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Synthesis of β-Functionalized Ethyl Polyfluoroaryl Sulfides, Sulfoxides, and Sulfones Underlain by Pentafluorobenzoic Acid

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Abstract—The reaction of pentafluorobenzoic acid with 2-mercaptoethanol followed by modification of the reaction product by oxidationm halohydroxylation and (or) decarboxylation led to the formation of β-halo- and β-oxyethyl polyfluoroaryl sulfides, sulfoxides, and sulfones, initial compounds for the synthesis of fluorine-containing 2,3-dihydro-1,4-benzothiazines, 2,3-dihydro-1,4-benzoxathiynes, and 2,3-dihydro-1,4-benzodithiynes and also of their S-oxides and S-dioxides based on intramolecular nucleophilic sybstitution.

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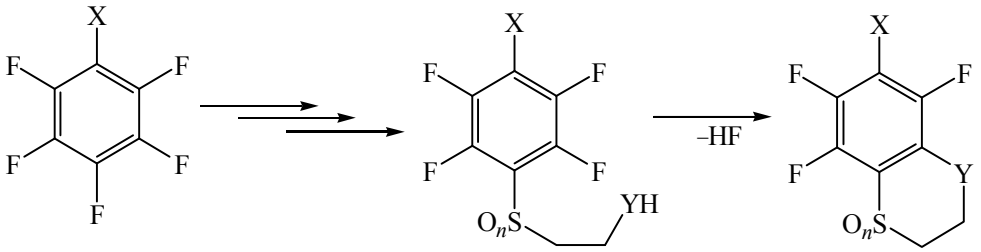
Among the sulfur-containing benzoheterocycles physiologically active compounds were found of a wide range of action [1]. From this viewpoint 2,3-dihydro-1,4-benzothiazines, 2,3-dihydro-1,4-benzoxathiynes, and 2,3-dihydro-1,4-benzodithiynes and also their S-oxides and S-dioxides are especially interesting [2–5]. The introduction of fluorine into a heterocyclic compound may significantly affect the character and power of its biological action [6–10]. Besides the presence in the benzene fragment of the benzoheterocycle of several fluorine atoms provides a possibility of a repeated modification of the compound by a nucleophilic substitution [11–13]. This information underlies the interest to fluorinated derivatives of the mentioned heterocyclic systems.

The synthesis of 2,3-dihydro-1,4-benzothiazine is commonly based on the application as initial compounds of the 2-aminothiophenol [1, 14–16] or of a *o*-halo-substituted nitroarene [3, 17–19]. Other ways to 2,3-dihydro-1,4-benzothiazine derivatives were also described [15, 16, 20]. 2,3-Dihydro-1,4-benzoxathiynes are prepared by the reductive cyclization of *o*-oxyarylthioketones [5, 21], by the addition of *o*-mercaptophenol to α,β-unsaturated ethers [14], by Diels–Alder heteroreaction of *o*-thioquinone with vinyl compounds [22], or by intramolecular alkoxydechlorination of S-(2'-hydroxyethyl)-2-chlorothiophenol derivatives [23]. The syntheses of 2,3-dihydro-1,4-benzodithiynes involve the reactions of benzopentathiepines with unsaturated compounds [24], cyclohexanone or cyclohexenone with 1,2-ethanedithiol in the presence of 1,1'-(ethane-1,2-diyl)dipyridinium bistribromide [25], and also intramolecular cyclization of 2-phenylsulfanylethylthiosulfonates or the reactions of dithiopyrocatechol derivatives with 1,2-dibromoethane [26].

Thus the introducing into the sulfur-containing ring of the second heteroatom is due to its presence in the initial compound, but the methods of building up the heterocyclic fragment underlain by its character are not general. In their turn the syntheses of compounds contain-ing sulfur in the oxidized state (sulfoxide or sulfone) are performed commonly by the oxidation of the sulfide unit of the already formed heterocycle [2, 3, 5, 23]. This fact provides certain limitations for the preparation by this procedure of compounds containing easily oxidizable groups. Besides it is impossible to prepare derivatives substituted in the

[†] Deceased.

Scheme 1.



$n = 0, 1, 2$; YH = OH, NH_2, NHR, SH

benzene ring requiring the presence in the precursor of a substituent whose nature is incompatible with the synthesis conditions.

With respect to the synthesis of polyfluoro-2,3-dihydro-1,4-benzothiazines, -oxathiynes and -dithiynes, and also of the corresponding S-oxides and S-dioxides it seemed possible to overcome the above-mentioned difficulties using a common approach to all cases based on the presence in the initial compound of several fluorine atoms. This approach makes it possible to use as the general basic compound an available polyfluoroarene, and as the method of building up on this compound of the heterocycle, the introducing by the nucleophilic substitution of the fluorine an ethylsulfide moiety containing a functional group in the β-position either directly playing the role of the reaction site for the final nucleophilic cyclization or easily converted into it (Scheme 1). If the sulfide sulfur required oxidation then depending on the structure of the heterocycle precursor it can be carried out either before cyclization or in the cyclic sulfide. Therewith the presence of a sulfur-containing group in the *ortho*-position to the fluorine substituted at the cyclization in any case favors the intramolecular cyclization.

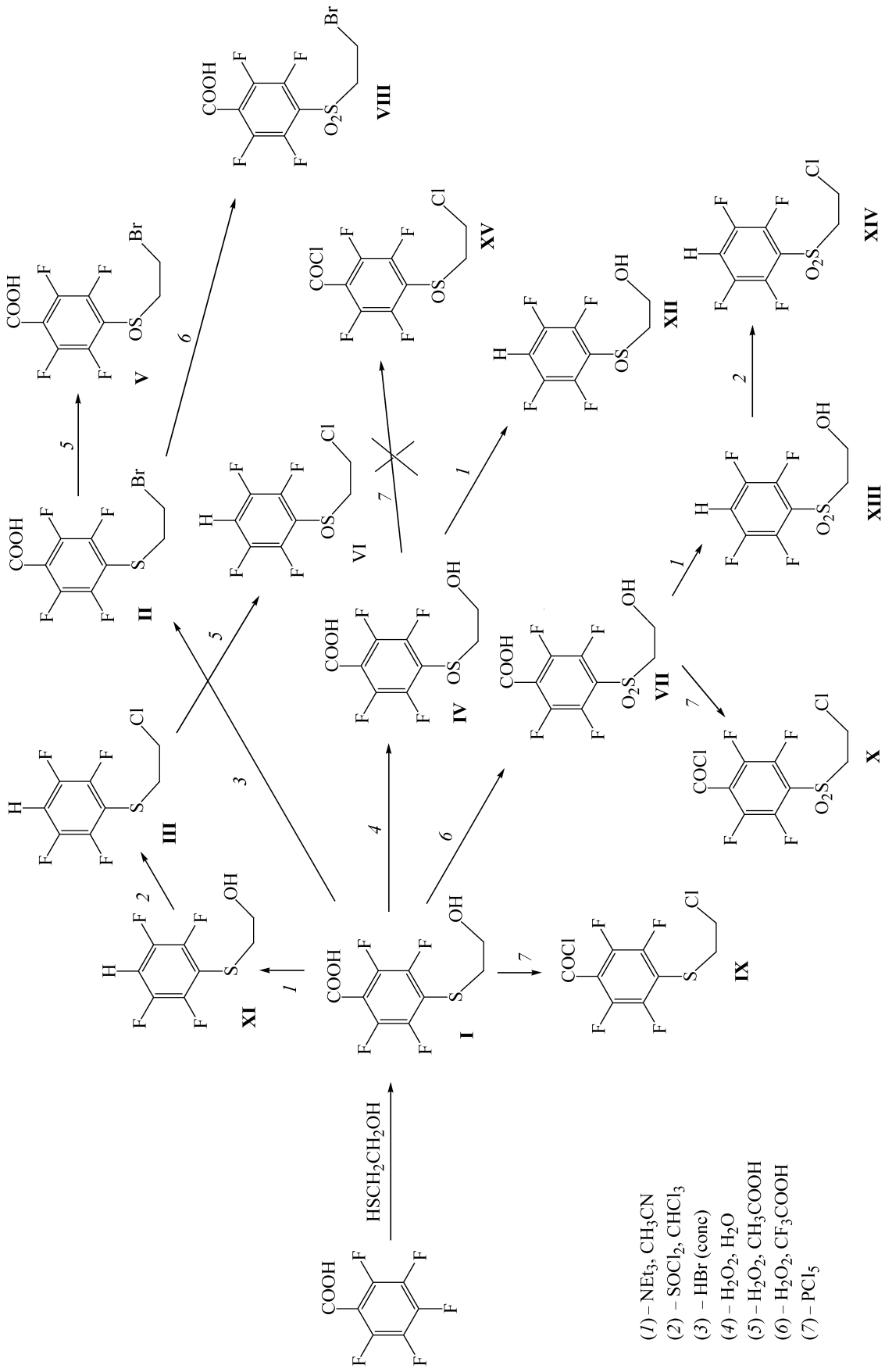
Some examples of this approach were described in the literature, for instance, the synthesis of the derivative of bis(5,8-vinylsulfanyl)-6-fluoro-2,3-dihydro-1,4-benzothiazine by the reaction of bis(1,4-vinylsulfanyl)tetrafluorobenzene with 2-aminoethanethiol [27]. Amosova et al for the preparation of di- and tetraoxides of the fluorinated benzo-di-1,4-thiazines used the addition to the vinyl group of 1,4-bis(vinylsulfinyl- and -sulfonyl)-tetrafluorobenzenes followed by the nucleophilic cyclization [28].

The suitable type of the underlying compound for putting this synthetic scheme into operation are polyfluoroarenecarboxylic acids. This choice beside the accessibility of these compounds is supported by the presence of a carboxy group that at least does not hamper the introduction of the β-functionalized ethylsulfide into the *para*-position with respect to it by the nucleophilic substitution of a fluorine atom and the subsequent cyclization furnishes wide opportunities for further functionalization of the synthesized heterocyclic compound both at the carboxy group and by the nucleophilic substitution of fluorine atoms. The attractive feature of this function is also the easy opportunity of its removal from the polyfluoroaromatic ring by decarboxylation giving a place for a wide range of modifications by means of electrophilic substitution of the hydrogen.

As the first step to the performance of the above defined procedure with respect to the synthesis of the building blocks for the sulfur-containing polyfluorobenzoheterocycles we studied in this research the reactions of the pentafluorobenzoic acid with 2-mercaptoethanol. The choice of this compound is stipulated by the fact that after the substitution of the first fluorine atom by the β-hydroxyethylthiol group the hydroxy group of the latter may be used in the final heterocyclization in two ways (cf. [29]): both as a nucleophilic site and for introducing other nucleophilic groups by successive replacement of the hydroxyl by halogen atom any further by (alkyl)amino or mercapto group. Therewith the primarily introduced sulfide sulfur atom may if required be oxidized with retaining either the hydroxy group or the opportunity of its replacement. This approach allows the application of the same bifunctional reagent for the synthesis of sulfur-containing heterocycles differing by the nature of the second heteroatom and the state of sulfur oxidation.

The reaction of pentafluorobenzoic acid with 2-mercaptoethanol cleanly provided 4-(2-hydroxyethylsulfanyl)-2,3,5,6-tetrafluorobenzoic acid (**I**) (Scheme 2). The conversion of acid **I** into other compounds being potential precursors of heterocycles may be performed

Scheme 2.


HSCH2CH2OH
(1) – NEt3, CH3CN
(2) – SOCl2, CHCl3
(3) – HBr (conc)
(4) – H2O2, H2O
(5) – H2O2, CH3COOH
(6) – H2O2, CF3COOH
(7) – PCl5

by modification of three functional groups present in the molecule: carboxy, hydroxy, and sulfide moieties. In the present study we performed the oxidation of sulfur, halodehydroxylation, and decarboxylation. It turned out that in the former two cases depending on the reaction conditions different degree of modification was attained.

For instance, a cautious oxidation of sulfide **I**, and also of 4-(2-bromomethylsulfanyl)-2,3,5,6-tetrafluoro-benzoic acid (**II**) and 2,3,5,6-tetrafluoro(2-chloroethylsulfanyl)-benzene (**III**) with a stoichiometric amount of hydrogen peroxide in water or AcOH gave the corresponding compounds containing a sulfoxide moiety: 4-(2-hydroxy-ethylsulfinyl)- and 4-(2-bromoethylsulfinyl)-2,3,5,6-tetrafluorobenzoic acids (**IV, V**), and also 2,3,5,6-tetrafluoro(2-chloroethylsulfinyl)benzene (**VI**). Vigorous oxidation of sulfides **I** and **II** with a 5-fold amount of hydrogen peroxide in trifluoroacetic acid gave sulfones: 4-(2-hydroxyethylsulfonyl)- and 4-(2-bromoethyl-sulfonyl)-2,3,5,6-tetrafluorobenzoic acids (**VII, VIII**).

By treating compound **I** with hydrobromic acid we succeeded in clean replacement of the alcohol hydroxyl by bromine to obtain acid **II**. In reactions of compounds **I** and **VII** with phosphorus pentachloride both hydroxy groups were replaced by chlorine to give acid chlorides of 4-(2-chloroethylsulfanyl)- and 4-(2-chloroethylsul-fonyl)-2,3,5,6-tetrafluorobenzoic acids (**IX, X**) respectively. The building blocks containing acyl chloride groups, on the one hand, may be easily converted into versatile other functional groups, and on the other hand, provide a possibility of additional fusion of heterocycle and going over to tricyclic structures, also interesting for the synthesis of potential biologically active substances. The possibility of heterocyclization of polyfluorobenzoic acids chlorides was demonstrated in [30,31].

By easy decarboxylation at short boiling in a mixture acetonitrile–triethylamine acids **I**, **IV**, and **VII** were converted into analogous derivatives of tetrafluoro-benzene: (2-hydroxyethylsulfanyl)-, (2-hydroxyethyl-sulfinyl)-, and (2-hydroxyethylsulfonyl)-2,3,5,6-tetra-fluorobenzenes (**XI–XIII**). By treating with thionyl chloride compounds **XI** and **XIII** were readily converted into sulfide **III** and 2,3,5,6-tetrafluoro(2-chloroethyl-sulfonyl)benzene (**XIV**) respectively. Sulfide **XI** was also obtained by the reaction of pentafluorobenzene with 2-mercaptoethanol. Same as with pentafluorobenzoic acid, this reaction proceeded regioselectively. We failed to convert sulfoxides **IV** and **XII** into sulfoxides **XV** and **VI** by treating with phosphorus pentachloride or thionyl chloride: according to ^{1}H and ^{19}F NMR spectra formed sulfides **IX** and **III** respectively.

The composition and structure of all compounds obtained was proved by elemental analysis and ^{1}H and ^{19}F NMR spectra. In the ^{1}H NMR spectra of compounds **I, III, VII–XI, XIII**, and **XIV** in the region δ 3.0–4.5 ppm two signals of methylene groups appear in the form of triplets. In the spectra of compounds **II, IV–VI**, and **XII** the analogous signals have a more complex structure. In the spectra of sulfoxides **IV–VI, XII** this pattern is evidently caused by the nonequivalence of the geminal protons due to the asymmetry of the sulfur atom. In the spectrum of compound **II** the proton signals of ethylene bridge are overlapped and appear as a common multiplet. In the ^{1}H NMR spectra of all tetrafluorobenzene derivatives the characteristic signal of the proton of the aromatic ring at δ ~7–7.5 ppm regularly shifts downfield in going from sulfides **III** and **XI** to sulfoxides **VI** and **XII** and further to sulfones **XIV** and **XIII**. The protons of the alcohol hydroxy groups appear at δ ~2–3.5 ppm. In the spectra of acids **I** and **IV** in the region δ 6–10 ppm the averaged signal of two hydroxy groups is observed. This signal was not found in the spectrum of compound **VII** due to its complete broadening. In the spectra of bromine-containing acis the intensity and chemical shifts of the broadened signals of hydroxy protons are somewhat distorted apparently due to the water or ethanol impurity in the deuterated solvents used in the registering of the spectra. In the ^{19}F NMR spectra two multiplets in the region δ 20–30 ppm typical of 1,4-di-substituted tetrafluorophenyl fragment are present.

EXPERIMENTAL

^{1}H and ^{19}F NMR spectra wee registered on spectrometers Bruker WP-200SY (frequency 200.13 (^{1}H), 188.28 MHz (^{19}F)] and Bruker AV-300 [frequency 300.13 (^{1}H), 282 MHz (^{19}F)], internal references hexamethyldisiloxane (δ_H 0.0 ppm) and C_6F_6 (δ_F 0.0 ppm).

4-(2-Hydroxyethylsulfanyl)-2,3,5,6-tetrafluoro-benzoic acid (I). To a dispersion of 6.83 g (0.032 mol) of pentafluorobenzoic acid in 30 ml of water was added at stiring 2.77 g (0.035 mol) of 2-mercaptoethanol and 7.16 g (0.071 mol) of triethylamine. The mixture was left overnight, then acidified to pH 0, the separated precipitate was filtered off, washed with a little cold water, and recrystallized from water. Yield 7.24 g (83%), mp 144–145°C. ^{1}H NMR spectrum [$CDCl_3$, $(CD_3)_2SO$], δ, ppm: 3.08 t [2H, $S(CH_2)_2O$, J 6.2 Hz], 3.67 t [2H, $S(CH_2)_2O$, J 6.2 Hz], 6.86 br.s (2H, COOH + CH_2OH). ^{19}F NMR

spectrum, δ, ppm.: 24.6 m (2F), 28.4 m (2F). Found, %: C 40.11; H 2.33; F 28.57; S 12.20. $C_9H_6F_4O_3S$. Calculated, %: C 40.00; H 2.22; F 28.15; S 11.85.

4-(2-Bromoethylsulfanyl)-2,3,5,6-tetrafluorobenzoic acid (II). A mixture of 0.54 g(2 mmol) of compound **I** and 5 ml of concn. HBr was stirred for 5 h at 90°C. Then the reaction mixture was cooled to room temperature, the precipitate was filtered off, dried on the filter, and recrystallized from a mixture benzene–hexane, 1:2. Yield 0.55 g (83%), mp 118–120°C. ^{1}H NMR spectrum [$CDCl_3$, $(CD_3)_2SO$], δ, ppm: 3.21 br.s (OH), 3.38 m [4H, $S(CH_2)_2Br$]. ^{19}F NMR spectrum, δ, ppm: 24.6 m (2F), 29.3 m (2F). Found, %: C 32.49; H 1.72; Br 24.46; F 24.14; S 9.03. $C_9H_5BrF_4O_2S$. Calculated, %: C 32.53; H 1.51; Br 23.8; F 22.9; S 9.64.

2,3,5,6-Tetrafluoro(2-chloroethylsulfanyl)benzene (III). A mixture of 0.74 g (3.3 mmol) of compound **XI**, 3 ml of chloroform, and 0.64 g (5.4 mmol) of thionyl chloide was heated at reflux for 2 h. Then the reaction mixture was evaporated in a vacuum, the dry residue was washed with water and dried on the filter to obtain 0.77 g (97%) of compound **III** with the content of the main substance ~95% (by the data of ^{1}H and ^{19}F NMR spectra). The analytical sample was prepared by sublimation in a vacuum at 100–110°C (3 mm Hg). mp 39–40°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.17 t [2H, $S(CH_2)_2Cl$, *J* 7.7 Hz], 3.55 t [2H, $S(CH_2)_2Cl$, *J* 7.7 Hz], 7.03 m (1H, C_6F_4H). ^{19}F NMR spectrum, δ, ppm: 24.3 m (2F), 28.6 m (2F). Found, %: Cl 14.52; F 31.08; S 13.09. $C_8H_5ClF_4S$. Calculated, %: Cl 14.18; F 31.09; S 13.26.

4-(2-Hydroxyethylsulfinyl)-2,3,5,6-tetrafluorobenzoic acid (IV). A mixture of 0.99 g (4 mmol) of sulfide **I** and 4.35 g (4 mmol) of 3% hydrogen peroxide was heated for 12 h at 85°C, the reaction mixture was evaporated in a vacuum, the residue was recrystallized from a mixture chloroform–acetone, 3:1. Yield 0.72 g (68%), mp 143–145°C. ^{1}H NMR spectrum [$CDCl_3$, $(CD_3)_2SO$], δ, ppm: 3.31–3.40 m [1H, $SO(CH_2)_2O$], 3.59–3.66 m [1H, $SO(CH_2)_2O$], 3.90–3.97 m [1H, $SO(CH_2)_2O$], 4.02–4.10 m [1H, $SO(CH_2)_2O$], 6.79 br.s (2H, COOH + CH_2OH) ^{19}F NMR spectrum, δ, ppm: 22.8 m (2F), 24.1 m (2F). Found, %: C 37.58; H 2.07; F 26.52; S 11.12. $C_9H_6F_4O_4S$. Calculated, %: C 37.76; H 2.09; F 26.57; S 11.19.

4-(2-Bromoethylsulfinyl)-2,3,5,6-tetrafluorobenzoic acid (V). A mixture of 0.48 g (1.5 mmol) of sulfide **II** and a solution of 0.12 g (1.7 mmol) of 50% hydrogen peroxide in 0.5 ml of glacial acetic acid was heated for 6 h at 55°C, then the reaction mixture was diluted with 1.5-fold volume of water and was heated to boiling. The precipitate separated on cooling was filtered off and dried on the filter. Yield 0.31 g (63%), mp 89–91°C. ^{1}H NMR spectrum [$CDCl_3$, $(CD_3)_2SO$], δ, ppm: 3.48–3.57 m [1H, $SO(CH_2)_2Br$], 3.65–3.83 m [2H, $SO(CH_2)_2Br$], 3.94–4.02 m [1H, $SO(CH_2)_2Br$], 6.82 br.s (OH). ^{19}F NMR spectrum, δ, ppm: 23.0 m (2F), 24.8 m (2F). Found, %: C 30.21; H 1.92; Br 23.34; F 21.75; S 9.47. $C_9H_5BrF_4O_3S$. Calculated, %: C 31.03; H 1.44; Br 22.99; F 21.84; S 9.2.

2,3,5,6-Tetrafluoro(2-chloroethylsulfinyl)benzene (VI). A mixture of 0.39 g (1.6 mmol) of sulfide **III** and a solution of 0.13 g (1.8 mmol) of 50% hydrogen peroxide in 0.7 ml of glacial acetic acid was heated for 7 h at 55°C. Then the reaction mixture was diluted with 1.5-fold volume of water and was heated to boiling. On cooling 0.3 g (73%) of compound **VI** was filtered off, mp 50–52°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.35–3.47 m [1H, $SO(CH_2)_2Cl$], 3.83–4.04 m [3H, $SO_2(CH_2)_2Cl$], 7.25 m (1H, C_6F_4H). ^{19}F NMR spectrum, δ, ppm: 22.47 m (2F), 26.53 m (2F). Found, %: C 36.84; H 1.93; F 29.2; S 12.58. $C_8H_5ClF_4OS$. Calculated, %: C 36.9; H 1.92; F 29.92; S 12.32.

4-(2-Hydroxyethylsulfonyl)-2,3,5,6-tetrafluorobenzoic acid (VII). In 2 ml of boiling trifluoroacetic acid was dissolved 2.4 g (9 mmol) of sulfide **I**. To the hot solution was added dropwise at stirring 3.02 g (44 mmol) of 50% hydrogen peroxide. After keeping at room temperature for 24 h the reaction mixture was cooled to –10°C, the precipitate was filtered off and recrystallized from a mixture chloroform–acetonitrile, 3:1. Yield 2.14 g (79%), mp 178–180°C. ^{1}H NMR spectrum [$CDCl_3$, $(CD_3)_2SO$], δ, ppm: 3.52 t [2H, $SO_2(CH_2)_2O$, *J* 5.3 Hz], 3.99 t [2H, $SO_2(CH_2)_2O$, *J* 5.3 Hz]. ^{19}F NMR spectrum, δ, ppm: 24.1 m (2F), 25.5 m (2F). Found, %: C 35.70; H 2.16; F 24.47; S 10.50. $C_9H_6F_4O_5S$. Calculated, %: C 35.76; H 1.98; F 25.17; S 10.59.

4-(2-Bromoethylsulfonyl)-2,3,5,6-tetrafluorobenzoic acid (VIII). In 0.7 ml of boiling trifluoroacetic acid was dissolved 0.25 g (0.8 mmol) of sulfide **II**. To the hot solution was added dropwise at stirring 0.26 g (3.8 mmol) of 50% hydrogen peroxide. After keeping for 24 h the precipitate was filtered off, the mother liquor was diluted with water, and the precipitate was filtered off. The combined precipitate was dried in air and recrystallized from a mixture benzene–hexane, 1:1. Yield 0.19 g (69%), mp a53–a55°C. ^{1}H NMR spectrum [$CDCl_3$, $(CD_3)_2SO$], δ, ppm: 3.63 t [2H, $SO_2(CH_2)_2Br$,

J 7.3 Hz], 3.82 t [2H, $SO_2(CH_2)_2Br$, *J* 7.3 Hz], 8.82 br.s (OH). ^{19}F NMR spectrum, δ, ppm: 25.6 m (2F), 26.4 m (2F). Found, %: C 30.21; H 1.85; F 19.78; S 9.47. $C_9H_5BrF_4O_4S$. Calculated, %: C 29.67; H 1.37; F 20.9; S 8.8.

4-(2-Chloroethylsulfanyl)-2,3,5,6-tetrafluorobenzoic acid chloride (IX). 0.47 g (1.7 mmol) of compound **I** was mixed with 0.73 g (3.5 mmol) of phosphorus pentachloride. After 5 min started a vigorous reaction, and on its completion a homogeneous solution formed of yellow color. The phosphorus oxychloride was distilled off in a vacuum to obtain 0.51 g (96%) of oily acyl chloride **IX** containing over 95% of the main substance (by the data of ^1H and ^{19}F NMR spectra). The analytical sample was prepared by sublimation in a vacuum at 140–150°C (3 mm Hg). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.31 t [2H, $S(CH_2)_2Cl$, *J* 7.3 Hz], 3.61 t [2H, $S(CH_2)_2Cl$, *J* 7.3 Hz]. ^{19}F NMR spectrum, δ, ppm: 23.8 m (2F), 30.1 m (2F). Found, %: C 36.09; H 1.47; Cl 23.18; F 24.57; S 10.31. $C_9H_4Cl_2F_4OS$. Calculated, %: C 35.18; H 1.3; Cl 23.13; F 24.76; S 10.42.

4-(2-Chloroethylsulfonyl)-2,3,5,6-tetrafluorobenzoic acid chloride (X). Similarly to the procedure described for compound **IX** from 0.089 g (0.3 mmol) of sulfone **VII** and 0.123 g (0.6 mmol) of phosphorus pentachloride we obtained 0.051 g (51%) of acyl chloride **X**, mp 65–67°C (benzene–hexane, 1 : 5). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.76 t [2H, $SO_2(CH_2)_2Cl$, *J* 6.4 Hz], 3.91 t [2H, $SO_2(CH_2)_2Cl$, *J* 6.4 Hz]. ^{19}F NMR spectrum, δ, ppm: 26.4 m (2F), 28.4 m (2F). Found, %: C 3a.25; H 1.19; F 24.48; S 9.36. $C_9H_4Cl_2F_4O_3S$. Calculated, %: C 31.86; H 1.18; F 22.42; S 9.44.

(2-Hydroxyethylsulfanyl)-2,3,5,6-tetrafluorobenzene (XI). A mixture of 0.17 g (0.63 mol) of acid **I**, 2 ml of acetonitrile, and 0.46 g (4.3 mmol) of triethylamine was heated at reflux for 1.5 h. Acetonitrile and triethylamine were evaporated in a vacuum to obtain 0.13 g (95%) of compound **XI** containing over 95% of the main substance (by the data of ^1H and ^{19}F NMR spectra). The analytical sample was prepared by sublimation in a vacuum at 115–125°C (3 mm Hg), mp 25–26°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.16 br.s (aH, CH_2OH), 3.04 t [2H, $S(CH_2)_2O$, *J* 5.8 Hz], 3.65 t [2H, $S(CH_2)_2O$, *J* 5.8 Hz], 7.01 m (aH, C_6F_4H). ^{19}F NMR spectrum, δ, ppm: 24.0 m (2F), 28.3 m (2F). Found, %: C 42.82; H 2.65; F 33.51; S 14.23. $C_8H_6F_4OS$. Calculated, %: C 42.48; H 2.65; F 33.63; S 14.16.

(2-Hydroxyethylsulfinyl)-2,3,5,6-tetrafluorobenzene (XII). The dry residue obtained as described in the preceding experiment from 0.074 g (0.26 mmol) of acid **IV** and 0.245 g (2.4 mmol) of triethylamine in 1 ml of acetonitrile after evaporating the reaction mixture in a vacuum was recrystallized from the mixture chloroform–hexane–tetrachloromethane, 1 : 1 : 1. Yield 0.047 g (75%), mp 81–83°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.26–3.35 m [1H, $SO(CH_2)_2O$], 3.53 br.s (1H, CH_2OH), 3.67–3.74 m [1H, $SO(CH_2)_2O$], 4.03–4.10 m [1H, $SO(CH_2)_2O$], 4.15–4.23 m [1H, $SO(CH_2)_2O$], 7.24 m (1H, C_6F_4H). ^{19}F NMR spectrum, δ, ppm: 22.3 m (2F), 26.1 m (2F). Found, %: C 39.57; H 2.34; F 31.14; S 12.87. $C_8H_6F_4O_2S$. Calculated, %: C 39.67; H 2.48; F 31.40; S 13.22.

(2-Hydroxyethylsulfonyl)-2,3,5,6-tetrafluorobenzene (XIII). Similarly to the procedure described for compound **XII** from 0.41 g (1.3 mmol) of acid **VII** and 0.73 g (7.2 mmol) of triethylamine in 2 ml of acetonitrile we obtained 0.24 g (70%) of compound **XIII**, mp 63–64°C (benzene–hexane, 1 : 2). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.25 br.s (1H, CH_2OH), 3.55 t [2H, $SO_2(CH_2)_2O$, *J* 5.3 Hz], 4.11 t [2H, $SO_2(CH_2)_2O$, *J* 5.3 Hz], 7.33 m (1H, C_6F_4H). ^{19}F NMR spectrum, δ, ppm: 25.1 m (2F), 27.0 m (2F). Found, %: C 37.35; H 2.51; F 29.69; S 12.4. $C_8H_6F_4O_3S$. Calculated, %: C 37.21; H 2.33; F 29.46; S 12.4.

2,3,5,6-Tetrafluoro(2-chloroethylsulfonyl)-benzene (XIV). A mixture of 0.95 g (3.7 mmol) of sulfone **XIII**, 5 ml of chloroform, and 1.32 g (11 mmol) of thionyl chloride was heated at reflux for 3 h. Then the reaction mixture was evaporated to dryness, and the residue was recrystallized from aqueous acetic acid. Yield 0.5 g (49%), mp 63–66°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.73 t [2H, $SO_2(CH_2)_2Cl$, *J* 6.6 Hz], 3.88 t [2H, $SO_2(CH_2)_2Cl$, *J* 6.6 Hz], 7.37 m (1H, C_6F_4H). ^{19}F NMR spectrum, δ, ppm: 25.5 m (2F), 27.4 m (2F). Found, %: C 35.33; H 1.54; F 26.9; S 11.82. $C_8H_5ClF_4O_2S$. Calculated, %: C 34.72; H 1.81; F 27.49; S 11.57.

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