111.0(2)
N(1)—C(7)—C(2)	115.6(2)	F(11b)—C(11)—C(10)	109.1(2)	F(14b)—C(14)—C(13)	108.3(3)
C(6)—C(7)—C(2)	119.8(2)	F(11a)—C(11)—C(10)	107.4(2)		

Table 5. The coordinates of nonhydrogen ($\times 10^4$) and hydrogen ($\times 10^3$) atoms and equivalent isotropic thermal parameters ($Å^2 \times 10^3$) in structure **3e**

Atom	*x*	*y*	*z*	U_{eq}	Atom	*x*	*y*	*z*	U_{eq}
S(1)	2558(1)	4861(1)	786(1)	49(1)	C(12)	7908(4)	2801(3)	4556(2)	42(1)
O(1)	6156(2)	2560(2)	1269(1)	40(1)	F(12b)	9621(2)	2399(2)	4131(1)	56(1)
C(1)	4977(3)	1735(3)	1844(1)	34(1)	F(12a)	7409(3)	4310(2)	4397(1)	65(1)
N(1)	2578(3)	504(2)	1518(1)	44(1)	C(13)	8111(4)	2225(3)	5572(2)	51(1)
N(2)	3030(3)	1909(2)	1531(1)	39(1)	F(13b)	8899(3)	748(2)	5729(1)	72(1)
C(2)	5764(4)	19(3)	1942(2)	41(1)	F(13a)	6361(3)	2439(3)	5994(1)	79(1)
N(3)	211(3)	3012(4)	894(2)	58(1)	C(14)	9388(4)	2981(4)	5998(2)	59(1)
C(3)	7484(4)	−483(3)	1313(2)	56(1)	F(14c)	11112(3)	2861(3)	5595(1)	92(1)
C(4)	7780(5)	−2186(4)	1360(3)	70(1)	F(14b)	9580(3)	2270(3)	6836(1)	93(1)
C(5)	6026(5)	−2611(4)	1106(3)	67(1)	F(14a)	8630(4)	4393(3)	5992(2)	102(1)
C(6)	4252(5)	−2148(4)	1717(2)	62(1)	H(10)	5614(29)	3456(26)	1056(13)	33(5)
C(7)	4055(4)	−524(3)	1752(2)	44(1)	H(2)	6152(35)	−418(29)	2515(18)	39(6)
C(8)	1880(3)	3175(3)	1089(2)	40(1)	H(3Nb)	−150(52)	2190(44)	1064(23)	71(10)
C(9)	4666(3)	2215(3)	2774(2)	38(1)	H(3Na)	−449(49)	3710(38)	576(22)	58(9)
F(9b)	3856(2)	1173(2)	3366(1)	53(1)	H(3b)	8708(55)	−229(38)	1459(22)	75(10)
F(9a)	3421(2)	3538(2)	2745(1)	56(1)	H(3a)	7166(44)	106(35)	668(22)	61(9)
C(10)	6520(3)	2354(3)	3153(2)	38(1)	H(4b)	8817(56)	−2430(41)	924(24)	77(10)
F(10b)	8020(2)	1284(2)	2947(1)	51(1)	H(4a)	8050(58)	−2792(45)	1994(27)	87(11)
F(10a)	6927(2)	3703(2)	2778(1)	54(1)	H(5b)	6127(53)	−3677(48)	1147(24)	81(10)
C(11)	6361(3)	2211(3)	4184(2)	42(1)	H(5a)	5702(58)	−2214(47)	573(29)	81(12)
F(11b)	4627(2)	2948(2)	4433(1)	64(1)	H(6b)	2950(73)	−2252(54)	1500(31)	115(15)
F(11a)	6533(3)	729(2)	4557(1)	61(1)	H(6a)	4472(58)	−2765(47)	2307(27)	92(12)

diastereomers. Note that this ratio remains unchanged in the ^{19}F NMR spectrum recorded 72 h after preparation of the solution of **3b** in $CDCl_3$, *viz.*, the predominant pair of enantiomers is stable, whereas in nonfluorinated 4-alkyl-5-hydroxy-2-pyrazolines, which also bear two chiral centers, the content of the other diastereomer is increased with time because of the tautomeric conversion into the acyclic form followed by recyclization.[9]

The ^1H NMR spectra of compounds **3b—f** exhibit three one-proton singlets at δ 6.20—8.89. With the aim of unambiguous assignment of these signals to the resonance absorption of the thiocarbamoyl and hydroxyl protons, we studied the ^1H NMR spectral pattern of compound **3e** in this region at different temperatures (Table 6). Coalescence of two high-field signals into a broad singlet with elevation of temperature allows one to identify these signals as those for the protons of the $CSNH_2$ group, while a third, low-field, signal was assigned to the hydroxyl proton.

Table 6. The dependence of the positions of the OH and $CSNH_2$ signals in the ^1H NMR spectra (DMSO-d_6) of compound **3e** on temperature

T/°C	δ ^1H	
	$CSNH_2$ (br.s, 2 H)	OH (br.s, 1 H)
50	8.16, 8.72 (each 1 H)	8.89
80	8.29	8.83
100	8.18	8.79
130	8.01	8.63

Experimental

IR spectra were recorded on a Specord 75-IR spectrophotometer. ^1H and ^{19}F NMR spectra were recorded on a Tesla BS-567A spectrometer (100 and 75.3 MHz, respectively) with Me_4Si and C_6F_6 as the internal standards.

1,3-Diketones **1a—f** were obtained by the condensation of cyclohexanone and the corresponding methyl polyfluorocarboxylates according to the known procedure.[11] The characteristics of **1a**,[1] **1b**,[12] and **1e,f** [13] agree with the data published earlier.

2-(2,2,3,3-Tetrafluoropropionyl)cyclohexanone (1c). Yield 69%, colorless liquid, b.p. 88—89 °C (10 Torr). Found (%): C, 47.94; H, 4.52; F, 33.78. $C_9H_{10}F_4O_2$. Calculated (%): C, 47.79; H, 4.46; F, 33.60. IR (thin film), ν/cm^{-1}: 1570 (C=O); 2400—3500 (OH). ^1H NMR ($CDCl_3$), δ: 1.62—1.72 (m, 4 H, 2 CH_2); 2.40—2.52 (m, 4 H, 2 CH_2); 6.19 (tt, 1 H, HCF_2, $^2J_{H-F}$ = 52.58 Hz, $^3J_{H-F}$ = 5.40 Hz); 15.34 (br.s, 1 H, OH).

2-Perfluoropentanoylcyclohexanone (1d). Yield 65%, colorless liquid, b.p. 84—85 °C (6 Torr). Found (%): C, 38.42; H, 2.73; F, 49.93. $C_{11}H_9F_9O_2$. Calculated (%): C, 38.38; H, 2.64; F, 49.68. IR (thin film), ν/cm^{-1}: 1595 (C=O); 2420—3490 (OH). ^1H NMR ($CDCl_3$), δ: 1.53—1.71 (m, 4 H, 2 CH_2); 2.47—2.56 (m, 4 H, 2 CH_2); 15.25 (br.s, 1 H, OH).

General procedure for the synthesis of 2*H*-indazoles (3a—i). A mixture of 1,3-diketone **1** and semicarbazide **2** (1 mol-equiv.) (for **3g—i**, a mixture of **1**, hydrochloride of **2b** (1 mol-equiv.), and Et_3N (1 mol-equiv.)) was refluxed in propan-2-ol for 12 h, and the reaction mixture was poured into 100 mL of water. Then, compounds **3a—i** were obtained as follows.

Compounds 3a,b were extracted with $CHCl_3$, and the combined extracts were dried with $MgSO_4$. The solvent was removed, and the residue was chromatographed on a column with SiO_2 in $CHCl_3$. The first yellow fraction was collected, the solvent removed, and the residue recrystallized.

Compounds 3c—f,h,i. The precipitate that formed was filtered off, washed with 20 mL of cold water, and recrystallized.

Compounds 3g were extracted with $CHCl_3$, and the combined extracts were dried with $MgSO_4$. The solvent was removed, and the residue recrystallized.

^{19}F NMR of **3b** ($CDCl_3$), δ: 81.31 (s, 3 F, CF_3); 85.67 (s, 1/14 F, 1/42 CF_3).

Reaction of 1a with 2b. A mixture of **1a** (2.64 g, 15 mmol), hydrochloride of **2b** (1.67 g, 15 mmol), and Et_3N (2.02 g, 20 mmol) was refluxed in propan-2-ol for 10 h. The reaction mixture was poured into 150 mL of water, and the products were extracted with $CHCl_3$. The combined extracts were dried with $MgSO_4$, and the solvent was removed. The residue was recrystallized from toluene to give colorless crystals of semicarbazone **4** (1.2 g, 50%), whose characteristics correspond to the literature data.[14]

X-ray diffraction analysis of compound 3e. The crystals of **3e** are triclinic, a = 7.131(2) Å, b = 9.288(3) Å, c = 15.395(3) Å, α = 77.32(2)°, β = 83.50(2)°, γ = 76.78(2)°, V = 996.3(4) Å^3 (20 °C), d_{calc} = 1.778 g cm^{-3}, space group $P\bar{1}$, Z = 2.

The parameters of the unit cell and the intensity values of 3550 independent reflections (R_{int} = 0.023) were measured on an automatic Siemens P3/PC diffractometer (Mo-Kα radiation, graphite monochromator, θ/2θ scanning mode, $2\theta_{max}$ = 60°).

The structure was solved by the direct method with the SHELXTL PLUS program system.[15] The hydrogen atoms were located by the difference synthesis of electron density. The full-matrix least-squares F^2-refinement was performed in the anisotropic (isotropic for the hydrogen atoms) approximation from 3150 reflections. Final residuals are wR_2 = 0.110 (R_1 = 0.042 from 2498 reflections with $F > 4\sigma(F)$), S = 1.21. The atomic coordinates are listed in Table 5.

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