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Reactions of Alkyl 1*H*,1*H*-Perfluoroalkyl Sulfones with Ammonia, Amines, and Hydrazines

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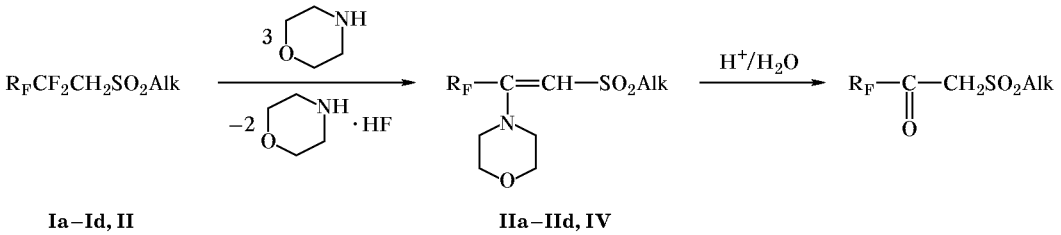
Abstract—2,2,3,3-Tetrafluoropropyl and 2,2,3,3,4,4,5,5-octafluoropentyl alkyl sulfones react with ammonia, primary and secondary amines, hydrazine hydrate, phenylhydrazine, and *N*,*N*-dimethylhydrazine to afford, depending on the length of the polyfluoroalkyl chain and reaction conditions, the corresponding enamines, imines, or mono- and bis-hydrazones. The bis-hydrazone obtained from phenylhydrazine and 2,2,3,3,4,4,5,5-octafluoropentyl benzyl sulfone is capable of undergoing further dehydrofluorination to give 5-difluoromethyl- or 5-unsubstituted 1-phenylpyrazole.

We previously reported on the reactions of 2,2,3,3-tetrafluoropropyl- and 2,2,3,3,4,4,5,5-octafluoropentyl alkyl sulfones **Ia**, **Id**, and **II** with morpholine, which resulted in formation of enamines **IIIa**, **IIId**, and **IV**, respectively. These products can be used in the synthesis of fluorinated ketones [1] (Scheme 1). The ease and preparative simplicity of the above reactions prompted us to study reactions of sulfones **I** and **II** with amino compounds in more detail. Primarily, we intended to elucidate the effect on the product yield of such factors as the nature of the amino compound and the length of the polyfluoroalkyl chain.

Obviously, the first stage of the reaction of amines with sulfones **I** and **II** is dehydrofluorination leading to polyfluoroalkenyl sulfones **V** and **VI** (Scheme 2). The dehydrofluorination is reversible. For example, the ^{19}F NMR spectrum of the reaction mixture obtained from compound **II** and triethylamine in benzene, regardless of the amount of triethylamine, reaction time, and temperature (from 20 to 80°C), contained signals of alkenyl fluoride **VI** and initial sulfone at a molar ratio of 1.5:1. We succeeded in displacing the equilibrium to the right and isolating alkenyl fluorides **V** and **VI** in 60 and 87% yield, respectively, when triethylamine hydrofluoride was removed from the reaction mixture by adding water.

Alkenyl fluoride **V** is formed as a mixture of *cis* and *trans* isomers at a ratio of 1:5 (Tables 1, 2). The isomers are thermally stable, and they can be distilled under reduced pressure at 150°C without decomposition. Alkenyl fluoride **VI** is formed only as *trans* isomer [2]. The equilibrium can also be displaced by removing alkenyl fluoride from the mixture via reaction with ammonia or primary or secondary amines. Treatment of sulfones **Ic** and **II** with excess ammonia yields enamines **VIIa** and **VIIb** (Scheme 3).

Scheme 1.



Ia–Id, II **IIa–IId, IV**

I, **III**, R_F = HCF_2, Alk = CH_2Ph (**a**), C_3H_7 (**b**), C_4H_9 (**c**), C_5H_{11} (**d**); **II**, **IV**, R_F = $H(CF_2)_3$, Alk = CH_2Ph.

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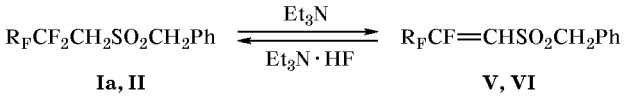
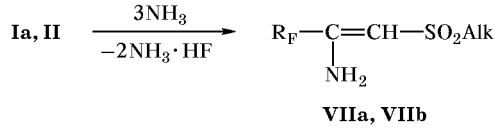
Scheme 2.



V, R_F = HCF_2; **VI**, R_F = $H(CF_2)_3$.

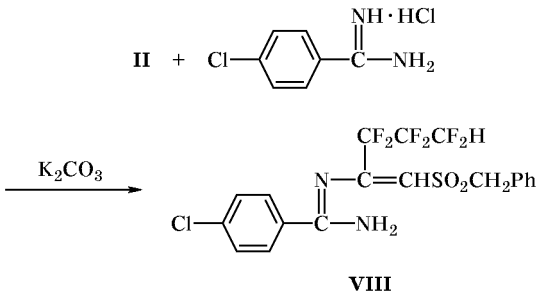
Scheme 3.



VII, R_F = HCF_2, Alk = C_4H_9 (**a**); RF = $H(CF_2)_3$, Alk = CH_2Ph (**b**).

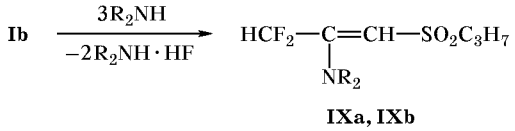
Compounds **VIIa** and **VIIb** are crystalline substances. The presence of only one set of signals in the ^1H and ^{19}F NMR spectra of both reaction mixtures and isolated products suggests that the latter are formed as a single isomer. Only one isomer, enamine **VIII**, was also obtained by reaction of sulfone **II** with *p*-chlorobenzamidine.

Scheme 4.



On the other hand, the reactions of sulfone **Ib** with dimethyl- and dipentylamine gave enamines **IXa** and **IXb** (Scheme 5) as mixtures of two isomers with respect to the double bond, one isomer prevailing (presumably, thermodynamically more stable one). The ^{19}F NMR spectra of the reaction mixtures obtained from sulfone **Ib** and dimethylamine or dipentylamine, recorded by the end of the process, contained signals from two isomers at a ratio of 4 : 1 or 2.5 : 1, respectively. The major isomers were isolated in the pure state.

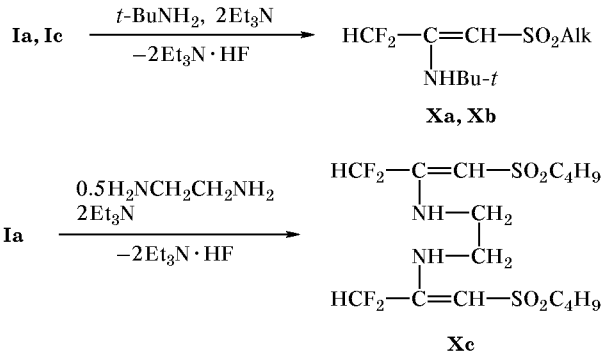
Scheme 5.



IX, R = Me (**a**), C_5H_{11} (**b**).

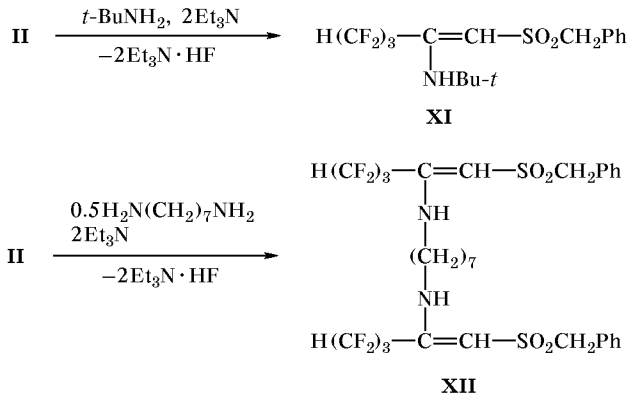
The effect of the length of the polyfluoroalkyl chain is clearly observed in the reactions of sulfones **I** and **II** with primary amines. Short-chain sulfones **Ia** and **Ic** react with alkylamines to form enamines **Xa**–**Xc** (Scheme 6), whereas analogous reactions of sulfone **II** lead to formation of Schiff bases **XI** and **XII** [2] (Scheme 7).

Scheme 6.



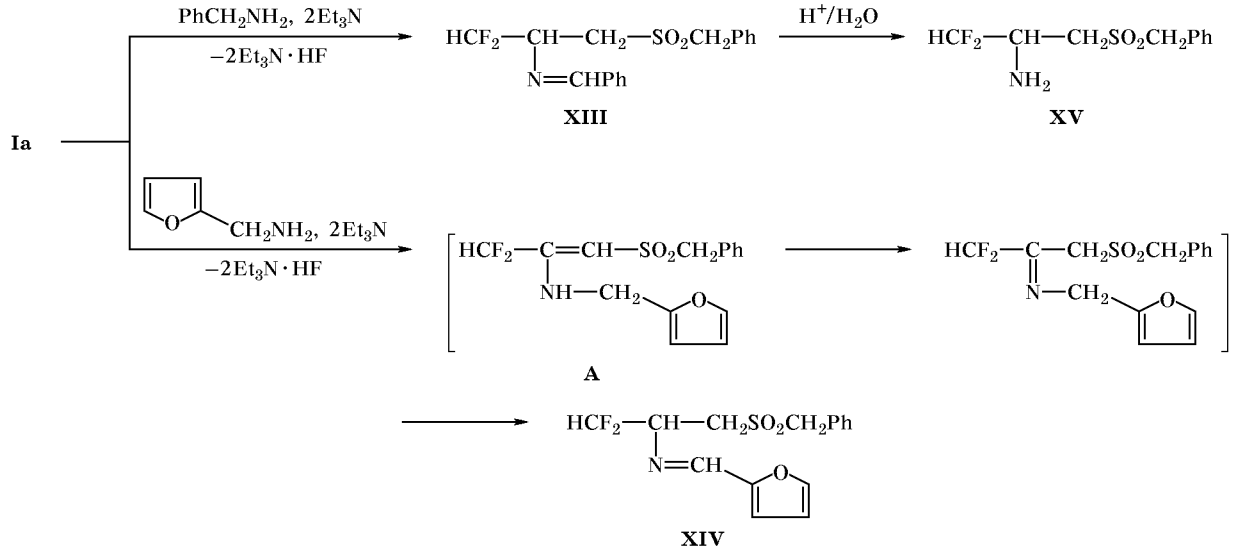
X, Alk = C_4H_9 (**a**), CH_2Ph (**b**).

Scheme 7.



Enamines **Xa**–**Xc** are formed as a single isomer. According to published data [3], the spin–spin coupling constant $^4J_{HF}$ for the *trans* isomer containing a F−C−C=C−H fragment is about 2 Hz; the corresponding coupling constant for the *cis* isomer is equal to zero. Thus compounds **Xa** and **Xb** have *trans* structure, for the coupling constant $^4J_{HF}$ is equal to 1.8 Hz. Unfortunately, $^4J_{HF}$ values for compounds **VII**, **IX**, and **Xc** range from 0.5 to 1 Hz, so that we cannot determine their geometric structure with certainty.

Scheme 8.



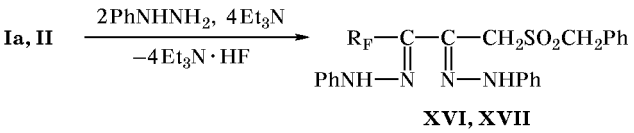
The strong effect of the polyfluoroalkyl chain length on the structure of final products may be explained by increase of electron-acceptor power of the substituent in going from HCF_2 to R_FCF_2 [4]. However, this factor is likely to be not the only one determining formation of enamines or imines as final products. As shown below using the reactions with hydrazines as examples, imino compounds can also be obtained from sulfone **Ia** having a short polyfluoroalkyl chain.

Another essential factor is the amine nature. The reactions of sulfone **Ia** with benzylamine and 2-furfurylamine gave *N*-benzylidene- and *N*-furfurylideneamines **XIII** and **XIV**, presumably as a result of a series of prototropic rearrangements (Scheme 8, cf. [5]). This assumption is indirectly supported by the ^{19}F NMR spectrum of the reaction mixture obtained from sulfone **Ia** and 2-furfurylamine. Initially, the spectrum contained two signals at δ_F –121.24 and –134.56 ppm, which (by analogy with the ^{19}F NMR spectra of enamines **IX** and **X**) could be assigned to *Z* and *E* isomers of intermediate **A**. After 24 h (room temperature), these signals disappeared, and those belonging to the final product appeared. A similar pattern was observed in the ^{19}F NMR spectrum of the reaction mixture obtained from **Ia** and benzylamine. Hydrolysis of compound **XIII** with dilute hydrochloric acid yields fluorinated primary amine **XV**.

The result of reactions of sulfones **I** and **II** with hydrazines essentially depends on the hydrazine nature and reaction conditions. It is known that in reactions with phenylhydrazine difluoromethylene groups of polyfluorinated aldehydes or ketones can be converted into phenylhydrazono groups [6, 7]. Analogous successive dehydrofluorination processes can also occur in reactions of **I** and **II** with hydrazines.

Sulfones **I** and **II** reacted with excess phenylhydrazine to afford mixtures of products from which we failed to isolate individual compounds as analytically pure samples. When the reaction was performed in the presence of triethylamine (molar ratio sulfone : phenylhydrazine : triethylamine 1 : 2 : 4) we obtained the corresponding bis-hydrazones **XVI** and **XVII** in 73 and 12% yield, respectively (Scheme 9).

Scheme 9.

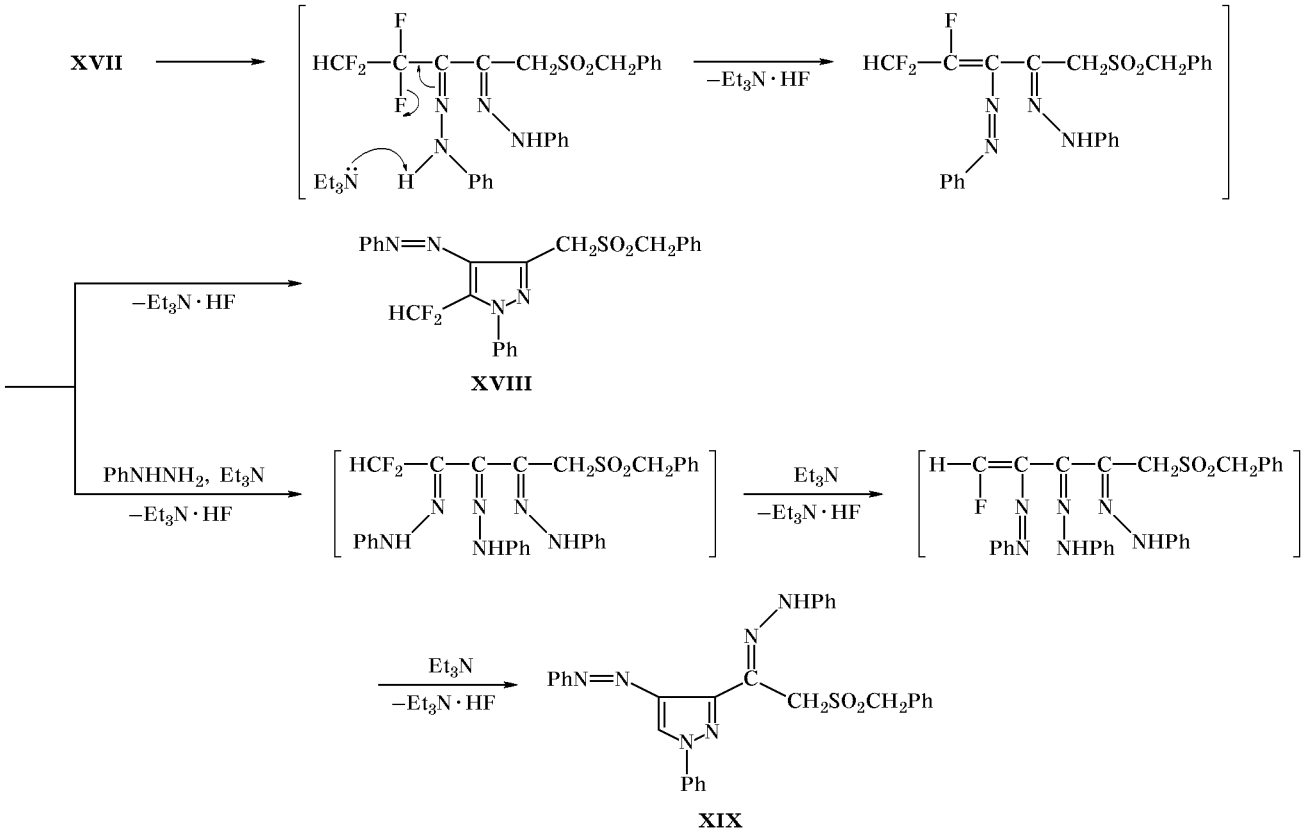


XVI, R_F = H; **XVII**, R_F = HCF_2CF_2.

A probable reason for the low yield of **XVII** is that the product contains a tetrafluoroethyl group which gives rise to further reaction with phenylhydrazine in the presence of triethylamine through a series of consecutive processes like those described in [6]. Depending on the reactant ratio, pyrazoles **XVIII** or **XIX** are formed (Scheme 10). From the preparative viewpoint, it is convenient to obtain compounds **XVIII** and **XIX** directly from sulfone **II**, without isolation of bis-hydrazone **XVII** (the optimal reactant ratio is given in Experimental).

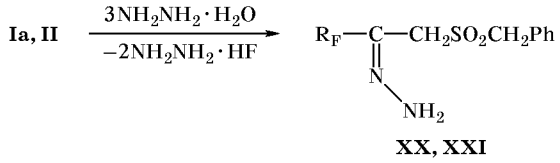
By reactions of sulfones **Ia** and **II** with excess hydrazine hydrate in the absence of triethylamine we

Scheme 10.



obtained monohydrazones **XX** and **XXI** in 74–78% yield (Scheme 11).

Scheme 11.

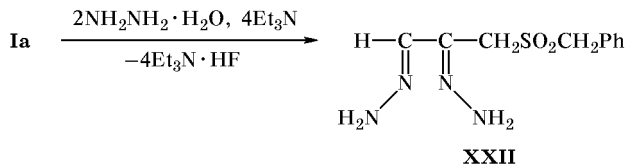


XX, XXI

XX, R_F = HCF_2; **XXI**, R_F = $H(CF_2)_3$.

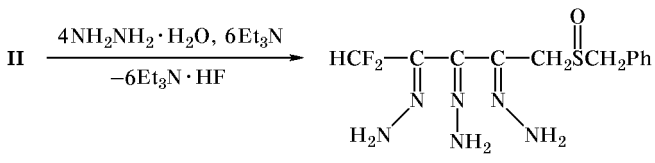
The result of the reaction in the presence of triethylamine also depends on the length of the polyfluoroalkyl radical in molecules **I** and **II**. Tetrafluoropropyl sulfone **Ia** reacts with 2 equiv of hydrazine hydrate and 4 equiv of triethylamine, affording 88% of bis-hydrazone **XXII** due to replacement of fluorine in both difluoromethylene groups (Scheme 12). Reactions of octafluoropentyl sulfone **II** with hydrazine hydrate and triethylamine at various reactant ratios led to formation of complex mixtures of products. The only isolated product was 1-benzylsulfinyl-5,5-difluoropentane-2,3,4-trione trishydrazone (**XXIII**) which was obtained using 4 equiv of hydrazine hydrate and 6 equiv of triethylamine per equivalent of sulfone **II** (Scheme 13). A part of the hydrazine hydrate taken was consumed in the reduction of the sulfonyl group.

Scheme 12.



XXII

Scheme 13.

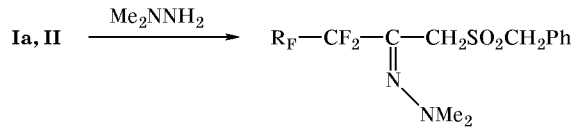


XXIII

In the reaction of **Ia** and **II** with *N*,*N*-dimethylhydrazine successive dehydrofluorination processes

are impossible. In this case, regardless of the presence or absence of triethylamine, only monohydrazones **XXIV** and **XXV** were obtained (Scheme 14).

Scheme 14.



XXIV, XXV

XXIV, $R_F = HCF_2$; **XXV**, $R_F = H(CF_2)_3$.

EXPERIMENTAL

The ^1H and ^{19}F NMR spectra were recorded on a Varian VXR-300 spectrometer at 299.943 and 282.203 MHz, respectively. Tetramethylsilane (^1H) and hexafluorobenzene (^{19}F, δ_F –162.9 ppm relative to CCl_3F) were used as internal references. The progress of reactions was monitored by ^{19}F NMR spectroscopy. The yields, constants, elemental analyses, and spectral parameters of the newly synthesized compounds are given in Tables 1 and 2. Compounds **Ia**, **Id**, **II**, **VI**, **VIIb**, and **XI** were described in [2]. Sulfones **Ib** and **Ic** were synthesized by the procedure reported in [2] and were used without additional purification.

1-(Benzylsulfonyl)-2,3,3-trifluoro-1-propene (V). To a solution of 0.01 mol of sulfone **Ia** in 30 ml of diethyl ether we added with stirring at 20°C 0.01 mol of triethylamine and 3 ml of water. The mixture was stirred for 14 h, and the ether layer was separated, washed with water (2 × 5 ml), dried over Na_2SO_4, and evaporated under reduced pressure (10–20 mm). The residue was purified by recrystallization.

2-Amino-1-butylsulfonyl-3,3-difluoro-1-propene (VIIa) and 3,3-difluoro-2-(dimethylamino)-1-propylsulfonyl-1-propene (IXa). Gaseous ammonia or dimethylamine was slowly passed over a period of 2 h through a solution of 0.05 mol of the corresponding sulfone in 100 ml of benzene, stirred at 20°C. The precipitate was filtered off, the filtrate was washed with water and dried over Na_2SO_4, the solvent was removed under reduced pressure (10–20 mm), and the residue was purified by vacuum distillation (compound **VIIa**) or recrystallization (**IXa**).

2-(α-Amino-*p*-chlorobenzylideneamino)-1-benzylsulfonyl-3,3,4,4,5,5-hexafluoro-1-pentene (VIII). A mixture of 0.01 mol of sulfone **II** and 0.03 mol of anhydrous potassium carbonate in 15 ml of acetonitrile was refluxed for 5 min, 0.01 mol of *p*-chlorobenzamidine hydrochloride was added, and the mixture was refluxed for an additional 4 h. The precipitate was filtered off, the filtrate was evaporated, and the residue was recrystallized.

2-Dipentylamino-3,3-difluoro-1-propylsulfonyl-1-propene (IXb), 1-butylsulfonyl-2-*tert*-butylamino-3,3-difluoro-1-propene (Xa), 1-benzylsulfonyl-2-*tert*-butylamino-3,3-difluoro-1-propene (Xb), 1,2-bis(2-butylsulfonyl-1-difluoromethylvinylamino)ethane (Xc), 1,7-bis(1-benzylsulfonylmethyl-2,2,3,3,4,4-hexafluorobutylideneamino)heptane (XII), 1-benzylsulfonyl-2-dimethylhydrazono)-3,3-difluoropropane (XXIV), and 1-benzylsulfonyl-2-dimethylhydrazono)-3,3,4,4,5,5-hexafluoropentane (XXV) (*general procedure*****).** A solution of 0.01 mol of appropriate sulfone and 0.02 mol of triethylamine in 10 ml of benzene was refluxed for 10 min. The corresponding amine or *N*,*N*-dimethylhydrazine, 0.01 mol, was added to the hot solution, the mixture was refluxed for 2.5 h, and the solvent was removed under reduced pressure (10–20 mm). The residue was washed with water, filtered off, dried, and purified by recrystallization.

2-Benzylideneamino-1-benzylsulfonyl-3,3-difluoropropane (XIII) and 1-benzylsulfonyl-3,3-difluoro-2-furfurylideneaminopropane (XIV). A solution of 0.011 mol of triethylamine and 0.011 mol of benzylamine or furfurylamine in 10 ml of benzene was added with stirring at 20°C to a solution of 0.005 mol of sulfone **Ia** in 20 ml of benzene. The mixture was stirred for 4 days at 20–25°C, washed with water, dried over Na_2SO_4, and evaporated under reduced pressure (10–20 mm).

2-Amino-1-benzylsulfonyl-3,3-difluoropropane (XV). Concentrated hydrochloric acid, 5 ml, was added with stirring at room temperature to a suspension of 0.0089 mol of compound **XIII** in 30 ml of ethanol. The mixture was refluxed for 2 h. Volatile products were removed under reduced pressure (10–20 mm), and the residue was washed with ether. The solid product was dissolved in water, the solution was filtered, and 10 ml of 20% aqueous sodium hydroxide was added to the filtrate. The colorless crystals of amine **XV** were filtered off, washed with water, and dried.

1-Benzylsulfonyl-2,3-bis(phenylhydrazono)-propane (XVI) and 1-benzylsulfonyl-4,4,5,5-hexafluoro-2,3-bis(phenylhydrazono)pentane (XVII). Phenylhydrazine, 0.02 mol, was added at 20°C to a solution of 0.01 mol of appropriate sulfone and 0.04 mol of triethylamine in 10 ml of benzene. The mixture was stirred for 4 h, and the precipitate was filtered off, washed with water, dried, and purified by recrystallization.

Table 1. Yields, melting points, and elemental analyses of compounds **Ib**, **Ic**, **V**, **VII**–**X**, and **XII**–**XXV**

Comp. no.	Yield, %	mp, °C (solvent), or bp, °C (*p*, mm)	Found, %			Formula	Calculated, %		
			C	H	S		C	H	S
Ib	81	39–40	32.58	4.53	14.49	$C_6H_{10}F_4O_2S$	32.43	4.54	14.43
Ic	78	27–28	36.02	5.40	13.06	$C_7H_{12}F_4O_2S$	35.59	5.12	13.57
V	60	53–55 (CCl_4–hexane, 4 : 1)	47.98	3.60	12.84	$C_{10}H_9F_3O_2S$	48.00	3.63	12.81
VIIa	81	119–121 (0.05)	39.78	6.03	15.25	$C_7H_{13}F_2NO_2S$	39.43	6.14	15.04
VIII	56	98–100 (Et_2O)	47.34	2.88	[a]	$C_{19}H_{15}ClF_6N_2O_2S$	47.07	3.12	[a]
IXa	90	65–67 (ether–hexane, 1 : 3)	42.56	6.71	13.96	$C_8H_{15}F_2NO_2S$	42.28	6.65	14.11
IXb	90	Viscous liquid	56.55	9.32	9.60	$C_{16}H_{31}F_2NO_2S$	56.61	9.20	9.44
Xa	67	116–118 (0.06)	49.46	7.66	11.94	$C_{11}H_{21}F_2NO_2S$	49.05	7.86	11.90
Xb	80	81–82 (benzene)	55.60	6.30	10.57	$C_{14}H_{19}F_2NO_2S$	55.43	6.31	10.57
Xc	53	126–128(EtOH)	42.45	6.20	14.17	$C_{16}H_{28}F_4N_2O_4S_2$	42.47	6.24	14.17
XII	42	107–109 (EtOH)	47.26	4.30	8.30	$C_{31}H_{34}F_{12}N_2O_4S_2$	47.08	4.33	8.11
XIII	73	90–92 (EtOH)	60.79	5.10	9.48	$C_{17}H_{17}F_2NO_2S$	60.52	5.08	9.50
XIV	86	Viscous liquid	55.34	4.69	9.58	$C_{15}H_{15}F_2NO_3S$	55.04	4.62	9.79
XV	65	97–100 (EtOH–H_2O, 2 : 1)	48.14	5.12	13.16	$C_{10}H_{13}F_2NO_2S$	48.18	5.26	12.86
XVI	73	190–192 (EtOH)	64.85	5.53	7.83	$C_{22}H_{22}N_4O_2S$	65.00	5.46	7.89
XVII	12	192–193 (benzene)	56.65	4.04	6.70	$C_{24}H_{22}F_4N_4O_2S$	56.91	4.38	6.33
XVIII[b]	63	141–143 (EtOH)	62.03	4.30	6.96	$C_{24}H_{20}F_2N_4O_2S$	61.79	4.32	6.87
XIX[c]	78	242–244 (CH_3NO_2)	67.60	4.81	6.38	$C_{30}H_{26}N_6O_2S$	67.40	4.90	6.00
XX	74	89–90 (hexane–EtOH, 3 : 2)	45.20	4.96	12.28	$C_{10}H_{12}F_2N_2O_2S$	45.80	4.61	12.22
XXI	78	166–168 (EtOH)	39.92	3.37	9.07	$C_{12}H_{12}F_6N_2O_2S$	39.78	3.34	8.85
XXII	88	158–160 (benzene)	47.26	5.58	12.74	$C_{10}H_{14}N_4O_2S$	47.23	5.55	12.61
XXIII	66	123–124 (benzene)	43.79	4.79	9.70	$C_{12}H_{16}F_2N_6OS$	43.63	4.88	9.71
XXIV	87	93–94 (hexane)	49.61	5.71	10.90	$C_{12}H_{16}F_2N_2O_2S$	49.64	5.55	11.04
XXV	62	130–132 (EtOH)	43.07	4.13	8.21	$C_{14}H_{16}F_6N_2O_2S$	43.08	4.13	8.21

[a] Found, %: Cl 7.28. Calculated, %: Cl 7.31.

[b] Mass spectrum (EI), *m*/*z*: 466 $[M]^+$, 311 $[M - PhCH_2SO_2]^+$.

[c] Mass spectrum (EI): 534 $[M]^+$, 379 $[M - PhCH_2SO_2]^+$, 287 $[M - PhCH_2SO_2 - PhNH]^+$.

3-Benzylsulfonylmethyl-1-phenyl-4-phenylazo-5-difluoromethylpyrazole (XVIII). Phenylhydrazine, 0.02 mol, was added with stirring at 20°C to a solution of 0.01 mol of sulfone **II** and 0.06 mol of triethylamine in 20 ml of benzene. The mixture was stirred for 4 days, and the precipitate was filtered off and twice recrystallized from alcohol with addition of charcoal.

3-(2-Benzylsulfonyl-1-phenylhydrazonoethyl)-1-phenyl-4-phenylazopyrazole (XIX) was synthesized as described above for compound **XVIII** from 0.01 mol of sulfone **II**, 0.08 mol of triethylamine, and 0.03 mol of phenylhydrazine. The precipitate of **XIX** was filtered off and washed with benzene and water on a filter. An analytical sample of **XIX** was obtained by recrystallization from nitromethane.

1-Benzylsulfonyl-3,3-difluoro-2-hydrazonopropane (XX) and 1-benzylsulfonyl-3,3,4,4,5,5-hexafluoro-2-hydrazonopentane (XXI). Hydrazine hydrate, 0.03 mol, was added with stirring at 20°C to a solution of 0.01 mol of appropriate sulfone in 10 ml of benzene. The mixture was stirred for 3 h, and the precipitate was filtered off, dried, and purified by recrystallization.

1-Benzylsulfonyl-2,3-dihydrazonopropane (XXII). Triethylamine, 0.04 mol, and hydrazine hydrate, 0.025 mol, were added with stirring at 20°C to a solution of 0.01 mol of sulfone **Ia** in 10 ml of

Table 2. NMR spectra of compounds **Ib**, **Ic**, **V**, **VII**–**X**, and **XII**–**XXV**

Comp. no.	^{1}H NMR spectrum ($CDCl_3$), δ, ppm	^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm
Ib	6.08 t.t (1H, CHF_2, $^2J_{H,F}$ = 53.4, $^3J_{H,F}$ = 5.3 Hz), 3.67 t (2H, CH_2CF_2, $^2J_{H,F}$ = 14.7 Hz), 3.14 m (2H, CH_2), 1.91 m (2H, CH_2), 1.11 t (3H, CH_3)	–115.32 m (2F, CF_2), –138.04 d.m (2F, CF_2H, $^2J_{F,H}$ = 53.4 Hz)
Ic	6.49 t.t (1H, CHF_2, $^2J_{H,F}$ = 53.1, $^3J_{H,F}$ = 5.3 Hz), 4.11 t (2H, CH_2CF_2, $^2J_{H,F}$ = 14.8 Hz), 3.56 m (2H, CH_2), 2.24 m (2H, CH_2), 1.91 m (2H, CH_2), 1.37 t (3H, CH_3)	–114.69 m (2F, CF_2), –137.41 d.m (2F, CF_2H, $^2J_{F,H}$ = 53.1 Hz)
V	7.41 m (5H, C_6H_5), 6.26[a] d (1H, CH=, $J_{H,F\text{-}cis}$ = 17.1 Hz), 6.15[b] d (1H, CH=, $J_{H,F\text{-}trans}$ = 30.6 Hz), 6.074[b] t (1H, CHF_2, $^2J_{H,F}$ = 53.4 Hz), 6.068[a] t (1H, CH=, $^2J_{H,F}$ = 55.2 Hz), 4.26[b] s (2H, CH_2), 4.35[a] s (2H, CH_2)	–104.82[b] d.t (1F, CF=, $J_{F,H\text{-}trans}$ = 30.6, $^3J_{F,F}$ = 19.2, $^3J_{F,F}$ = 13.8 Hz), –109.04[a] m (1F, CF_2), –127.09[b] d.d (2F, CF_2, $^2J_{F,H}$ = 55.2, $^3J_{F,F}$ = 19.2, $^3J_{F,F}$ = 13.8 Hz), –128.96[a] d.d (2F, CF_2, $^2J_{H,F}$ = 53.4, $^3J_{F,F}$ = 20.2 Hz)
VIIa	6.04 t (1H, CHF_2, $^2J_{H,F}$ = 54.9 Hz), 5.86 br.s (2H, NH_2), 4.99 s (1H, CH=), 2.99 t (2H, CH_2), 1.76 m (2H, CH_2), 1.45 m (2H, CH_2), 0.99 t (3H, CH_3)	–121.47 d (2F, CF_2H, $^2J_{F,H}$ = 54.9 Hz)
VIII	7.61 d.m and 7.37 d.m (4H, C_6H_4), 7.30 m (5H, C_6H_5), 6.05 s (1H, CH=), 5.98 t.t (1H, CHF_2, $^2J_{H,F}$ = 52.0, $^3J_{H,F}$ = 6.0 Hz), 5.26 br.s (2H, NH_2), 4.26 s (2H, CH_2)	–117.56 m (2F, CF_2), –131.98 m (2F, CF_2), –138.29 d.m (2F, CF_2H, $^2J_{F,H}$ = 52.0 Hz)
IXa	7.58 t (1H, CHF_2, $^2J_{H,F}$ = 52.2 Hz), 4.86 s (1H, CH=), 3.01 m [8H, $(CH_3)_2N+CH_2SO_2$], 1.82 m (2H, CH_2), 1.04 t (3H, CH_3)	–121.76 d (2F, CF_2H, $^2J_{F,H}$ = 52.2 Hz)
IXb	8.09 t (1H, CHF_2, $^2J_{H,F}$ = 52.5 Hz), 5.03 s (1H, CH=), 2.88 t (2H, CH_2), 1.67 m (2H, CH_2), 1.31 m (2H, CH_2), 1.13 m (2H, CH_2), 0.82 t (3H, CH_3)	–119.79 d (2F, CF_2H, $^2J_{F,H}$ = 52.5 Hz)
Xa	7.31 t (1H, CHF_2, $^2J_{H,F}$ = 54.3 Hz), 5.06 t (1H, CH=, $^4J_{H,F}$ = 1.8 Hz), 4.78 br.s (1H, NH), 2.96 t (2H, CH_2), 1.71 m (2H, CH_2), 1.37 m (2H, CH_2), 1.31 c [9H, $(CH_3)_3C$], 0.87 t (3H, CH_3)	–121.89 d (2F, CF_2H, $^2J_{F,H}$ = 54.3 Hz)
Xb	7.35 m (5H, C_6H_5), 6.92 t (1H, CHF_2, $^2J_{H,F}$ = 54.3 Hz), 4.86 t (1H, CH=, $^4J_{H,F}$ = 1.8 Hz), 4.81 br.s (1H, NH), 4.26 s (2H, CH_2Ph), 1.27 s [9H, $C(CH_3)_3$]	–123.03 d (2F, CF_2H, $^2J_{F,H}$ = 54.3 Hz)
Xc	7.24 t (2H, CHF_2, $^2J_{H,F}$ = 57.3 Hz), 5.81 br.s (2H, NH), 5.02 s (2H, CH=), 3.19 m (4H, CH_2N), 2.91 m (4H, CH_2), 1.63 m (4H, CH_2), 1.37 m (4H, CH_2), 0.81 t (6H, CH_3)	–113.69 d (4F, CF_2H, $^2J_{F,H}$ = 57.3 Hz)
XII	7.39 m (10H, C_6H_5), 6.35 t.t (1H, CHF_2, $^2J_{H,F}$ = 52.9, $^3J_{H,F}$ = 5.9 Hz), 4.30 s (4H, CH_2SO_2), 4.00 s (4H, $CH_2C_6H_5$), 3.47 m (4H, CH_2N=), 1.59 m (4H, CH_2), 1.23 m (6H, CH_2)	113.70 m (4F, CF_2), –132.4 m (4F, CF_2), –138.15 d.m (4F, CF_2H, $^3J_{F,H}$ = 52.9 Hz)
XIII[c]	8.08 s (1H, CH=N), 7.63 m (2H, H_{arom}), 7.25 m (2H, H_{arom}), 7.04 m (6H, H_{arom}), 5.24 t.d (1H, CHF_2, $^2J_{H,F}$ = 55.3, $^3J_{H,H}$ = 4.1 Hz), 3.97 m (1H, CH), δ_A 3.83, δ_B 3.62 (*AB*, CH_2Ph, J_{AB} = 13.7 Hz), δ_A 3.24, δ_B 2.82 (*AB*, CH_2SO_2, J_{AB} = 15.0, $^3J_{H,H}$ = 10.4 Hz)	δ_A –125.08, δ_B –126.40 (*AB*, CF_2H, J_{AB} = 282.3, $^2J_{F,H}$ = 55.3, $^3J_{F,H}$ = 12.4 Hz)

Table 2. (Contd.)

Comp. no.	^{1}H NMR spectrum ($CDCl_3$), δ, ppm	^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm
XIV	8.19 s (1H, CH=N), 7.54 d (1H, 5-H, $^3J_{H,H}$ = 1.5 Hz), 7.34 m (5H, C_6H_5), 6.90 d (1H, 3-H, $^3J_{H,H}$ = 3.0 Hz), 6.48 d.d (1H, 4-H, $^3J_{H,H}$ = 3.0, $^3J_{H,H}$ = 1.5 Hz), 5.76 t.d (1H, CHF_2, $^2J_{H,F}$ = 55.0, $^3J_{H,H}$ = 1.5 Hz), δ_A 4.18, δ_B 4.12 (*AB*, CH_2Ph, J_{AB} = 14.0 Hz), 4.05 m (1H, CH), 3.45 d.d (1H, C**H**$_a$H$_b$SO$_2$, $^2J_{H,H}$ = 14.7, $^3J_{H,H}$ = 9.9 Hz), 3.12 d.m (1H, CH$_a$**H**$_b$SO$_2$, $^2J_{H,H}$ = 14.7 Hz)	–126.54 br.d.d (2F, CF_2H, $^2J_{F,F}$ = 234.7, $^2J_{F,H}$ = 55.0, $^3J_{F,H}$ = 14.0 Hz)
XV	7.43 m (5H, C_6H_5), 5.74 t.d (1H, CHF_2, $^2J_{H,F}$ = 55.8, $^3J_{H,H}$ = 1.2 Hz), δ_A 4.47, δ_B 4.35 (*AB*, CH_2Ph, J_{AB} = 13.8 Hz), 3.66 m (1H, CH), 3.03 m (2H, CH_2SO_2), 1.61 br.s (2H, NH_2)	δ_A –127.67, δ_B –131.45 (*AB*, CF_2H, J_{AB} = 282.0, $^2J_{F,H}$ = 55.8, $^3J_{F,H}$ = 12.7 Hz)
XVI	10.41 br.s (1H, NH), 9.90 br.s (1H, NH), 7.67 s (1H, CH), 7.4–6.7 m (15H, 3C_6H_5), 4.84 s (2H, CH_2), 4.61 s (2H, CH_2)	
XVII	13.02 br.s (1H, NH), 9.81 br.s (1H, NH), 7.5–7.2 m (10H, C_6H_5), 7.09 m (5H, C_6H_5), 6.55 t.t (1H, CHF_2, $^3J_{H,F}$ = 57.2 Hz), 4.51 s (2H, CH_2), 4.45 s (2H, CH_2)	–107.02 m (2F, CF_2), –138.33 d.m (2F, CF_2H, $^2J_{F,H}$ = 57.2 Hz)
XVIII	7.84–7.21 m (16H, CHF_2 + C_6H_5), 4.78 s (2H, CH_2Ph), 4.45 s (2H, CH_2SO_2)	–113.75 d (2F, CF_2H, $^2J_{F,H}$ = 55.2 Hz)
XIX	12.67 s (1H, NH), 8.43 s (1H, CH=), 7.88–7.00 m (20H, C_6H_5), 5.05 s (2H, CH_2Ph), 4.45 s (2H, CH_2)	
XX	7.43 m (5H, C_6H_5), 6.73 br.s (2H, NH_2), 6.17 t (1H, CHF_2, $^2J_{H,F}$ = 55.2 Hz), 4.38 s (2H, CH_2), 4.05 s (2H, CH_2)	–115.23 d (2F, CF_2H, $^2J_{F,H}$ = 55.2 Hz)
XXI	7.44 m (5H, C_6H_5), 6.97 br.s (2H, NH_2), 6.28 t.t (1H, CHF_2, $^2J_{H,F}$ = 52.4, $^3J_{H,F}$ = 5.7 Hz), 4.37 s (2H, CH_2Ph), 4.07 s (2H, CH_2)	–110.33 m (2F, CF_2), –132.10 m (2F, CF_2), –138.52 d (2F, CF_2H, $^2J_{F,H}$ = 52.4 Hz)
XXII	7.40 m (6H, C_6H_5 + CH), 7.00 br.s (2H, NH_2), 6.67 br.s (2H, NH_2), 4.51 s (2H, CH_2Ph), 4.41 s (2H, CH_2SO_2)	
XXIII[d]	7.39 s (5H, C_6H_5), 7.08 br.s (2H, NH_2), 7.01 br.s (2H, NH_2), 6.72 br.s (2H, NH_2), 6.36 t (1H, CHF_2, $^2J_{H,F}$ = 56.4 Hz), 4.7–4.4 m (4H, 2CH_2, two overlapped *AB* systems)	–113.3, δ_A –112.35, δ_B –114.24 (*AB*, CF_2H, J_{AB} = 293.7, $^2J_{F,H}$ = 56.4 Hz)
XXIV	6.14 t (1H, CHF_2, $^2J_{H,F}$ = 56.7 Hz), 4.37 s (2H, CH_2Ph), 4.14 s (2H, CH_2SO_2), 3.08 s [6H, $N(CH_3)_2$]	–112.48 d (2F, CF_2H, $^2J_{F,H}$ = 56.7 Hz)
XXV	7.36 m (5H, C_6H_5), 6.22 t.t (1H, CHF_2, $^2J_{H,F}$ = 53.2, $^3J_{H,F}$ = 6.0 Hz), 4.27 s (2H, CH_2), 4.03 s (2H, CH_2), 3.13 s [6H, $N(CH_3)_2$]	–106.25 m (2F, CF_2), –131.16 m (2F, CF_2), –137.50 d.m (2F, CF_2H, $^2J_{F,H}$ = 53.2 Hz)

[a] *cis* Isomer. [b] *trans* Isomer. [c] Solvent C_6D_6. [d] Solvent DMSO-d_6.

benzene. The mixture was stirred for 3 h, and the precipitate was filtered off, washed with water, dried, and purified by recrystallization.

1-Benzylsulfinyl-5,5-difluoro-2,3,4-trihydrazonopentane (XXIII). Triethylamine, 0.06 mol, and hydrazine hydrate, 0.04 mol, were added to a solution of 0.01 mol of sulfone **II** in 20 ml of acetonitrile. The mixture was refluxed for 3 h, and the precipitate was filtered off and washed with 5 ml of acetonitrile. The filtrate was evaporated under reduced pressure (10–20 mm), and the crystalline residue was washed with water, dried, and purified by recrystallization.

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