frequencies, the absorption of complex I was subtracted from the total absorption of the solutions with different concentrations of Ind:

$$D^{\nu}_{\mathrm{Ind\cdot HCl}} = \varepsilon^{\nu}_{\mathrm{Ind\cdot HCl}} \cdot l_{\nu} \cdot C_{\mathrm{Ind\cdot HCl}} = D_{\nu} - \varepsilon^{\nu}_{\mathrm{I}} \cdot l_{\nu} \cdot C_{\mathrm{I}}. \quad (4)$$

The CA is absent in pure DMF. The $\varepsilon^{\nu}_{\mathrm{I}} \cdot l_{\nu}$ coefficients were measured in the HCl—DMF system. The concentrations of complex I in Eq. (4) were determined from Eq. (3). The coefficients of CA of the ionized form of the indicator were obtained from the linear dependences of $D^{\nu}_{\mathrm{Ind\cdot HCl}}$ on C°_{Ind}.

The spectra of the ionized form of Ind and the complexes of HCl with DMF (I and II) at $\nu > 1900$ cm^{-1} differ substantially in the 1900—2740 cm^{-1} frequency range (Fig. 3). At lower frequencies, CA in the IR spectrum of the Ind · HCl species is almost absent.

Thus, during the equilibrium ionization of the indicator in the HCl—DMF system, species are formed, whose IR spectrum contains intense CA at $\nu > 1900$ cm^{-1}. The presence[1,9] of CA in the spectra of the Ind · HCl complexes indicates that a species with the strong quasi-symmetrical H bond (N...H...Cl) is formed during the substitution of the DMF molecule in the DMF · HCl complex by the Ind molecule.

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Reactions of 2-polyfluoroalkylchromones with aliphatic diamines

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2-Polyfluoroalkylchromones react with aliphatic 1,2-diamines to give 2,3-dihydro-1*H*-1,4-diazepines. A similar reaction with 1,3-diaminopropane yields *N,N'*-trimethylenebis(2-hydroxyacetophenonimines) as a result of scission of the original chromones.

Key words: 2-polyfluoroalkylchromones, aliphatic diamines; 2,3-dihydro-1*H*-1,4-diazepines, *N,N'*-trimethylenebis(2-hydroxyacetophenonimines).

It is known[1—3] that chromones, when treated with ammonia or primary amines, undergo opening to give the corresponding enamino ketones. Reactions with ethylenediamine are ambiguous and, depending on the reaction conditions, yield either *N,N'*-ethylenebisenamino ketones or mixtures of 2,3-dihydro-1,4-diazepines with *N,N'*-ethyleneiminoenamino ketones and *N,N'*-ethylenebis(2-hydroxyacetophenonimines) resulting from chromone scission.[4]

We found that, unlike nonfluorinated analogs, 2-polyfluoroalkylchromones (**1a—l**), obtained by condensation of the corresponding 2-hydroxyacetophenones with alkyl polyfluorocarboxylates,[5] react with ethylenediamine in an ethanolic solution at room temperature to give only 5-aryl-7-polyfluoroalkyl-2,3-dihydro-1*H*-1,4-diazepines (**2a—l**) (Scheme 1). In the absence of a solvent, chromone **1l** gives a mixture of diazepine **2l** with *N,N'*-ethylenebis(2-hydroxy-5-chloroacetophe-

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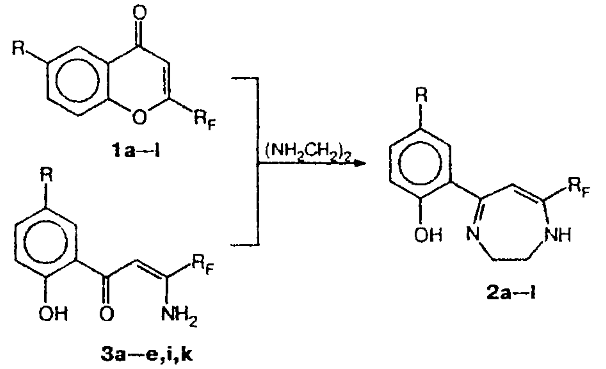
Scheme 1



	R	R_F		R	R_F
a	H	CF_3	**g**	MeO	$(CF_2)_2H$
b	Me	CF_3	**h**	Cl	$(CF_2)_2H$
c	MeO	CF_3	**i**	H	CF_2H
d	Cl	CF_3	**j**	Me	CF_2H
e	H	$(CF_2)_2H$	**k**	MeO	CF_2H
f	Me	$(CF_2)_2H$	**l**	Cl	CF_2H

Scheme 2

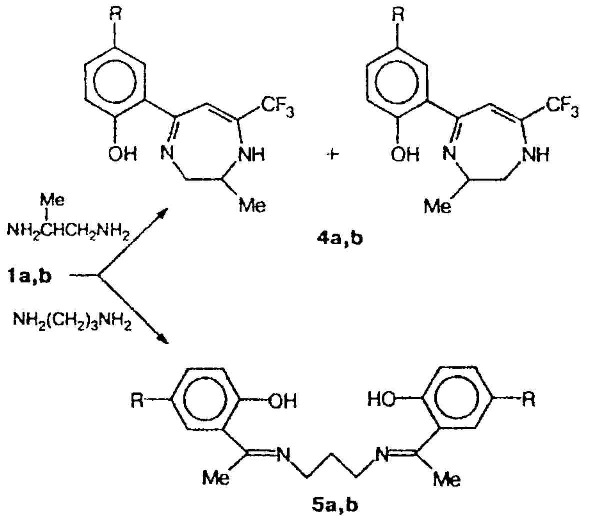


Table 1. Main characteristics of 2,3-dihydro-1*H*-1,4-diazepines **2f—h,j,l** and **4a,b**

Compound	Yield (%)	M.p./°C	Found/Calculated (%) C	H	N	Molecular formula	^1H NMR, δ (*J*/Hz)	IR, ν/cm^{-1}
2f	80	152—153	55.71 55.63	4.51 4.67	9.24 9.27	$C_{14}H_{14}F_4N_2O$	2.29 (s, 3 H, Me); 3.63 (m, 2 H, CH_2); 4.08 (m, 2 H, CH_2); 5.2 (br.s, 1 H, NH); 5.80 (s, 1 H, =CH); 5.92 (tt, 1 H, CF_2CF_2H, $^2J_{H,F}$ = 53.6, $^3J_{H,F}$ = 3.4); 6.82 (d, 1 H, H(3), ^3J = 8.3); 7.10 (dd, 1 H, H(4), ^4J = 1.7); 7.31 (d, 1 H, H(6))	3250, 1630, 1610, 1530
2g	80	157—158	52.71 52.83	4.46 4.43	8.76 8.80	$C_{14}H_{14}F_4N_2O_2$	3.60 (m, 2 H, CH_2); 3.78 (s, 3 H, MeO); 4.09 (m, 2 H, CH_2); 5.2 (br.s, 1 H, NH); 5.74 (s, 1 H, =CH); 5.92 (tt, 1 H, CF_2CF_2H, $^2J_{H,F}$ = 53.8, $^3J_{H,F}$ = 3.3); 6.88—6.91 (m, 2 H, H(3), H(4)); 7.09 (br.s, 1 H, H(6))	3250, 1635, 1535
2h	91	193—194	48.32 48.39	3.42 3.44	8.58 8.68	$C_{13}H_{11}ClF_4N_2O$	3.64 (m, 2 H, CH_2); 4.08 (m, 2 H, CH_2); 5.3 (br.s, 1 H, NH); 5.71 (s, 1 H, =CH); 5.94 (tt, 1 H, CF_2CF_2H, $^2J_{H,F}$ = 53.7, $^3J_{H,F}$ = 3.2); 6.86 (d, 1 H, H(3), ^3J = 8.9); 7.21 (dd, 1 H, H(4), ^4J = 2.5); 7.49 (d, 1 H, H(6)); 16.2 (br.s, 1 H, OH)	3230, 1620, 1515
2j	88	182—183	59.66 59.76	5.76 5.79	10.53 10.72	$C_{13}H_{14}F_2N_2O \cdot 0.5\ H_2O$	2.28 (s, 3 H, Me); 3.61 (m, 2 H, CH_2); 4.07 (m, 2 H, CH_2); 5.2 (br.s, 1 H, NH); 5.65 (s, 1 H, =CH); 6.19 (t, 1 H, CF_2H, $^2J_{H,F}$ = 55.2); 6.82 (d, 1 H, H(3), ^3J = 8.5); 7.09 (dd, 1 H, H(4), ^4J = 1.9); 7.33 (d, 1 H, H(6))	3390, 3230, 1630, 1530
2l	77	225—226	52.61 52.86	4.14 4.07	10.05 10.27	$C_{12}H_{11}ClF_2N_2O$	3.65 (m, 2 H, CH_2); 4.06 (m, 2 H, CH_2); 5.4 (br.s, 1 H, NH); 5.56 (s, 1 H, =CH); 6.21 (t, 1 H, CF_2H, $^2J_{H,F}$ = 55.2); 6.85 (d, 1 H, H(3), ^3J = 9.0); 7.22 (dd, 1 H, H(4), ^4J = 2.5); 7.52 (d, 1 H, H(6))	3350, 3240, 1630, 1530

(*to be continued*)

Table 1. (*continued*)

Compound	Yield (%)	M.p./°C	Found/Calculated (%)			Molecular formula	^{1}H NMR, δ (*J*/Hz)	IR, ν/cm^{-1}
			C	H	N			
4a	75	152—153	57.57 57.78	4.74 4.85	10.27 10.37	$C_{13}H_{13}F_3N_2O$	1.31 and 1.52 (both d, 3 H, Me, *J* = 6.2, *J* = 7.0); 3.15—4.13 (m, 3 H, CH_2CH); 5.3 (br.s, 1 H, NH); 5.97 (s, 1 H, =CH); 6.64—7.61 (m, 4 H, C_6H_4)	3210, 1635, 1620, 1540
4b	76	138—139	58.97 59.15	5.43 5.32	9.77 9.85	$C_{14}H_{15}F_3N_2O$	1.32 and 1.53 (both d, 3 H, Me, *J* = 6.2, *J* = 6.8); 3.17—4.17 (m, 3 H, CH_2CH); 5.1 (br.s, 1 H, NH); 5.96 (s, 1 H, =CH); 6.82 (d, 1 H, H(3), ^3J = 8.3); 7.12 (dd, 1 H, H(4), ^4J = 1.6); 7.33 (br.s, 1 H, H(6))	3210, 1635, 1530

nonimine). Diazepines **2a—e,i,k** have been obtained by us earlier[6] by the reaction of ethylenediamine with aryl β-amino-β-polyfluoroalkylvinyl ketones (**3a—e,i,k**).

As expected, reactions of chromones **1a,b** with 1,2-diaminopropane yield a 1:1 mixture of regioisomeric dihydrodiazepines (**4a,b**), while the action of 1,3-diaminopropane results in scission of chromones **1a,b** to give 2-hydroxy- and 2-hydroxy-5-methylacetophenones. The latter further react with 1,3-diaminopropane to give the corresponding Schiff's bases (**5a,b**) (Scheme 2).

Thus, the reaction of 2-polyfluoroalkylchromones with ethylenediamine is a simple and convenient method for the synthesis of fluorine-containing 5-(2-hydroxyaryl)-2,3-dihydro-1*H*-1,4-diazepines.

Experimental

IR spectra were recorded on an IKS-29 instrument (Vaseline oil). ^{1}H NMR spectra were recorded on a Tesla BS-567A spectrometer (100 MHz) in $CDCl_3$ with tetramethylsilane as the internal standard.

5-Aryl-7-polyfluoroalkyl-2,3-dihydro-1*H*-1,4-diazepines (2a—l, 4a,b). 1,2-Diamine (6 mmol) was added to a solution of chromone **1** (2 mmol) in 10 mL of EtOH. The reaction mixture was kept at ~20 °C for 3 h. Then water (20 mL) was added, and the orange precipitate that formed was filtered off and recrystallized from EtOH or benzene.

Diazepines **2a—e,i,k** are identical with those described earlier.[6] The yields, melting points, elemental compositions, and IR and ^{1}H NMR spectral data for compounds **2f—h,j,l** and **4a,b** are given in Table 1.

***N,N'*-Trimethylenebis(2-hydroxyacetophenonimine) (5a)** was obtained from chromone **1a** and 1,3-diaminopropane under similar conditions, yield 69%, m.p. 124—125 °C. Found (%): C, 73.52; H, 7.07; N, 8.91. $C_{19}H_{22}N_2O_2$. Calculated (%): C, 73.52; H, 7.14; N, 9.03. IR, ν/cm^{-1}: 1620 (C=N); 1575, 1500 (benzene ring). ^{1}H NMR, δ: 2.21 (quint, 2 H, CH_2, *J* = 6.5 Hz); 2.33 (s, 6 H, 2 Me); 3.73 (t, 4 H, 2 H_2N, *J* = 6.5 Hz); 6.75 (td, 1 H, H(5), ^3J = 8.0 Hz, ^4J = 1.5 Hz); 6.90 (dd, 1 H, H(3)); 7.29 (td, 1 H, H(4)); 7.50 (dd, 1 H, H(6)); 16.2 (br.s, 1 H, OH).

***N,N'*-Trimethylenebis(2-hydroxy-5-methylacetophenonimine) (5b).** Yield 85%, m.p. 113—114 °C. Found (%): C, 74.40; H, 7.82; N, 8.42. $C_{21}H_{26}N_2O_2$. Calculated (%): C, 4.53; H, 7.74; N, 8.28. IR, ν/cm^{-1}: 1625 (C=N); 1610, 1595, 1510 (benzene ring). ^{1}H NMR, δ: 2.28 (quint, 2 H, CH_2, *J* = 6.5 Hz); 2.28 (s, 6 H, 2 MeAr); 2.32 (s, 6 H, 2 Me); 3.72 (t, 4 H, 2 CH_2N, *J* = 6.5 Hz); 6.81 (d, 1 H, H(3), ^3J = 8.4 Hz); 7.10 (dd, 1 H, H(4), ^4J = 1.9 Hz); 7.29 (d, 1 H, H(6)).

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