

# TRANSFORMATIONS OF POLYFLUOROARENESULFONYL HALIDES WITH ALKENES, POLYFLUOROARENETHIOLS AND ALKALI METAL HALIDES

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**Abstract:** The reactions of polyfluoroarenesulfonyl chlorides or bromides with polyfluoroarenethiols gave mixtures of polyfluorinated diaryl disulfides, whereas replacement of fluorine atom at the 4-position of aromatic ring of C<sub>6</sub>F<sub>5</sub>SO<sub>2</sub>F occurred. The reactions of polyfluoroarenesulfonyl chlorides or bromides with some *n*-nucleophiles such as alkali metal halides probably proceed with electron transfer.

The reactions of polyfluoroarenesulfonyl bromides with alkenes such as hexene-1 or allyl chloride provided the corresponding adducts in high yields, while the conversion of polyfluoroarenesulfonyl chlorides at the same conditions was poor and C<sub>6</sub>F<sub>5</sub>SO<sub>2</sub>F was unreactive. The reaction of polyfluoroarenesulfonyl bromides with allyl bromide resulted in allyl polyfluoroaryl sulfones. The formation of the products in reactions of polyfluoroarenesulfonyl bromides with alkenes apparently occurs with participation of polyfluoroarenesulfonyl radicals.

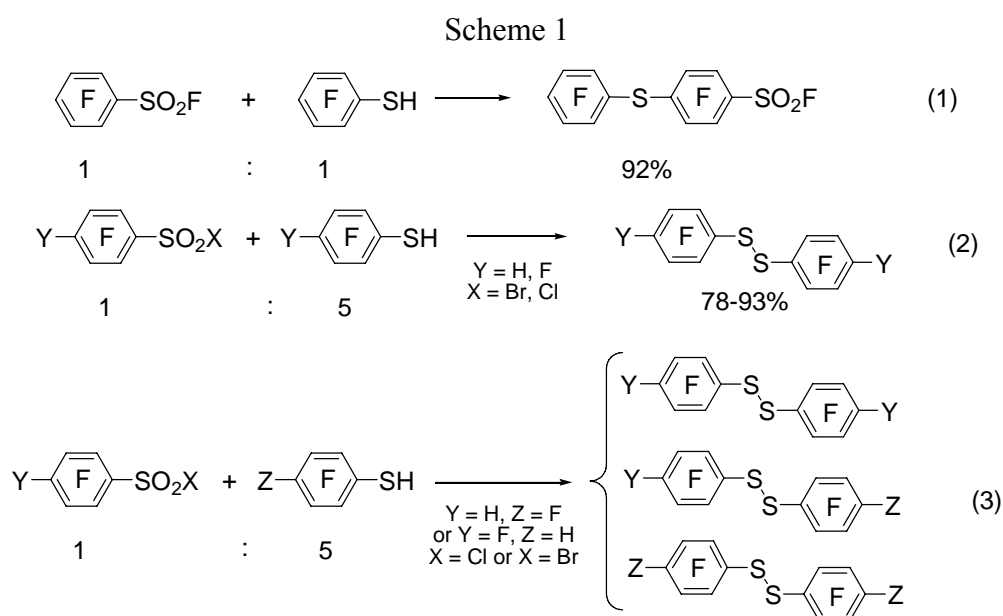
**Keywords:** polyfluoroaromatic compounds, sulfonyl bromide, sulfonyl chloride, alkenes, radical addition, allyl polyfluoroaryl sulfone, thiols, metal halides, electron transfer, diaryl disulfide

## INTRODUCTION

Non-fluorinated arenesulfonyl chlorides and bromides are widely used in organic synthesis. For example, these compounds readily react with amines<sup>1</sup> or alcohols<sup>2</sup> and undergo the addition reaction to the double bond<sup>3</sup>. Some transformations of polyfluorinated arenesulfonyl chlorides were also described. So, pentafluorobenzenesulfonyl chloride reacted with amines, alcohols, potassium fluoride to give the corresponding sulfonamides<sup>4</sup>, esters<sup>5</sup>, sulfonyl fluoride<sup>6</sup>. At the same time little there is few knowledge about the chemistry of polyfluoroarenesulfonyl bromides<sup>7</sup>. Recently we have shown that polyfluoroarenesulfonyl bromides could be obtained by reaction of polyfluoroarenethiols with bromine and nitric acid<sup>8</sup>. Among the chemical transformations of polyfluoroarenesulfonyl halides their reactions with nucleophiles are of great interest as a result of wide variety of different products that could be obtained. Hence, some reactions of polyfluorinated arenesulfonyl halides with polyfluoroarenethiols, alkali metal halides and alkenes are presented in this paper.

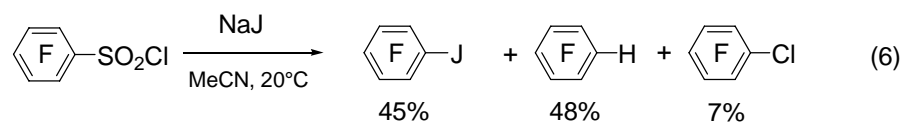
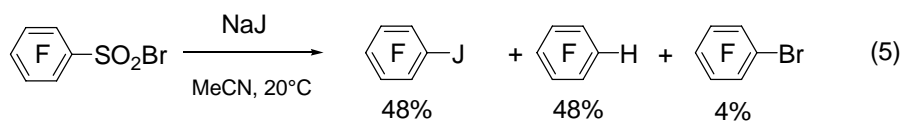
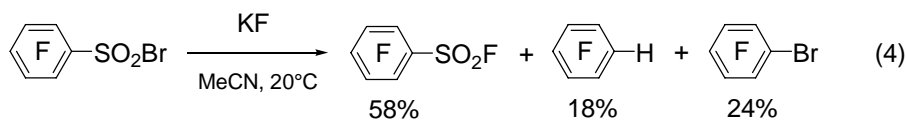
## RESULTS AND DISCUSSION

Polyfluoroarenesulfonyl halides like sulfonic acid anhydrides could be acylating agents for polyfluoroarenethiols. Nevertheless, the reaction of pentafluorobenzenesulfonyl fluoride and pentafluorobenzenethiol gave only the product of substitution of fluorine atom at the 4-position of sulfonyl fluoride (eqn. (1), Scheme 1). The same reaction route is usually observed for reactions of pentafluorobenzenesulfonyl fluoride with nucleophiles<sup>9</sup>. Unexpectedly, the reaction of pentafluorobenzenesulfonyl chloride or sulfonyl bromide with pentafluorobenzenethiol gave only decafluorodiphenyl disulfide. The similar result has been obtained in reactions of 2,3,5,6-tetrafluorobenzenesulfonyl chloride or sulfonyl bromide with 2,3,5,6-tetrafluorobenzenethiol (eqn. (2), Scheme 1). The reactions of polyfluoroarenesulfonyl halides with polyfluoroarenethiols carrying different substitutes in aromatic rings gave mixture of all possible diaryl disulfides (eqn. (3), Scheme 1).



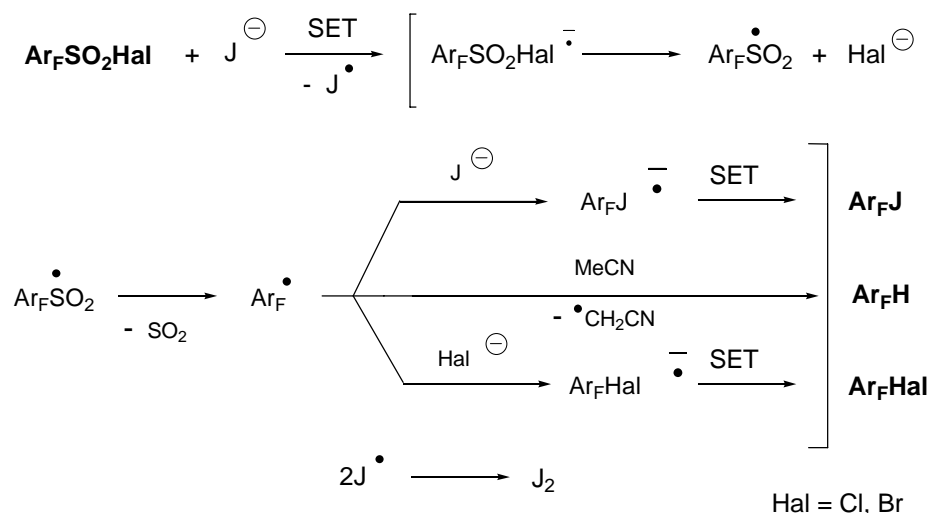
While the reaction of pentafluorobenzenesulfonyl chloride with potassium or sodium fluoride gave the corresponding sulfonyl fluoride<sup>9</sup>, the reaction of pentafluorobenzenesulfonyl bromide with potassium fluoride unexpectedly provided significant amounts of pentafluorobenzene and bromopentafluorobenzene alongside the expected sulfonyl fluoride (eqn. (4), Scheme 2). Reaction of pentafluorobenzenesulfonyl bromide with sodium chloride or pentafluorobenzenesulfonyl chloride with sodium bromide also gave mixtures of sulfonyl halides, halogenpolyfluoroarenes and pentafluorobenzene. As it turned out, pentafluorobenzene and iodopentafluorobenzene were the major products in reaction of pentafluorobenzenesulfonyl bromide or pentafluorobenzenesulfonyl sulfonyl chloride with sodium iodide alongside insignificant amounts of the corresponding halogenpentafluorobenzenes (eqn (5) and (6), Scheme 2).

Scheme 2



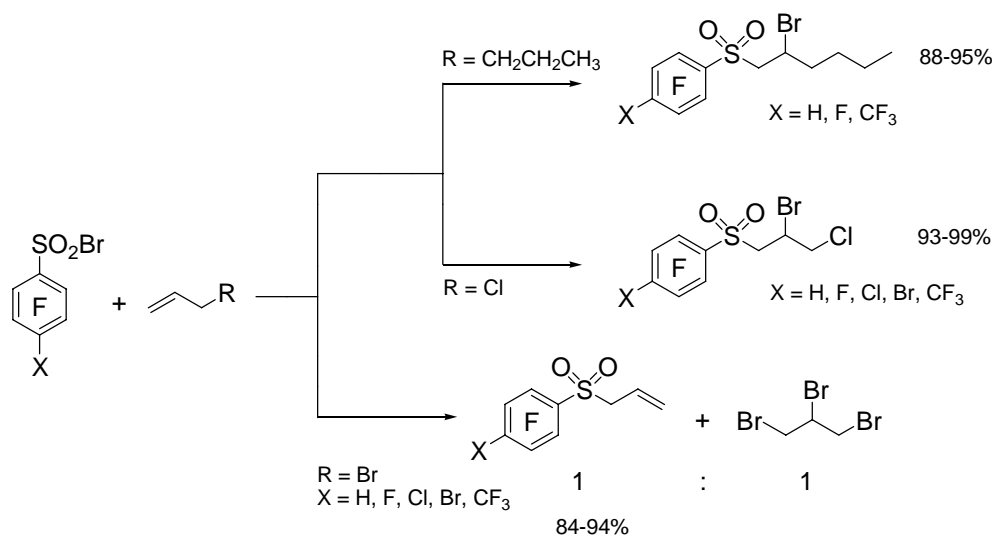
It could be suggested that at first sulfonyl halide forms radical anion as a result of the electron transfer from the iodide-anion. The radical anion formed undergoes fragmentation with formation of halide-anion and polyfluoroarenesulfonyl radical. The latter obviously transforms into the polyfluoroaryl radical, which reacts with a nucleophile or with a solvent with formation of reaction products (Scheme 3).

Scheme 3



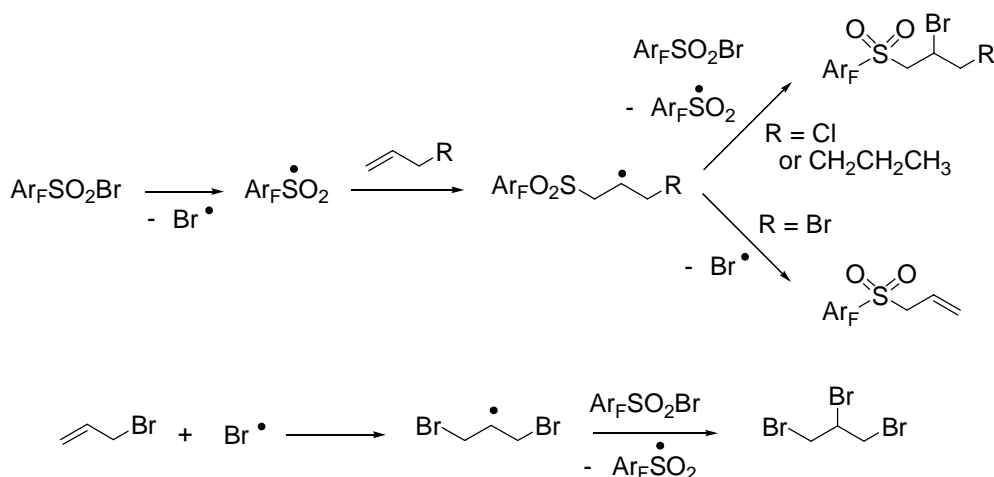
Thereupon it seemed reasonable to study the reactions of polyfluoroarenesulfonyl halides with  $\pi$ -nucleophiles. We have shown that reaction of polyfluoroarenesulfonyl bromides with hexene-1 at room temperature and scattered daylight irradiation give the adducts in high yields. The same transformations were observed in reaction of polyfluoroarenesulfonyl bromides with allyl chloride at room temperature or on heating in a sealed tube. At the same time the reaction of polyfluoroarenesulfonyl bromides with allyl bromide suddenly provided allyl polyfluoroaryl sulfones and 1,2,3-tribromopropane in high yields (Scheme 4).

Scheme 4



The possible route of the process could be illustrated by the following scheme. Polyfluoroarenesulfonyl radical formed as a result of homolytic cleavage of sulfur-bromine bond adds to the double bond of alkene. The radical thus formed probably reacts with sulfonyl bromide to form the reaction product and another polyfluoroarenesulfonyl radical. An other way is observed when bromine is in the neighboring position to the radical center. In this case the elimination of bromine occurs with formation of allyl polyfluoroaryl sulfone (Scheme 5). The evidence in favor of radical nature of the process is catalysis of the process by copper(I) salts, increasing the rate of the process under scattered daylight irradiation and inhibition of the process in the presence of hydroquinone. It should be noted that conversion of pentafluorobenzenesulfonyl chloride in such process is low, even in presence of copper(I) iodide as a catalyst.<sup>10</sup>

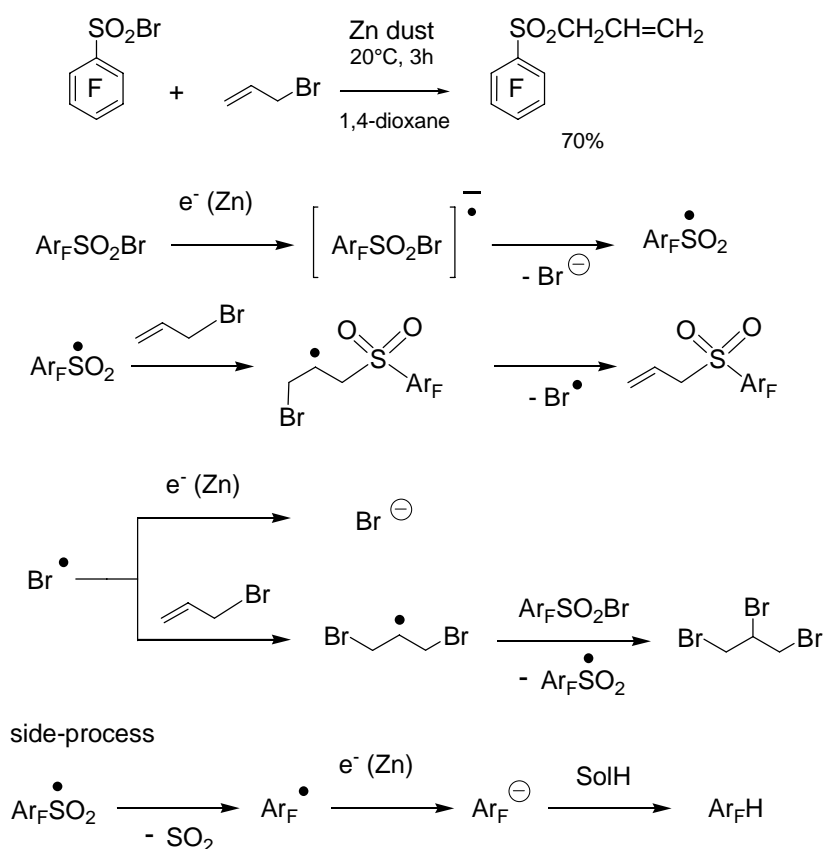
Scheme 5



It seemed reasonable to obtain allyl polyfluoroaryl sulfones at room temperature without the formation of 1,2,3-tribromopropane. It was previously shown that the formation of allyl aryl sulfones was observed in reaction of benzenesulfonyl chloride with allyl bromide in the presence of indium<sup>11</sup>. It turned out that the reaction of pentafluorobenzenesulfonyl bromide with allyl bromide in the presence

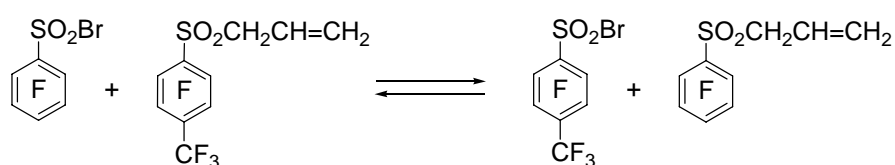
of zinc dust in 1,4-dioxane gave allyl pentafluorophenyl sulfone in 70% yield without the side formation of 1,2,3-tribromopropane. Zinc seems to work as an initiator. Polyfluoroarenesulfonyl bromide forms apparently radical anion by the action of zinc and, finally, polyfluoroarenesulfonyl radical. It is possible, that the decrease of the amount of tribromopropane formed is a result of the reaction of bromine with zinc with formation of bromide-anion. The other solvents used (MeCN, Et<sub>2</sub>O) demonstrated preferable formation of pentafluorobenzene, while in hexane no reaction was observed.

Scheme 6



Polyfluoroarenesulfonyl bromides could also react with allyl polyfluoroaryl sulfones. A mixture of pentafluorobenzenesulfonyl bromide and allyl 4-trifluoromethylphenyl sulfone was heated for 24h to give a mixture of 4-trifluoromethyl-2,3,5,6-tetrafluorobenzenesulfonyl bromide and allyl pentafluorophenyl sulfone alongside with the starting compounds. The analogous result was obtained when a mixture of 4-trifluoromethyl-2,3,5,6-tetrafluorobenzenesulfonyl bromide and allyl pentafluorophenyl sulfone was heated in the same conditions. Thus, the reversibility of allyl polyfluoroaryl sulfone formation could be suggested (Scheme 7).<sup>10</sup>

Scheme 7



## EXPERIMENTAL

$^{19}\text{F}$  and  $^1\text{H}$  NMR spectra were recorded on a Bruker AV-300 instrument at 282 and 300 MHz respectively for solutions in  $\text{CCl}_4$  with addition of acetone- $d_6$ . Chemical shifts are given in  $\delta$  (ppm); the internal standards were  $\text{C}_6\text{F}_6$  (-162.9 ppm from  $\text{CCl}_3\text{F}$ ) and HMS (0.04 ppm from TMS). The  $^{19}\text{F}$  and  $^1\text{H}$  chemical shifts are reported vs.  $\text{C}_6\text{F}_6$  and TMS. Coupling constants ( $J$ ) are given in Hz. IR spectra were measured on a Bruker Vector 22 IR spectrophotometer. UV spectra were recorded on a Hewlett Packard 8453 UV spectrophotometer for solutions in hexane. High resolution mass spectra were recorded on the Thermo DFT mass-spectrometer (EI mode, 70eV). GC-MS analyses were performed with a Hewlett-Packard G1800A system consisting of an HP 5890 Series II gas chromatograph and an HP 5971 mass selective detector (HP-5 capillary column, 30 m  $\times$  0.25 mm, stationary phase 5% of diphenyl- and 95% of dimethylpolysiloxane; carrier gas helium, flow rate 1 mL/min; injector temperature 280°C; ion source temperature 173°C, EI mode, 70eV, a.m.u. range 30–650). The melting points were determined on a Kofler hot stage apparatus. Polyfluoroarenethiols were synthesized according to literature data<sup>12,13</sup>. Polyfluoroarenesulfonyl bromides were obtained as described<sup>8</sup>.

*Reactions of polyfluoroarenesulfonyl halides with polyfluoroarenethiols.* General procedure. A solution of polyfluoroarenethiol in MeCN was added dropwise to a solution of polyfluoroarenesulfonyl halide in MeCN and the resulted yellow solution was stirred at room temperature. The resulted mixture was analyzed by  $^{19}\text{F}$  NMR-spectroscopy.

**Table 1** Reactions of polyfluoroarenesulfonyl halides with polyfluoroarenethiols

Substrate (g, mmol)	Reagent (g, mmol)	MeCN, mL	Time, h	Products
$\text{C}_6\text{F}_5\text{SO}_2\text{F}$ (0.25g, 1.00mmol)	$\text{C}_6\text{F}_5\text{SH}$ (0.20g, 0.99mmol)	5.0	1.5	4-pentafluorophenylthio-2,3,5,6-tetrafluorobenzenesulfonyl fluoride (isolated 0.39g, 0.98mmol, 98%)
$\text{C}_6\text{F}_5\text{SO}_2\text{Cl}$ (0.40g, 1.50mmol)	$\text{C}_6\text{F}_5\text{SH}$ (1.53g, 7.49mmol)	10.0	1	$\text{C}_6\text{F}_5\text{SSC}_6\text{F}_5 : \text{C}_6\text{F}_5\text{SH} : \text{C}_6\text{F}_5\text{H} = 69 : 22 : 9$
$\text{C}_6\text{F}_5\text{SO}_2\text{Br}$ (0.51g, 1.64mmol)	$\text{C}_6\text{F}_5\text{SH}$ (1.64g, 8.18mmol)	10.0	1	$\text{C}_6\text{F}_5\text{SSC}_6\text{F}_5 : \text{C}_6\text{F}_5\text{SH} = 94 : 6$
4- $\text{HC}_6\text{F}_4\text{SO}_2\text{Cl}$ (0.50g, 2.01mmol)	4- $\text{HC}_6\text{F}_4\text{SH}$ (1.79g, 9.85mmol)	14.0	1	$\text{HC}_6\text{F}_4\text{SSC}_6\text{F}_4\text{H} : 4\text{-HC}_6\text{F}_4\text{SH} : 1,4\text{-C}_6\text{F}_4\text{H}_2 = 82 : 15 : 3$
4- $\text{HC}_6\text{F}_4\text{SO}_2\text{Br}$ (1.39g, 4.74mmol)	4- $\text{HC}_6\text{F}_4\text{SH}$ (4.32g, 23.73mmol)	24.0	14	$\text{HC}_6\text{F}_4\text{SSC}_6\text{F}_4\text{H} : 4\text{-HC}_6\text{F}_4\text{SH} = 89 : 11^*$
$\text{C}_6\text{F}_5\text{SO}_2\text{Cl}$ (0.53g, 2.00mmol)	$\text{HC}_6\text{F}_4\text{SH}$ (0.37g, 2.02mmol)	1.0	0.1667	$\text{C}_6\text{F}_5\text{SO}_2\text{Cl} : \text{HC}_6\text{F}_4\text{SSC}_6\text{F}_4\text{H} : 4\text{-HC}_6\text{F}_4\text{SSC}_6\text{F}_5 : \text{C}_6\text{F}_5\text{H} : \text{C}_6\text{F}_5\text{SSC}_6\text{F}_5 = 53 : 30 : 12 : 4 : 1$
$\text{C}_6\text{F}_5\text{SO}_2\text{Br}$ (1.11g, 3.57mmol)	4- $\text{HC}_6\text{F}_4\text{SH}$ (0.63g, 3.46mmol)	5.0	0.3333	$\text{C}_6\text{F}_5\text{SO}_2\text{Br} : \text{HC}_6\text{F}_4\text{SSC}_6\text{F}_4\text{H} : 4\text{-HC}_6\text{F}_4\text{SSC}_6\text{F}_5 : \text{C}_6\text{F}_5\text{SSC}_6\text{F}_5 = 53 : 26 : 18 : 3$
$\text{C}_6\text{F}_5\text{SO}_2\text{Br}$ (0.31g, 0.99mmol)	4- $\text{HC}_6\text{F}_4\text{SH}$ (0.91g, 5.00mmol)	2.0	0.5	$\text{HC}_6\text{F}_4\text{SSC}_6\text{F}_4\text{H} : 4\text{-HC}_6\text{F}_4\text{SSC}_6\text{F}_5 : \text{C}_6\text{F}_5\text{SSC}_6\text{F}_5 : 4\text{-HC}_6\text{F}_4\text{SH} = 67 : 28 : 3 : 2$

\*alongside traces of 1,2,4,5-tetrafluorobenzene were observed.

*Reactions of polyfluoroarenesulfonyl halides with alkali metal halides.* General procedure. A solution of polyfluoroarenesulfonyl halide in MeCN was added dropwise to a suspension of alkali metal halide in MeCN at room temperature. The reaction mixture was stirred at room temperature and the resulted solution was analyzed by  $^{19}\text{F}$  NMR.

**Table 2** Reactions of polyfluoroarenesulfonyl halides with alkali metal halides

Substrate (g, mmol)	Reagent (g, mmol)	MeCN, mL	Time, h	Products
C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Br (0.61g, 1.96mmol)	KF (0.22g, 3.79mmol)	5.5	7	C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> F : C <sub>6</sub> F <sub>5</sub> Br : C <sub>6</sub> F <sub>5</sub> H = 60 : 23 : 17
C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Br (0.32g, 1.03mmol)	NaCl (0.06g, 1.03mmol)	9.5	22	C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Cl : C <sub>6</sub> F <sub>5</sub> Br : C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Br : C <sub>6</sub> F <sub>5</sub> H : C <sub>6</sub> F <sub>5</sub> Cl = 25 : 23 : 23 : 17 : 13*
C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Br (0.31g, 1.00mmol)	NaI (0.31g, 2.07mmol)	10.0	**	C <sub>6</sub> F <sub>5</sub> H : C <sub>6</sub> F <sub>5</sub> I : C <sub>6</sub> F <sub>5</sub> Br = 48 : 48 : 4
C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Cl (0.09g, 0.34mmol)	NaBr (0.06g, 1.03mmol)	4.0	19	C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Br : C <sub>6</sub> F <sub>5</sub> Br : C <sub>6</sub> F <sub>5</sub> H : C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Cl : C <sub>6</sub> F <sub>5</sub> Cl = 33 : 23 : 19 : 13 : 11*
C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Cl (0.09g, 0.34mmol)	NaI (0.11g, 0.73mmol)	4.0	**	C <sub>6</sub> F <sub>5</sub> I : C <sub>6</sub> F <sub>5</sub> H : C <sub>6</sub> F <sub>5</sub> Cl = 48 : 45 : 7

\*and unidentified products (<10%)

\*\*the reaction was complete after 3-5 minutes

*Reactions of polyfluoroarenesulfonyl halides with alkenes.* General procedure. A mixture of polyfluoroarenesulfonyl bromide and alkene in a glass ampoule under argon was heated at 100-150°C for 20-24h (a) or kept at room temperature for several weeks (b). The reaction mixture was dissolved in 10mL CH<sub>2</sub>Cl<sub>2</sub> and analyzed by <sup>1</sup>H, <sup>19</sup>F NMR. The solvent and excess alkene were removed under reduced pressure. In case of allyl chloride or hexene-1 the residue contained the corresponding adduct, while in case of allyl bromide the residue consisted of a mixture of allyl polyfluoroaryl sulfone and 1,2,3-tribromopropane in the ratio 1 : 1. Tribromopropane was removed by washing with hexane 3×10mL. The crude products were purified by sublimation or recrystallization from EtOH.

*Reaction of polyfluoroarenesulfonyl bromides with allyl polyfluoroaryl sulfones.* An ampule was charged with polyfluoroarenesulfonyl bromide and allyl polyfluoroaryl sulfone and the mixture was heated for 25 h at 145–155°C on an oil bath. The mixture was dissolved in 5mL of CCl<sub>4</sub> and analyzed by GC–MS and <sup>19</sup>F and <sup>1</sup>H NMR.

**Table 3** Reactions of polyfluoroarenesulfonyl halides with alkenes

Substrate (g, mmol)	Reagent (g, mmol)	T, °C	Time	Products
C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Br (0.93g, 2.99mmol)	hexene-1 (0.50, 5.94mmol)	20-23	24days	C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CHBrCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> (1.04g, 2.63mmol, 88%)
C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Br (0.63g, 2.03mmol)	hexene-1 (0.40, 4.75mmol)	20-23	5days	C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CHBrCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> (100% conversion)*
4-HC <sub>6</sub> F <sub>4</sub> SO <sub>2</sub> Br (0.64g, 2.18mmol)	hexene-1 (0.37g, 4.40mmol)	16-20	24days	4-HC <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CHBrCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> (0.78g, 2.07mmol, 95%)
4-CF <sub>3</sub> C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Br (0.91g, 2.52mmol)	hexene-1 (0.47g, 5.58mmol)	16-20	21days	4-CF <sub>3</sub> C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CHBrCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> (1.00g, 2.25mmol, 89%)
C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Br (0.80g, 2.57mmol)	allyl chloride (0.78, 10.19mmol)	20-23	42days	C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CHBrCH <sub>2</sub> Cl (0.99g, 2.55mmol, 99%).
C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Br (1.60g, 5.14mmol)	allyl chloride (1.66g, 21.69mmol)	95-100	16h	C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CHBrCH <sub>2</sub> Cl (1.86g, 4.80mmol, 93%)
4-HC <sub>6</sub> F <sub>4</sub> SO <sub>2</sub> Br (0.78g, 2.66mmol)	allyl chloride (0.84g, 10.98mmol)	20-23	49days	4-HC <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CHBrCH <sub>2</sub> Cl (0.98g, 2.65mmol, 99%)
4-HC <sub>6</sub> F <sub>4</sub> SO <sub>2</sub> Br (0.92g, 3.14mmol)	allyl chloride (1.11g, 14.50mmol)	140-144	14h	4-HC <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CHBrCH <sub>2</sub> Cl (1.14g, 3.08mmol, 98%)
4-ClC <sub>6</sub> F <sub>4</sub> SO <sub>2</sub> Br (0.42g, 1.28mmol)	allyl chloride (0.45g, 5.88mmol)	20-23	49days	4-ClC <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CHBrCH <sub>2</sub> Cl (0.48g, 1.19mmol, 93%)
4-ClC <sub>6</sub> F <sub>4</sub> SO <sub>2</sub> Br (0.82g, 2.50mmol)	allyl chloride (0.85g, 11.11mmol)	108-110	9h	4-ClC <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CHBrCH <sub>2</sub> Cl (0.96g, 2.39mmol, 95%)
4-BrC <sub>6</sub> F <sub>4</sub> SO <sub>2</sub> Br (2.41g, 6.48mmol)	allyl chloride (2.00g, 26.14mmol)	18-24	50days	4-BrC <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CHBrCH <sub>2</sub> Cl (2.82g, 6.29mmol, 97%)
4-CF <sub>3</sub> C <sub>6</sub> F <sub>4</sub> SO <sub>2</sub> Br (2.53g, 7.01mmol)	allyl chloride (2.17g, 28.36mmol)	18-20	40days	4-CF <sub>3</sub> C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CHBrCH <sub>2</sub> Cl (3.03g, 6.92mmol, 99%)
C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Br (1.25g, 4.02mmol)	allyl bromide (1.22g, 10.08mmol)	145-155	25h	C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> (1.03g, 3.79mmol, 94%).
4-HC <sub>6</sub> F <sub>4</sub> SO <sub>2</sub> Br (2.18g, 7.44mmol)	allyl bromide (3.80g, 31.41mmol)	145-155	25h	4-HC <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> (1.59g, 6.32mmol, 85%)
4-ClC <sub>6</sub> F <sub>4</sub> SO <sub>2</sub> Br (1.52g, 4.64mmol)	allyl bromide (2.89g, 23.89mmol)	145-155	25h	4-ClC <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> (1.13g, 3.90mmol, 84%, 60% isolated)
4-BrC <sub>6</sub> F <sub>4</sub> SO <sub>2</sub> Br (1.45g, 3.90mmol)	allyl bromide (2.34g, 19.34mmol)	145-155	25h	4-BrC <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> (1.13g, 3.39mmol, 87%, 62% isolated)
4-CF <sub>3</sub> C <sub>6</sub> F <sub>4</sub> SO <sub>2</sub> Br (1.76g, 4.87mmol)	allyl bromide (3.04g, 25.13mmol)	145-155	25h	4-CF <sub>3</sub> C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> (1.41g, 4.38mmol, 90%)
C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Br (0.25g, 0.80mmol)	4-CF <sub>3</sub> C <sub>6</sub> F <sub>4</sub> SO <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> 0.25 g (0.78 mmol)	145-155	25h	C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Br : 4-CF <sub>3</sub> C <sub>6</sub> F <sub>4</sub> SO <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> : 4-CF <sub>3</sub> C <sub>6</sub> F <sub>4</sub> SO <sub>2</sub> Br : C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> = 46 : 26 : 11 : 18 ( <sup>19</sup> F, <sup>1</sup> H NMR) 4-CF <sub>3</sub> C <sub>6</sub> F <sub>4</sub> SO <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> : C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> = 60 : 40 (GC-MS).
4-CF <sub>3</sub> C <sub>6</sub> F <sub>4</sub> SO <sub>2</sub> Br (0.08g, 0.22mmol)	C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> 0.06 g (0.22 mmol)	145-155	25h	C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Br : 4-CF <sub>3</sub> C <sub>6</sub> F <sub>4</sub> SO <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> : 4-CF <sub>3</sub> C <sub>6</sub> F <sub>4</sub> SO <sub>2</sub> Br : C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> = 9 : 22 : 33 : 37 ( <sup>19</sup> F, <sup>1</sup> H NMR) 4-CF <sub>3</sub> C <sub>6</sub> F <sub>4</sub> SO <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> : C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> = 37 : 63 (GC-MS).

\*CuI (0.0376g, 0.197 mmol, 10mol.%) was added to reagents.



**Table 4** Reactions of pentafluorobenzenesulfonyl bromide with allyl bromide

Substrate (g, mmol)	Allyl bromide (g, mmol)	Conditions	T, °C	Time	Products (Conversion)
C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Br (1.60g, 5.14mmol)	1.83g, 15.13mmol	in the dark	17-21	15days	C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Br : C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> = 56 : 44 (44%)
C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Br (1.38g, 4.44mmol)	1.54g, 12.73mmol	scattered daylight	17-21	15days	C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> : C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Br = 94 : 6 (94%)
C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Br (1.37g, 4.40mmol)	2.49g, 20.58mmol	hydroquinone (0.12g, 1.09mmol, 25mol.%)	20-23	17days	C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Br : C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> = 90 : 10 (10%)
C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Br (1.37g, 4.40mmol)	2.10g, 17.36mmol	CuI (0.1672g, 0.88mmol, 20mol.%)	145-155	3h	C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> (100%)
C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Br (1.37g, 4.40mmol)	2.10g, 17.36mmol	-	145-155	3h	C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> : C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Br = 80 : 20 (80%)
C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Cl (1.19g, 4.46mmol)	2.10g, 17.36mmol	CuI (0.1716g, 0.90mmol, 20mol.%)	149-154	3h	C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Cl : C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> = 94 : 6 (6%)
C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Br (1.47g, 4.72mmol)	0.64g, 5.29mmol	1,4-dioxane 10.0mL, Zn (0.33g, 5.05mmol),	21	3h	C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> (0.90g, 3.31mmol, 70%)
C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Br (0.31g, 1.00mmol)	0.14g, 1.16mmol	MeCN 2.0mL, Zn (0.0712g, 1.09mmol),	25	3h	C <sub>6</sub> F <sub>5</sub> H : C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> = 82 : 18
C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Br (0.31g, 1.00mmol)	0.14g, 1.16mmol	Et <sub>2</sub> O 2.0mL, Zn (0.0713g, 1.09mmol),	25	3h	C <sub>6</sub> F <sub>5</sub> H : C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> = 84 : 16
C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Br (0.32g, 1.03mmol)	0.14g, 1.16mmol	hexane 2.0mL, Zn (0.0708g, 1.08mmol),	25	3h	No reaction
C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Br (0.31g, 1.00mmol)	0.14g, 1.16mmol	1,4-dioxane 2.0mL	25	3h	C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Br : C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> = 98 : 2 (2%)
C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Cl (0.27g, 1.01mmol)	0.15g, 1.24mmol	1,4-dioxane 2.0mL, Zn (0.0753g, 1.15mmol),	21	3h	C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Cl : C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> : C <sub>6</sub> F <sub>5</sub> H = 78 : 14 : 7

Analytical data for selected compounds are given below.

2-Bromohexyl pentafluorophenyl sulfone: mp. 62-65°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ, ppm, *J*, Hz: 0.84 t (3H, CH<sub>3</sub>, *J* = 7.2), 1.16-1.52 m (4H, <sup>5</sup>CH<sub>2</sub><sup>4</sup>CH<sub>2</sub>), 1.85 m (1H, <sup>3</sup>CH<sub>2</sub>), 1.95 m (1H, <sup>3</sup>CH<sub>2</sub>), 3.74 d.d (1H, CH<sub>2</sub>SO<sub>2</sub>, *J* = 15.3, *J* = 5.0), 3.90 d.d (1H, CH<sub>2</sub>SO<sub>2</sub>, *J* = 15.3, *J* = 7.8), 4.38 m (1H, -CHBr-). <sup>13</sup>C NMR (CDCl<sub>3</sub>), δ, ppm.: 13.59 (CH<sub>3</sub>), 21.61 (<sup>5</sup>CH<sub>2</sub>), 28.80 (<sup>4</sup>CH<sub>2</sub>), 38.11 (<sup>3</sup>CH<sub>2</sub>), 44.62 (CHBr), 64.89 (CH<sub>2</sub>SO<sub>2</sub>), 115.4 (C<sub>6</sub>F<sub>5</sub>, C<sup>1</sup>), 138.0 (C<sub>6</sub>F<sub>5</sub>, C<sup>3,5</sup>), 145.4 (C<sub>6</sub>F<sub>5</sub>, C<sup>2,4,6</sup>). <sup>19</sup>F NMR (CDCl<sub>3</sub>), δ, ppm, *J*, Hz: 26.37 m (2F<sup>2,6</sup>), 19.01 t.t (1F<sup>4</sup>, *J*<sub>F<sup>4</sup>-F<sup>3,5</sup></sub> = 21.0, *J*<sub>F<sup>4</sup>-F<sup>2,6</sup></sub> = 7.8), 3.81 m (2F<sup>3,5</sup>). Found: [M]<sup>+</sup> 393.9666. C<sub>12</sub>H<sub>12</sub>BrF<sub>5</sub>O<sub>2</sub>S. Calculated M 393.9656.

2-Bromo-3-chloropropyl 4-trifluoromethyl-2,3,5,6-tetrafluorophenyl sulfone: mp 68-69°C; IR, ν, cm<sup>-1</sup>: 3005, 2955, 1497, 1347, 1331, 1227, 1191, 1153, 990, 945, 716, 669, 648, 569, 501. UV, λ<sub>max</sub>, nm (lg ε): 220 (4.03), 290 (3.51). <sup>1</sup>H NMR, δ, ppm, *J*, Hz: 3.86 d.d (1H, CH<sub>2</sub>, *J* = 15.5, 7.5), 3.88 d.d (1H, CH<sub>2</sub>, *J* = 12.0, 6.7), 4.06 d.d (1H, CH<sub>2</sub>, *J* = 12.0, 4.3), 4.07 d.d (1H, *J* = 15.5, 5.1), 4.65 m (1H, -CHBr-). <sup>13</sup>C NMR, δ, ppm, *J*, Hz: 40.70 (CHBr, *J*<sub>C-H</sub> = 158), 47.19 (CH<sub>2</sub>Cl, *J*<sub>C-H</sub> = 156), 61.81 (CH<sub>2</sub>SO<sub>2</sub>, *J*<sub>C-H</sub> = 140), 115.32 q.t (<sup>4</sup>C, *J*<sub>C-F<sup>CF</sup>3</sub> = 35, *J*<sub>C-F<sup>3,5</sup></sub> = 23), 120.07 q (CF<sub>3</sub>, *J*<sub>C-F</sub> = 276), 123.16 t (<sup>1</sup>C, *J*<sub>C-F<sup>2,6</sup></sub> = 14), 144.77 (C<sup>2,3,5,6</sup>, *J*<sub>C-F</sub> ≈ 265). <sup>19</sup>F NMR, δ, ppm, *J*, Hz: 105.53 t (3F, CF<sub>3</sub>, *J*<sub>CF<sub>3</sub>-F<sup>3,5</sup></sub> = 22.0), 28.33 m (2F<sup>2,6</sup>), 25.89 m (2F<sup>3,5</sup>). Found, %: C 27.88; H 1.14; F 30.04; S 7.48; [M]<sup>+</sup> 435.8769, C<sub>10</sub>H<sub>5</sub>BrClF<sub>7</sub>O<sub>2</sub>S. Calculated, %: C 27.45; H 1.15; Br 18.10; F 30.39; S 7.33; M 435.8765.

Allyl pentafluorophenyl sulfone: mp 67-68°C; IR,  $\nu$ ,  $\text{cm}^{-1}$ : 2978, 2920, 1643, 1519, 1503, 1383, 1356, 1294, 1243, 1158, 1095, 996, 952, 883, 781, 727, 657, 547. UV,  $\lambda_{\text{max}}$ ,  $\text{HM}$  ( $\lg \epsilon$ ): 209 (3.97), 243 (2.50), 270 (3.12).  $^1\text{H}$  NMR,  $\delta$ , ppm,  $J$ , Hz: 3.96 d (2H,  $\text{CH}_2\text{SO}_2$ ,  $J = 7.4$ ), 5.29 d.d (1H,  $=\text{CH}_2$ ,  $J = 17.0$ ,  $J = \sim 1$ ), 5.41 d.d (1H,  $=\text{CH}_2$ ,  $J = 10.1$ ,  $J = \sim 1$ ), 5.89 m (1H,  $-\text{CH}=\text{}$ ).  $^{13}\text{C}$  NMR,  $\delta$ , ppm,  $J$ , Hz: 62.0 ( $\text{CH}_2\text{SO}_2$ ), 113.6 ( $\text{C}^1$ ,  $J_{\text{C-F}^{2,6}} = 14.3$ ,  $J_{\text{C-F}^4} = 4.0$ ,  $J_{\text{C-F}^{3,5}} = 2.0$ ), 123.2 ( $-\text{CH}=\text{}$ ), 126.2 ( $=\text{CH}_2$ ), 137.9 ( $\text{C}^{3,5}$ ,  $J_{\text{C-F}^{3(5)}} = 259.3$ ), 144.9 ( $\text{C}^4$ ,  $J_{\text{C-F}^4} = 264.1$ ,  $J_{\text{C-F}^{3,5}} = 13.4$ ,  $J_{\text{C-F}^{2,6}} = 5.0$ ), 145.4 ( $\text{C}^{2,6}$ ,  $J_{\text{C-F}^{2(6)}} = 261.0$ ).  $^{19}\text{F}$  NMR,  $\delta$ , ppm,  $J$ , Hz: 26.6 m (2F,  $\text{F}^{2,6}$ ), 17.2 t.t (1F,  $\text{F}^4$ ,  $J_{\text{F}^4 \text{F}^{3,5}} = 20.7$ ,  $J_{\text{F}^4 \text{F}^{2,6}} = 7.3$ ), 2.9 m (2F,  $\text{F}^{3,5}$ ). Found, %: C 40.03; H 1.80; F 34.74; S 11.86.  $[\text{M}]^+$  271.9911.  $\text{C}_9\text{H}_5\text{O}_2\text{F}_5\text{S}$ . Calculated, %: C 39.71; H 1.85; F 34.90; S 11.78. M 271.9925.

## CONCLUSIONS

Polyfluoroarenesulfonyl bromides can be used for introduction of polyfluoroarenesulfonyl group in organic compounds by interaction with the double bond of alkenes. Polyfluoroarenesulfonyl chlorides are less reactive in such transformations. Polyfluoroarenesulfonyl halides are sensitive to reducing agents.

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