Heteroatom Chemistry
Volume 3, Number 4, 1992

Preparation of Polyfluorodihydrobenzothiophenes and Investigation of Some of Their Chemical Properties

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Received 6 November 1991.

ABSTRACT

Co-pyrolysis of thiophenol or diphenyl disulfide with tetrafluoroethylene or chlorotrifluoroethylene in the presence of oxidants gave 2,2,3,3-tetrafluoro-2,3-dihydrobenzo[b]thiophene (I) or the corresponding chlorotrifluorodihydrobenzothiophenes.

Reactions of compounds synthesized by use of electrophilic and nucleophilic reagents and with oxidants have been studied.

INTRODUCTION

In the previous studies on the behavior of aromatic compounds containing electron-donating groups (OH, SH, SCH_3, etc.) with polyfluoroolefins, a new reaction has been found in the aromatic series: *viz.* polyfluorocycloalkenylation of benzene [1], naphthalene [2], and pyridine derivatives and their polyfluorinated analogues [3]. Later on, the reaction was extended to thiophene derivatives. The products included 4,4,5,5,6,6-hexafluorocyclopenta[b]thiophene and 4,4,5,5,6,6,7,7-octafluorocyclohexa[b]thiophene [4]. Formation of polyfluoroarenecycloalkenes and their heteroanalogues in these reactions was suggested to take place *via* intermediate formation of α,α-difluorobenzyl type radicals and their subsequent reactions with polyfluoroolefins [5]. With benzyl type radicals substituted by their heteroanalogues $Ar\dot{X}$ where X is a heteroatom, one could expect, on reaction with polyfluoroolefins, formation of polyfluoroarenecycloalkenes with the heteroatom in the fluorinated alicyclic moiety. Possibly, such a process was observed in the formation of polyfluorocumaranes as by-products from benzene derivatives [5]. In this context, it seemed reasonable for us to try to find conditions for such types of reactions in the course of co-pyrolysis leading to formation of heteroanalogues of polyfluoroarenecycloalkenes. For that purpose, we have studied the behavior of sulfur containing benzene derivatives with polyfluoroolefins. The sulfur containing benzene derivatives were used because of the relative ease of generation of $Ar\dot{S}$ radicals. It is known that thiyl radicals are generated on thermolysis of disulfides [6] and oxidation of thiols to disulfides. An oxidant for thiols may be, for example, iodine [7].

In view of all the above, we have investigated the thermolytic reactions in a flow system of a number of thiophenols and the corresponding disulfides with tetrafluoroethylene (TFE) in the presence of iodine.

RESULTS AND DISCUSSION

It has been shown that, in the co-pyrolysis of thiophenol with TFE in the presence of iodine in a flow system, 2,2,3,3tetra-fluoro-2,3-dihydrobenzo-

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Dedicated to Professor Dr. Mult. Dr. H. C. Alois Haas on the occasion of his 60th birthday.

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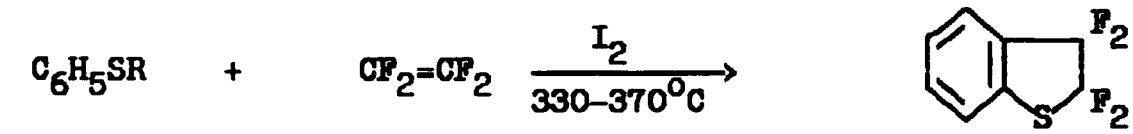


R = H, SC_6H_5 — I, 50%

[b]thiophene (*I*) is formed as the main product. We have also performed the co-pyrolysis of diphenyl disulfide with TFE under the same conditions. The reaction has been shown to proceed in a similar way, also with formation of compound (*I*) as the main product.

Earlier, formation of this compound as a by-product in the reaction of diphenyl disulfide with TFE in an autoclave has been reported [8].

In order to explore the general character of the process, we have investigated such types of transformations with some substituted diphenyl disulfides and other polyfluoroolefins. It has been shown for 4,4′-dibromo- and -dinitrodiphenyl disulfides, for example, that the reaction with TFE proceeds in a similar way to form 5-substituted tetrafluorodihydrobenzothiophenes.

The low yields of the desired products in these cases may be explained by the lower thermal stability of these 4,4′-disubstituted disulfides, leading to formation of a high amount of tar in the reaction mixtures.

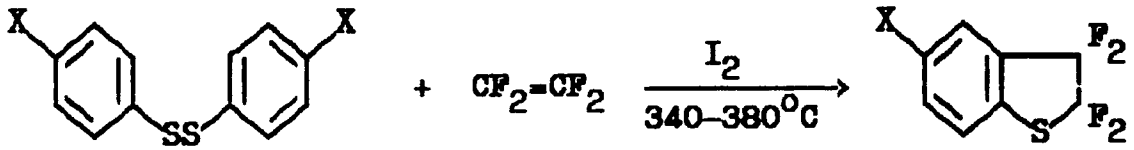
We have also studied the reaction of thiophenol with trifluorochloroethylene. The reaction route has been shown to be the same, 3-chloro-2,2,3-trifluoro-2,3-dihydrobenzo[b]thiophene (*IV*) being formed as the main product, together with 2-chloro-2,3,3-trifluoro-2,3-dihydrobenzo[b]thiophene (*V*). The co-pyrolysis of diphenyl disulfide with chlorotrifluoroethylene (CTFE) proceeds in a similar way.

Of specific interest are processes of such type with the use of other thiol group oxidants instead of iodine. One such oxidant was reported to be dimethylsulfoxide; its reaction with thiophenol gave diphenyl disulfide in a high yield [9].

We have shown that co-pyrolysis of thiophenol with tetrafluoroethylene in the presence of dimethylsulfoxide also gives compound *I* together with diphenyl disulfide.

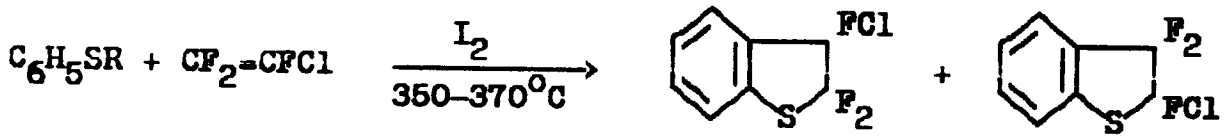
The reaction with CTFE proceeds in a similar way.

It should be noted that chlorotrifluorodihydrobenzothiophenes are formed with the same



X = Br, II, 10%

X = NO_2, III, 14%

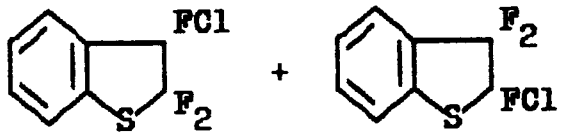


	IV		V
	4	1	1
R = H,		15%	
R = SC_6H_5,		26%	

$$C_6H_5SH + CF_2{=}CF_2 \xrightarrow[360\text{–}370^\circ C]{DMSO} I, + C_6H_5SSC_6H_5$$

30% 39%

$$C_6H_5SH + CF_2{=}CFCl \xrightarrow[350\text{–}370^\circ C]{DMSO}$$



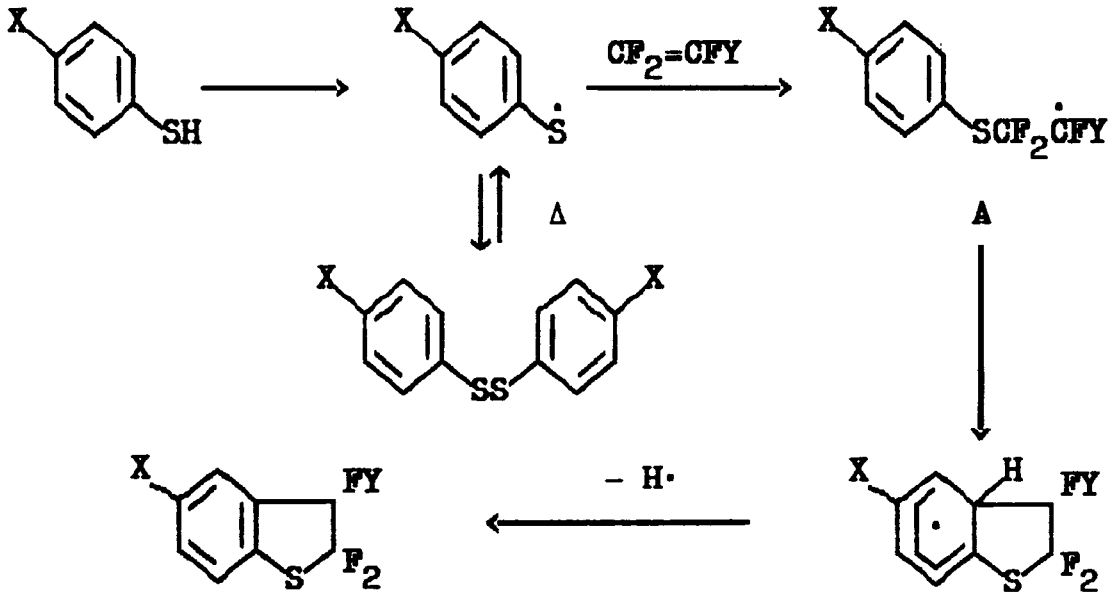
IV : V

4 : 1

10%

isomer ratio here as in the reaction in the presence of iodine. In the absence of iodine and dimethylsulfoxide, thiophenol essentially does not react with polyfluoroolefins.

Formation of polyfluorodihydrobenzothiophenes may be represented by the following scheme:



its content in the mixture should be comparable to that of compound *I*.

Participation of type *A* radicals in formation of polyfluorodihydrobenzothiophenes agrees with the results of co-pyrolysis of thiophenol and diphenyl disulfide with CTFE which gave predominantly

Formation of compound *I* does not seem to proceed by disproportionation of radical *A* with hydrogen transfer as suggested in ref. [8], because we did not find 1,1,2,2-tetrafluoroethylphenyl sulfide as a product. In the case of disproportionation, compound *IV*. It is known that thiyl radicals attack CTFE at the CF_2-group to form intermediate radicals of similar structure [10].

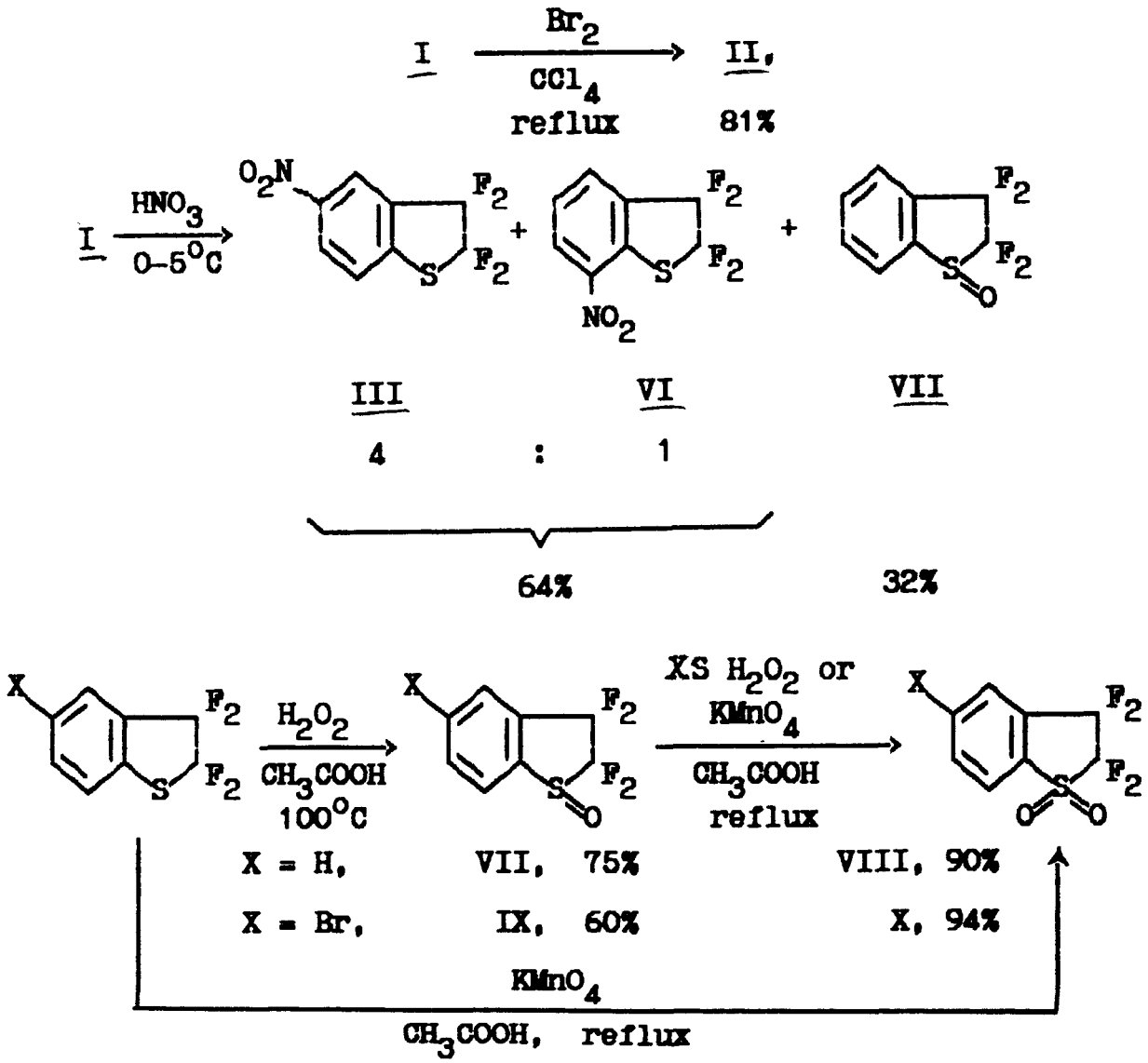
Another scheme of formation of polyfluorodihydrobenzothiophenes involving formation of the

2-iodopolyfluoroethyl radical $I-CF_2-\dot{C}FX$ (X=F, Cl) with its subsequent reaction with diphenyl disulfide seems to be less likely under the reaction conditions applied (cf. [8]). In this case, the intermediate compound $I-CF_2CFCl-SC_6H_5$ could lead on thermolysis to generation of the isomeric radical $\dot{C}F_2-CFCl-SC_6H_5$ *via* homolysis of the C—I bond and eventually to *V*. However, in the reactions studied, predominant formation of the isomer *IV* has been observed.

The route of formation of polyfluorodihydrobenzothiophenes in reactions of thiophenol with polyfluoroolefins in the presence of dimethylsulfoxide is less evident. It could also involve the thiophenoxyl radical possibly being generated, for example, on oxidation of thiophenol or on thermolysis of the diphenyl disulfide formed [11]. This assumption is in agreement with the result of co-pyrolysis of thiophenol with CTFE in the presence of dimethylsulfoxide which gave a mixture of chlorotrifluorodihydrobenzothiophenes *IV* and *V* of the same isomer ratio as in the presence of iodine.

We have studied some chemical properties of polyfluorodihydrobenzothiophenes.

In view of the low yields of the 5-derivatives of compound (*I*) in the co-pyrolysis of 4,4′-disubstituted derivatives of diphenyl disulfide with TFE, it seemed reasonable to develop alternative syntheses of these products. One approach might be found in electrophilic substitution reactions of compound *I*. In this case, the possible orientation could be inferred from the data on orientation in the electrophilic substitution of benzotrifluoride [12] and trifluoromethylphenyl sulfide [13]. In view of meta-orientation in the former case and predominant para-orientation in the latter, one could expect for compound *I* the orientation to be mainly in the 5-position and to a lesser degree, in the 7-position.



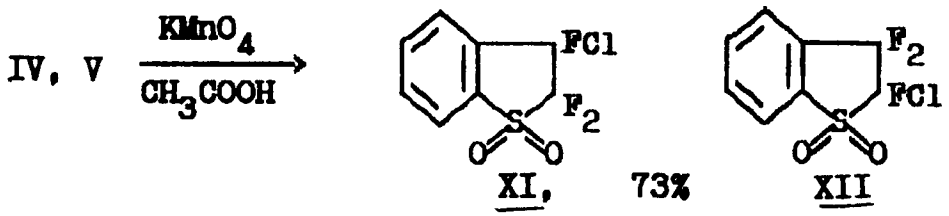
We have shown that the bromination of compound *I* affords the 5-bromo-derivative *II* in a high yield.

With nitric acid, the 5-nitro-derivative *III* was obtained together with the 7-nitro-isomer *VI* and sulfoxide *VII*.

Evidently, *VII* is a product of oxidation of compound *I*. Formation of sulfoxides from the corresponding sulfides with nitric acid is well known [14].

We have also obtained sulfoxide *VII* by oxidation of compound *I* with hydrogen peroxide. With an excess of H_2O_2, the sulfone *VIII* is formed. The latter has also been obtained in the oxidation of *I* or *VII* by potassium permanganate in acetic acid. Similar transformations were performed for the bromo-derivative *II*.

The reactions leading to sulfone formation have been extended to chlorotrifluorodihydrobenzothiophenes:



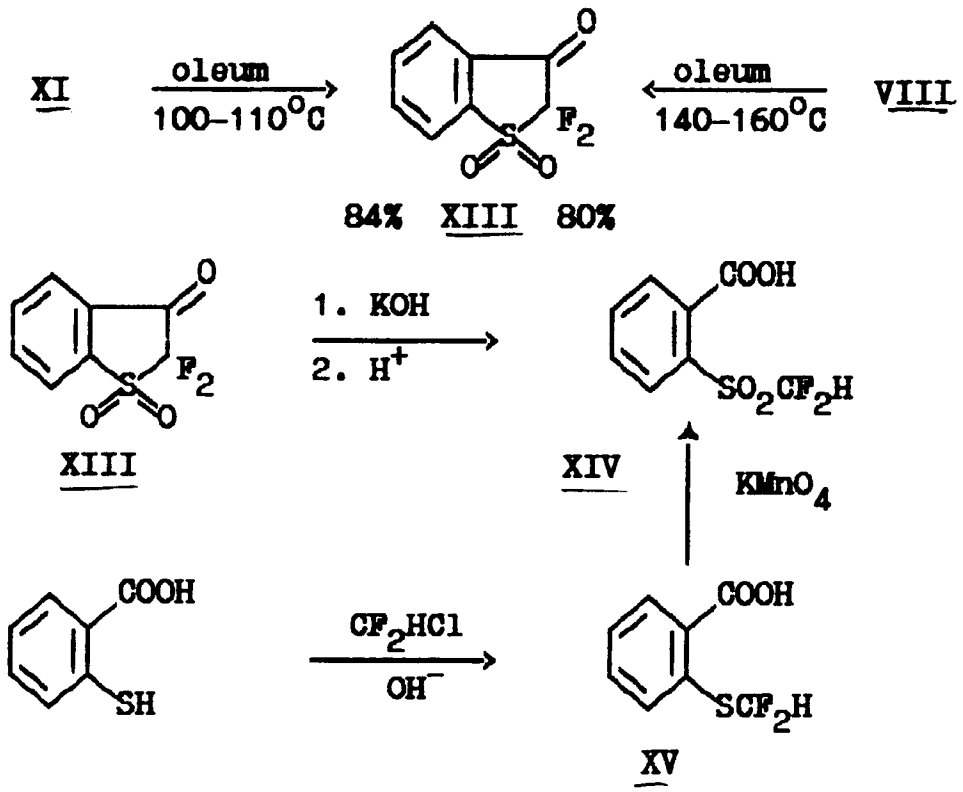
The reaction products are 3-chloro-2,2,3-trifluoro- and 2-chloro-2,3,3-trifluoro-2,3-dihydrobenzo[b]thiophene 1,1-dioxide (*XI*, *XII*). Compound *XI* may be isolated from the reaction mixture. It reacts with 15% oleum to give 3-oxo-2,2-difluoro-2,3-dihydrobenzo-[b]thiophene 1,1-dioxide (*XIII*). The latter was also obtained in the reaction with oleum of the sulfone *VIII*.

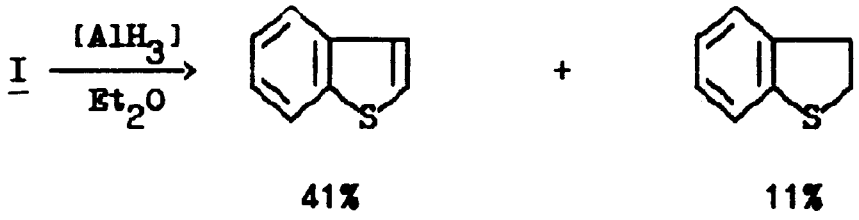
The ketosulfone *XIII* reacts with potassium hydroxide to form 2-(difluoromethylsulfonyl) benzoic acid (*XIV*). The latter was obtained by oxidation of 2-(difluoromethylthio)benzoic acid (*XV*), obtained by reaction of thiosalicylic acid with chlorodifluoromethane in alkaline media.

These transformations confirm the presence of the $—SO_2—CF_2—$ group in compound *XI* and, as a consequence, the $—S—CF_2—$ group in compound *IV*, a major isomer formed in the reactions of thiophenol and diphenyl disulfide with CTFE.

On the reduction of sulfoxide *VII* with zinc in acetic acid, *I* is smoothly formed. The latter was reduced with aluminum hydride (cf. [15]) to benzothiophene and 2,3-dihydrobenzothiophene.

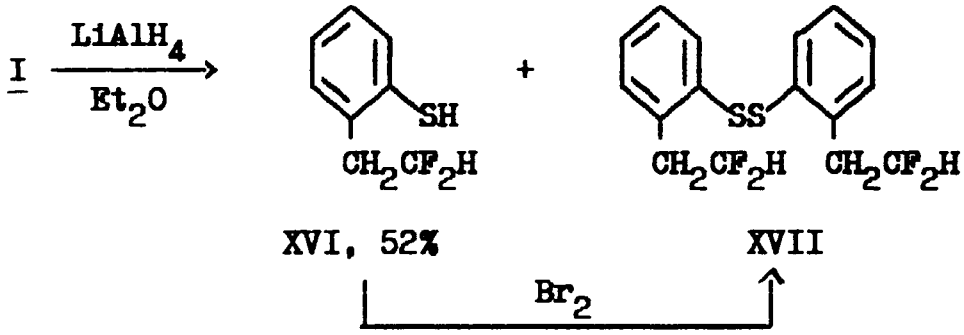
With lithium aluminum hydride, the polyfluorinated heterocyclic ring of I is cleaved. This leads to 2-(2,2-difluoroethyl)thiophenol (*XVI*) and 2,2'-





(2,2-difluoroethyl)diphenyl disulfide (*XVII*). Under certain conditions, the thiophenol *XVI* is the only product:

aluminum hydride, the reductive elimination of bromine takes place along with cleavage of the polyfluorinated heterocyclic ring to give eventually the thiophenol *XVI*.



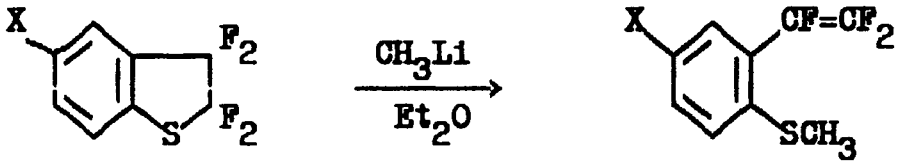
In the presence of bromine, the thiophenol *XVI* is oxidized to the disulfide *XVII* in a yield of 89%.

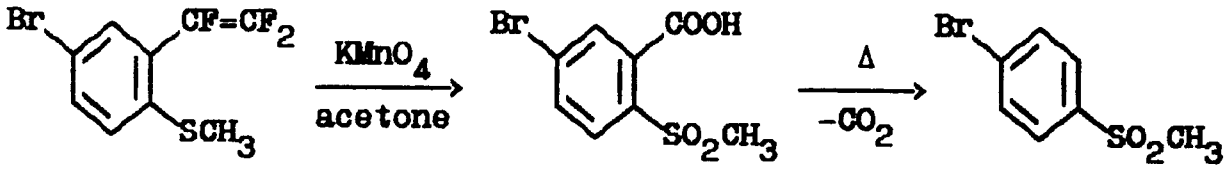
The reaction of compound *I* with methyllithium also leads to five-membered ring cleavage. The reaction product is 2-methylthio-α,β,β-trifluorostyrene (*XVIII*). A similar transformation is also observed for the bromo-derivative *II*, the product being 2-methylthio-5-bromo-α,β,β-trifluorostyrene (*XIX*).

In the reaction of compound *II* with lithium

The structures of the trifluorostyrene products *XVIII* and *XIX* have been confirmed by their oxidation to the corresponding 2-methylsulfonylbenzoic acids. 2-Methylsulfonyl-5-bromobenzoic acid (*XX*) has been decarboxylated to 4-bromophenylmethylsulfone. These findings confirm the orientation in the electrophilic substitution of compound *I*.

The NMR data of the polyfluorodihydrobenzothiophenes are given in Tables 1 and 2. Signal assignments in the ^{19}F NMR spectra of compound





XIX XX

TABLE 1 ^{19}F NMR Spectral Data of Polyfluorodihydrobenzothiophenes and Their Derivatives

Compound	Chemical Shift F^2	Chemical Shift F^3	$J_{F^2F^3}$ [Hz]
I	64.2	49.6	1.8
II	65.3	49.7	2.9
III	67.0	50.0	2.5
IV	63.4(t)	51.6	7.0
	77.3(c)		5.0
	J_{FF} = 198		
V	68.3	38.6(t)	9.0
		70.5(c)	2.0
		J_{FF} = 242	
VI	63.3	51.0	2.0
VIII	39.6	56.7	5.9
X	40.6	56.5	5.6
XI	38.7(t)	60.5	10.0
	52.8(c)		10.0
	J_{FF} = 214		
XII	41.3	45.7(t)	12.5
		74.5(c)	10.0
		J_{FF} = 264	
VII	44.5	58.9	7.0
	47.5	68.2	10.5
	J_{FF} = 220	J_{FF} = 264	9.5
IX	42.2	57.1	7.5
	44.4	61.6	9.5
	J_{FF} = 220	J_{FF} = 267	8.5

I and its sulfone *VIII* were made by comparison of chemical shift variations of fluorine at positions 3 (δ = −8.9) for compounds *IV* and *XI* and 2 (+27.0) for compounds *V* and *XII*, on the assumption that variations of δ^{19} F on going from sulfides *I*, *IV* and *V* to the corresponding sulfones *VIII*, *XI* and *XII* follow a similar tendency. The chemical shift variations for compounds *I* and *VIII* comprise −7.1 and +24.6 ppm, which is close to the values found for the chloro-derivatives *IV*, *XI* and *V*, *XII*. Similar chemical shift variations are also observed for the AB-systems of the geminal fluorine atoms: $\Delta\delta$F = +24.5, $\Delta\delta$F = +24.7 for compounds *IV* and *XI*; $\Delta\delta$F = −4.0, $\Delta\delta$F = −7.1 for compounds *V* and *XII*. Signal assignments of geminal fluorines in one and the same compound were based on the assumption that the chlorine atom affects the chemical shift of the nearest (cis) fluorine atom more than that of the remote (trans) one [16]. Similar signal assignments have been made for the 5-substituted compounds *II*, *III* and *X* (see Table 1).

Signal assignments in the NMR spectra of sulfoxides *VII* and *IX* were based on the assumption that $J_{F^2F^2} < J_{F^3F^3}$, which is observed for sulfones *XI* and *XII*, and was earlier observed for some polyfluoroindanes [17].

As to the NMR spectra of trifluorostyrenes *XVIII* and *XIX* (Table 3), signal assignments were made on the basis of the known order of signals and spin-spin coupling constants, their sequence being $J_{trans} > J_{gem} > J_{cis}$ [20].

Experimental

The ^{19}F and ^{1}H NMR spectra were recorded on a Varian A56/60A instrument, at frequencies 56.4 and 60 MHz, respectively. Internal standards were hexafluorobenzene and hexamethyldisiloxane. The spectra of individual compounds were measured in a 10% CCl_4 solution. The ^{1}H-NMR spectra of individual compounds were recorded on a Bruker WP-200SY instrument at a frequency of 200 MHz in the $CDCl_3$ solution. The IR spectra were measured on an UR-20 instrument for solid samples in KBr pellets at a concentration of 0.25%, for liquids as a film. Molecular weights and molecular formulas of compounds were determined mass-spectrometrically on MS-902 and Finnigan-MAT-8200 instruments. The nominal energy of ionizing electrons was 70 and 10 eV.

The GLC analyses were carried out on an "LHM-72" instrument with a thermal conductivity detector having linear programming of temperature 10°C per minute. The carrier gas was helium. Flow rate 60 ml/min. The columns 4000 × 4 mm (the solid carrier chromosorb W) a) silicon SKTFT-

TABLE 2 ^{1}H-NMR Spectral Data of Polyfluorodihydrobenzothiophenes and Their Derivatives

Compound	Chemical Shifts δ H^4	H^5	H^6	H^7	Spin-Spin Coupling Constants [Hz] H^4H^5	H^4H^6	H^5H^6	H^5H^7	H^6H^7
I	7.56	7.30	7.50	7.22	7.5		8.0		8.0
II	7.66		7.58	7.07		1.8			8.5
III	8.41		8.39	7.45					8.0
VI	8.07	7.64	8.55		7.5		8.0		
VIII	7.84	7.84	7.84	7.84					
X	8.05		8.02	7.80		~ 1			9.0
VII	7.75	7.85		7.92					~ 7
IX	7.96		7.96	7.82		1.3			8.5
XIII	8.14	8.08	7.95	8.08	6.5		7.5	2.5	8.0

TABLE 3 ^{19}F and ^{1}H NMR Spectral Data of Ortho-Substituted Trifluorostyrenes

Compound	XVIII	XIX
δF^{α}	1.3	0.35
δF^{β}_{trans}	58.4	61.2
δF^{β}_{cis}	44.4	46.9
J_{trans}	118	120
J_{gem}	74.5	70.5
J_{cis}	29.5	31.5
δH^{3}	7.05	7.13
δH^{4}	7.05	7.50
δH^{5}	7.05	—
δH^{6}	7.05	7.47

50, b) silicon SKTFV-803, c) methylsilicon E-301, d) fluorosilicon QF-1. The ratio of stationary phase to solid carrier was 15 : 100, column temperature 50–270°C, detector temperature 250°C. The components were identified by additions of authentic known compounds.

Methods of the Pyrolysis Experiments

The methods are similar to those described in ref. [21]. The experimental results are given in Table 4. The individual compounds were isolated by vacuum distillation (10–12 mm Hg). The analytical samples were obtained by preparative GLC (under conditions of analytical GLC).

Preparation of the Bromo Derivative II

Compound *I* (4.65 g) is dissolved in 60 ml of carbon tetrachloride, 0.2 g of iron is added, and a solution of 4.17 g of bromine in 10 ml of carbon tetrachloride is added dropwise with stirring for 0.5 hr with gradual heating of the reaction mixture to boiling. After the addition is complete, the mixture is refluxed with stirring for 4.5 hr. The resulting mixture is treated with $Na_2S_2O_5$ solution (20 g in 100 ml of water) until the color has been discharged, then with water. The organic layer is separated and dried with magnesium sulfate. The solvent is removed, and the residue distilled *in vacuo* (14 mm Hg) to give 5.97 g of a fraction with bp 80–81°C containing 88% of compound *II* as shown by the GLC data. Found: M 285.9091 $C_8H_3BrF_4S$. Calculated: M 285.9075.

Reaction of Compound I with Nitric Acid

Compound *I* (0.98 g) is added dropwise to 1.5 g of 100% nitric acid cooled down to 0°C, in such a way as to keep the temperature of the reaction mixture below +5°C. The mixture is allowed to stand at this temperature for 15 min and then poured onto ice. After separation, 1.18 g of a liquid is obtained containing 30% of compound *VII* and 67.5% of a mixture of nitro-isomers in the ratio 4 : 1 with predominant content of the 5-nitro-derivative (according to the ^{19}F NMR spectrum).

The reaction mixture (1.59 g) is chromatographed on a silica gel column (140–315 μm). The eluent is carbon tetrachloride. This gives 0.58 g of a fraction containing compound *III* and 0.10 g of a fraction containing compound *VI*.

Compound *III*: mp 74–75°C (hexane). IR spectrum: 1350, 1545 cm^{-1} (the NO_2 group). Found: M 252.9878 $C_8H_3F_4NO_2S$. Calculated: M 252.9820.

Compound *VI*: mp 171–173°C (in a sealed capillary). Found: M 252.9860.

Oxidation of Compound I with Hydrogen Peroxide

Compound *I* (82.2 g) is mixed with 415 ml of acetic acid and 95 g of 33% hydrogen peroxide and the mixture is heated on a boiling water bath for 24 hr. The reaction mixture, cooled to room temperature, is poured into 4.5 l of water. The liquid organic layer, 56.15 g, is separated, dried with magnesium

TABLE 4 Co-Pyrolysis of Thiophenol and Diaryl Disulfides with Polyfluoroolefins (Quartz Tube 400 × 15 mm)

Compound	Amount, g	Olefin	Time, min	Addition, g	Temperature °C	Yield of Reaction Mixture, g	Composition of Reaction Mixture, %	
							Product	Substrate
Thiophenol	2.39	TFE	8	I_2, 0.74	340–370	2.24	I, 79	12
Thiophenol	1.43	TFE	7	DMSO, 0.51	360–370	1.11*	I, 72	—
Diphenyl disulfide	689	TFE	770	I_2, 74.0	330–370	350**	I, 90	2.4
4,4′-dibromodiphenyl disulfide	4.12	TFE	13	I_2, 0.95	340–350	1.00	II, 68	—
4,4′-dinitrodiphenyl disulfide	1.02	TFE	11	I_2, 0.47	370–380	0.40	III, 57	—
Thiophenol	2.87	CTFE	7	I_2, 0.96	350–370	2.00	IV + V, 47	5.3
Thiophenol	2.76	CTFE	9	DMSO, 0.97	350–370	1.92	IV + V, 23	—
Diphenyl disulfide	11.94	CTFE	47	I_2, 2.96	350–360	12.89	IV + V, 33	30

* Residue 0.99 g contains 55% of diphenyl disulfide.
** Residue 517 g contains 70% of the starting diphenyl disulfide.

sulfate and analysed by GLC (84% of compound *VII* and 11% of sulfone *VIII*. The aqueous layer is extracted with methylene chloride. From the extract, 5.36 g of a liquid containing 93% of compound *VII* and 6% of compound *VIII* is isolated. The aqueous layer is then neutralized with sodium carbonate to give 14.23 g of practically pure sulfoxide *VII*. The continuous extraction of the aqueous layer with benzene affords an additional 3.12 g of sulfoxide *VII*, bp 124–125°C (14 mm Hg). Found: M 223.9919 $C_8H_4F_4OS$. Calculated: M 223.9919.

Oxidation of Compound II with Hydrogen Peroxide

Compound *II* (9.41 g) is mixed with 70 ml of acetic acid and 1.08 g of 33% hydrogen peroxide, heated for 5 hr on a boiling water bath and allowed to stand overnight. The solvent is then distilled off *in vacuo* at 14 mm Hg; the residue, 9.01 g, contains 62.6% of the starting compound and 32.7% of the sulfoxide *IX* according to the GLC data. The resulting mixture is distilled *in vacuo* (19 mm Hg) to give 3.00 g of a fraction containing 94% of compound *IX*, mp 70–70.5°C (hexane). Found: M 301.9030 $C_8H_3BrF_4OS$. Calculated: M 301.9025.

Oxidation of Compound I with Potassium Permanganate

Tetrafluorodihydrobenzothiophene *I* (3.00 g) is added with vigorous stirring to a suspension of 13.5 g of potassium permanganate in 200 ml of acetic acid. The mixture is refluxed with vigorous stirring for 9 hr. Then 40 ml of water is added to the mixture cooled to room temperature, and an SO_2 current is passed through it until the reaction mixture is decolourized. A precipitate is filtered off. Then 80% of the solvent is removed from the filtrate on a rotary evaporator and the residue is poured into a ten-fold excess of water. The organic layer (1.92 g of *VIII*) is isolated and separated, and the aqueous layer is neutralized with sodium carbonate until it is weakly alkaline and then it is extracted with ether. The ethereal layer is separated from the aqueous layer and dried with magnesium sulfate. The solvent is evaporated to give an additional 1.20 g of sulfone *VIII*, bp 70–75°C/5 mm Hg. Found: M 239.9865 $C_8H_4F_4O_2S$. Calculated: M 239.9868.

Oxidation of Compound II with Potassium Permanganate

Tetrafluorodihydrobenzothiophene *II* (5.01 g) is added with vigorous stirring to a suspension of 21.80 g of potassium permanganate in 300 ml of acetic acid. The mixture is refluxed with vigorous stirring for 8.5 hr. Then it is treated as described above, 4/5 of the solvent is evaporated and the residue poured into a ten-fold volume of water. The mixture is neutralized until it is weakly alkaline and extracted with ether. The ethereal layer is separated and dried with magnesium sulfate. The solvent is removed. The residue, 5.23 g, is practically pure sulfone (*X*), mp 100–101.5°C (pentane). Found: M 317.8966. $C_8H_3BrF_4O_2S$. Calculated: M 317.8973.

Oxidation of a Mixture of Chlorotrifluorodihydrobenzothiophenes IV and V with Potassium Permanganate

A mixture of compounds (*IV*) and (*V*) (3.00 g) is added with vigorous stirring to a suspension of 13.47 g of potassium permanganate in 20 ml of acetic acid. The reaction mixture is refluxed with stirring for 10 hr. Then it is treated as described above, and 2.50 g of an organic layer is isolated. The latter is allowed to stand, whereupon a solid product crystallizes out. The product is filtered off and 0.46 g of the mother liquor is separated which is a mixture of isomeric sulfones *XI* and *XII*. The precipitate on the filter is washed with pentane to give 1.24 g of sulfone *XI*, mp 45–46.5°C. Found: M 255.9646 $C_8H_4ClF_3O_2S$. Calculated: M 255.9572. After removal of pentane, and additional 0.51 g of a mixture of sulfones *XI* and *XII* is obtained.

Reaction of Compounds VIII and XI with Oleum

a) The sulfone *VIII* (0.40 g) and 15% oleum (0.2 ml) are heated at 140–160°C for 13 hr in a sealed tube. The mixture is cooled and poured onto 4 g of ice. The brownish red precipitate is filtered off, dried and sublimed at 100°C/1 mm Hg to give 0.21 g of compound *XIII*. The filtrate is extracted with ether, the organic layer is separated and dried over magnesium sulfate. The solvent is removed to give an additional 0.15 g of compound (*XIII*), mp 88.5–90°C (hexane). Found: M 217.9826 $C_8H_4F_2O_3S$. Calculated: M 217.9849.

b) The sulfone *XI* (2.50 g) and 1.3 ml of oleum are heated in a sealed tube at 100–110°C for 5 hr. After the mixture has been cooled, it is poured onto 30 g of ice. The precipitate is filtered off and dried. This gives 1.00 g of colourless crystals of compound *XIII*. The filtrate is extracted with ether, the organic layer is separated and dried over magnesium sulfate. After the solvent has been removed, an additional 0.80 g of compound *XIII* is obtained. The total yield is 84%. The product is purified by recrystallization from hexane. As shown by its ^{19}F-NMR and IR spectra, the compound is identical with that obtained in experiment a). A mixture mp test does not give a depression of the melting point.

Reduction of Sulfoxide (VII)

A mixture of 0.53 g of zinc, 5 ml of acetic acid and 0.47 g of sulfoxide *VII* is refluxed with vigorous stirring for 5 hr. After the mixture has been cooled to room temperature, it is poured into 100 ml of water, and 2 ml of concentrated hydrochloric acid is added to dissolve the zinc residue; 0.33 g of practically pure compound *I* is isolated.

Reduction of Compound I with Aluminum Hydride

Aluminum chloride (17.38 g) is suspended in 600 ml of absolute ether. The resulting suspension is cooled to −30°C, then 26.49 g of lithium aluminum hydride is added. The mixture is warmed to room temperature, and 3.00 g of compound *I* is added with vigorous stirring. The mixture is stirred at room temperature for 18 d. After stirring has been completed, 90 ml of water is added, then 60 ml of conc. HCl. The ethereal solution is separated and dried with $MgSO_4$. The solvent is removed on a rotary evaporator. The residue, 1.51 g, contains 50% of benzo[b]thiophene and 13% of 2,3-dihydrobenzo[b]thiophene (the remaining components were not identified. The amount of the main component is less than 3% of the theoretical yield).

Reaction of Compound I with Lithium Aluminum Hydride

Compound (*I*) (6.38 g) is dissolved in 700 ml of absolute ether in an argon current. Lithium aluminum hydride (2.15 g) is added with stirring. The mixture is stirred at room temperature in the argon current for 6 d. Then water and 10% hydrochloric acid are added to the reaction mixture in sequence and the mixture is stirred until two colourless layers are obtained. The aqueous layer is separated from the ethereal one and extracted with ether. The combined organic layer is treated with 10% NaOH solution. The resulting alkaline solution is separated and neutralized under an ethereal layer with 10% hydrochloric acid until pH < 1. The aqueous layer is separated and extracted with ether. The combined organic layer is dried over magnesium sulfate. The solvent is removed. The residue, 3.60 g, contains, according to the GLC data, 76% of thiophenol *XVI* and 21% of diethyl ether. The thiophenol is purified by vacuum distillation, bp 84–87°C/5 mm Hg. Found, %: C 55.3, 55.4; H 4.5, 4.7; F 21.5, 21.6; S 18.3, 18.5. M 174, $C_8H_8F_2S$. Calculated, %: C 55.2, H 4.6; F 21.8; S 18.4. M 174. ^{19}F NMR, $\delta = 47.9$ ($J_{FH^2} = 56.5$, $J_{FH^1} = 16.5$ Hz). ^1H-NMR, $\delta = 3.13$ (SH), 3.09 (CH_2, $J_{H^1H^2} = 4.5$ Hz), 6.00 (CHF_2), 7.00 ($4H_{Ar}$).

Reaction of a Mixture of Chlorotrifluorodihydrobenzothiophenes IV and V with Lithium Aluminum Hydride

A mixture of compounds *IV* and *V* (1.0 g) (isomer ratio 5 : 1) was reacted with 1.3 g of lithium aluminum hydride (3 d) as described above to give 1.98 g of a mixture containing the thiophenol *XVI*, the disulfide *XVII*, as well as benzo[b]thiophene and 2,3-dihydrobenzo[b]thiophene in the ratio of 8.7 : 4.4 : 6.0 : 1.9 respectively. Their total content is 21% of the theoretical yield. The rest is diethyl ether.

Oxidation of the Thiophenol XVI with Bromine

A solution of 0.48 g of bromine in 1.2 ml of acetic acid is added dropwise with stirring to a mixture of 1.07 g of the thiophenol *XV* and 6 ml of acetic acid. The reaction mixture is allowed to stand overnight. Then it is poured into 200 ml of water and $Na_2S_2O_5$ is added to remove the excess bromine. Then Na_2CO_3 is added until the pH = 8. The mixture is extracted with ether. The extract is separated and dried over magnesium sulfate. The solvent is then removed. The residue, 0.98 g, contains, according to the GLC data, 92% of the disulfide (*XVII*) which is purified by column chromatography on 140–315 μm silica gel. The eluent is carbon tetrachloride. This gives 0.21 g (the amount of the disulfide *XVII* 94%) and 0.54 g (the amount of the disulfide *XVII* 98%) of a liquid product. Found: M 346.0494 $C_{16}H_{14}F_4S_2$. Calculated: M 346.0473. ^{19}F NMR, $\delta = 47.8$ ($J_{FH^2} = 56.5$ Hz, $J_{FH^1} = 16.3$ Hz). ^1H-NMR, $\delta = 3.17$ (CH_2, $J_{H^1H^2} = 4.5$ Hz), 5.68 (CHF_2), 7.13 ($4H_{Ar}$).

Reaction of Compound I with Methyllithium

A solution of methyllithium in absolute ether obtained from 15.6 g of methyl iodide and 1.65 g of lithium by the methods of reference [22] is added slowly (0.5 hr) to a solution of 7.96 g of compound *I* in 200 ml of absolute ether at 20°C. After the addition is complete, the mixture is stirred for 2 hr at 20°C. Then the reaction mixture is treated with hydrochloric acid, the organic layer is washed and dried over magnesium sulfate. This affords 7.69 g of the reaction mixture containing 67.5% of the styrene *XVIII*. The pure compound is isolated by preparative GLC. Found: M 204.0226 $C_9H_7F_3S$. Calculated: M 204.0220.

Reaction of Compound II with Methyllithium

Similarly to the previous procedure, 28.9 g of compound *II* was treated with methyllithium obtained from 20.7 g of methyl iodide and 1.05 g of lithium

to give 30.9 g of a reaction mixture containing 58.9% of the styrene *XIX*, 24.5% of the starting compound and 9.5% of diethyl ether. The mixture is fractionated *in vacuo* (2 mm Hg) to give 4.2 g (the yield of the styrene *XIX* 79%), 4.0 g (the yield of the styrene *XIX* 95%) and 1.9 g (the yield of the styrene *XIX* 93%) of the product. The pure compound *XIX* is isolated by column chromatography on neutral aluminum oxide. The eluent is hexane. Found: M 281.9335 $C_9H_6BrF_3S$. Calculated: M 281.9326.

Oxidation of the Styrene XIX with Potassium Permanganate

To a solution of 3.90 g of compound *XIX* in 80 ml of acetone, 10.7 g of sodium bicarbonate is added, and then a solution of 8.75 g of potassium permanganate in 700 ml of acetone is added with stirring at room temperature (2 hr). The mixture is stirred for 5 hr and allowed to stand overnight. The solution is then concentrated to dryness, and 13.5 g of sodium pyrosulfite in 130 g of 15% of sulfuric acid is added to the residue. When stirred, the mixture gradually loses colour. When the mixture is allowed to stand, a liquid organic layer separates. It is isolated, and the aqueous layer is extracted with ether (3 × 75 ml). After the solvent has been evaporated from the extract, 0.78 g of the acid *XX* is obtained. The organic layer is dissolved in 50 ml of ether and the resulting solution is washed with 200 ml of water, then with 10% sodium carbonate solution (50 ml). The aqueous solution is evaporated to dryness, and the residue treated with diethyl ether. The ethereal solution is evaporated to give an additional 1.47 g of product *XX*. The sodium carbonate extract is acidified with hydrochloric acid to pH < 1. In this process, the acid *XX* precipitates, and the precipitate is filtered off to give 1.01 g. The mother solution is extracted with diethyl ether (3 × 50 ml). The solvent is removed, and an additional 0.43 g of acid (*XX*) is obtained. The total yield is 3.69 g of the crude product. Mp 178–180°C (recrystallization from water). Found, %: C 34.3; 34.5; H 2.4, 2.6; Br 28.4, 28.5; S 11.6, 11.8. M 279, $C_8H_7BrO_4S$. Calculated, %: C 34.4; H 2.5; Br 28.6; S 11.5. ^{1}H-NMR, δ = 3.05 (SO_2CH_3), 7.53 (H^4, $J_{H^4H^3}$ = 8.5 Hz, $J_{H^4H^6}$ = 2.0 Hz), 7.62 (H^6), 7.67 (H^3).

Decarboxylation of the Acid XX

The compound *XX* (0.32 g) is heated in an evacuated tube (1 mm Hg) at 350–370°C for 8 hr. After the compound has been cooled, it is treated with chloroform. The solvent is removed from the extract. The residue, 0.18 g, is pure 4-bromophenylmethylsulfone, mp 100–101°C [23]. The IR spectrum is identical with that of the authentic sample [24]. ^{1}H-NMR, δ = 3.02 (SO_2CH_3), 7.68 ($2H_{Ar}$), 7.78 ($2H_{Ar}$).

Reaction of Compound XIII with Potassium Hydroxide

Compound *XIII* (477 mg) is mixed with a solution of 149 mg of potassium hydroxide in 3.8 ml of water. The resulting solution is heated at 40–45°C for 5 hr. The mixture is then evaporated to dryness at a pressure of 14 mm Hg, and the residue is treated with ether and hydrogen chloride. The ethereal solution is separated and evaporated to give 468 mg of 2-difluoromethylsulfonylbenzoic acid. The product is purified by sublimation at 120°C (2 mm Hg). Mp 138.5–140°C. Found: M 236.0005 $C_8H_6F_2O_4S$. Calculated: M 235.9955. ^{1}H-NMR, δ = 6.95 (SO_2CF_2H, J_{HF} = 54.8 Hz), 7.81, 8.00, 8.26 ($4H_{Ar}$). ^{19}F NMR, δ = 39.8.

Preparation of 2-Difluoromethylthiobenzoic Acid (XV)

Thiosalicylic acid (4.0 g) is mixed with a suspension of 8.4 g of sodium hydroxide in 40 ml of aqueous dioxane (2:1 v/v). The mixture is heated to 70°C, and chlorodifluoromethane is bubbled through with vigorous stirring at a rate of 5 l/hr for 7 hr. After the reaction mixture has been cooled, it is poured into 800 ml of 15% hydrochloric acid. Then it is treated with 400 ml of methylene chloride. The organic layer is separated and the solvent is removed. This gives 4.07 g of the crude product. Mp 153.5–155°C (chromatography on silica gel 140–250 μm, eluent is methylene chloride). Found: M 204.0051 $C_8H_6F_2O_2S$. Calculated: M 204.0056. ^{1}H-NMR, δ = 7.01 (SCF_2H, J_{HF} = 56.6 Hz), 7.41, 7.55, 7.62, 8.08 ($4H_{Ar}$). ^{19}F NMR, δ = 68.7.

Oxidation of the Acid XV

2-Difluoromethylthiobenzoic acid (*XV*) (0.37 g) is added with stirring to a suspension of 2.28 g of potassium permanganate in 250 ml of acetone. The mixture is stirred at room temperature for 6 d. Then 10 ml of 10% sulfuric acid is added to it, and an SO_2 current is passed through it until the mixture is decolourized. The solvent is then evaporated and the residue treated with chloroform. The solution is evaporated to give 0.26 g of 2-difluoromethylsulfonylbenzoic acid (*XIV*). According to its ^{19}F NMR and IR spectra, the compound is identical with the one obtained by the hydrolysis of the ketosulfone *XIII*.

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