

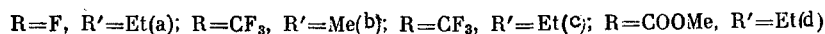
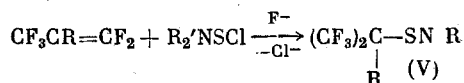
TABLE 1. Physicochemical Properties and NMR Spectra of Obtained Compounds

Com- pound	Yield, %	bp, °C (p, mm of Hg)	n_D^{20}	Found, %			Empirical formula	Calculated, %			^{19}F NMR spectrum (δ , ppm, singlet)	PMR spectrum (δ , ppm); J, Hz
				C	H	F		C	H	F		
(IIa)	62*	102-104 (760)	1,3360	25,82	1,95	61,33	$\text{C}_9\text{H}_5\text{F}_9\text{S}$	25,71	1,79	61,07	-11,3	1,0t (Me), 2,76q (CH_2), $J=8$ 7,2m (Ph)
(IIb)	82	50-52 (9)	1,4192	36,55	4,52	52,08	$\text{C}_{10}\text{H}_5\text{F}_9\text{S}$	36,59	4,52	52,13	-13,0	
(IIc)	68	mp 68-70	-	31,62	4,01	46,27	$\text{C}_{10}\text{H}_4\text{F}_9\text{NO}_2\text{S}$	32,17	4,07	45,84	-14,0	
(Va)	25	47-48 (32)	1,3644	30,81	3,76	48,75	$\text{C}_7\text{H}_{10}\text{F}_7\text{NS}$	30,77	3,66	48,71	†	0,9t (Me), $J=7,5$
(Vb)	72,5	63-66 (90)	1,3529	24,31	4,98	57,29	$\text{C}_8\text{H}_6\text{F}_9\text{NS}$	24,42	2,03	57,98	-13,0	2,6s (Me)
(Vc)	69,5	53-55 (20)	1,3649	29,83	2,97	53,43	$\text{C}_8\text{H}_{10}\text{F}_9\text{NS}$	29,72	3,10	52,94	-13,0	0,86t (Me), 2,89 and 2,94q (CH_2); $J=7,5$
(Vd)	52	54-55 (4)	1,4071	34,62	4,33	36,29	$\text{C}_9\text{H}_{13}\text{F}_6\text{NO}_2\text{S}$	34,50	4,15	36,74	-13,2	0,96t (Me), 2,94 and 2,98q (CH_2), 3,62s (Me), $J=7$
(VI)	-	80-82 (2)	1,4545	41,55	2,34	35,80	$\text{C}_{11}\text{H}_8\text{F}_6\text{O}_2\text{S}$	41,50	2,51	35,84	-12,6	3,52s (Me), 7,25m (Ph), 6,85m (Ph)
(VIII)	61	60-62 (2)	1,4681	37,41	1,69	35,54	$\text{C}_{10}\text{H}_5\text{ClOS}$	37,20	1,55	35,34	-14,2	3,84s (Me)
(IXb)	67,5	50 (18)	1,3922	22,10	1,12	41,27	$\text{C}_3\text{H}_3\text{ClF}_6\text{O}_2\text{S}$	21,70	1,08	41,22	-13,1	

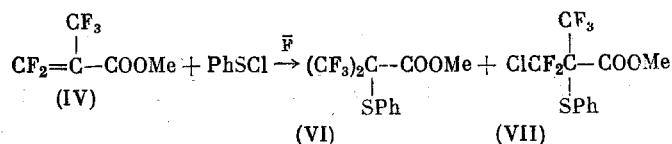
*After distillation over conc. H_2SO_4 .

†-2.6 d (CF_3), +90 h (CF); $J_{\text{CF}_3-\text{F}} = 14$ Hz.

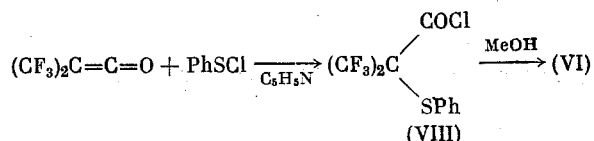
Chloride (III) was also obtained in high yield by reacting carbanion (I) with trichloromethanesulfonyl chloride, in which connection the corresponding sulfide (II) was not detected in the reaction products. At the same time, we found that carbanion (I), and also the carbanions generated from perfluoropropylene and methyl perfluoromethacrylate (IV), are smoothly sulfonylated by dialkylaminosulfonyl chlorides.



This reaction is a convenient method for the synthesis of a number of N,N-dialkylperfluoroalkanesulfenamides (V). Compounds of this class were previously obtained by the reaction of perfluoroalkanesulfonyl chlorides with amines [2] and by the sulfonylation of fluorinated CH acids with sulfonyl chlorides in the presence of tertiary amines [3]. Ester (IV) also reacts easily with benzenesulfonyl chloride in the presence of either KF or CsF. Together with sulfide (VI), chloro sulfide (VII) is formed in this reaction, which we had obtained previously in a similar reaction when catalyzed by pyridine [1].

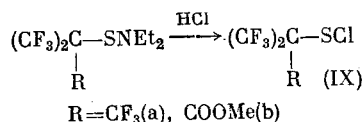


Sulfide (VI) was also obtained by independent synthesis by a scheme that includes the pyridine-catalyzed addition of benzenesulfonyl chloride to bis(trifluoromethyl)ketene to give acid chloride (VIII), and its subsequent alcoholysis.



As is known, perfluoropropylene, esters of perfluoromethacrylic acid, and bis(trifluoromethyl)ketene are easily dimerized when treated with either alkali-metal fluorides or tertiary amines, with the intermediate formation of fluorocarbanions. Such dimerization fails to occur in the cases studied by us. As a result, the obtained results testify to the fact that sulfonyl chlorides are efficient "traps" for fluorocarbanions.

Sulfenamides (Vc, d) when treated with dry HCl are cleaved in the usual manner at the S-N bond [2] to give sulfonyl chlorides (IX).



As a result, the sequence of transformations, which includes the amidosulfonylation of fluorocarbanions by dialkylaminosulfonyl chlorides and replacement of the dialkylamino group by chlorine, represents a method for the chlorosulfonylation of fluorocarbanions. The direct synthesis of sulfonyl chlorides by reacting fluorocarbanions with SCl_2 could not be accomplished. Thus, carbanion (I) reacts with SCl_2 in diglyme to give a complex mixture of products, in which, besides sulfonyl chloride (IXa), was identified chloride (III); i.e., here SCl_2 reacts the same as sulfonyl chlorides with electron-acceptor substituents. It should be mentioned that, based on the PMR spectral data (Table 1), the methylene groups in N,N-diethylsulfenamides (Vc, d) are nonequivalent, which is evidently associated with the hindered rotation around the S-N bond.

EXPERIMENTAL

The NMR spectra were recorded on Perkin-Elmer R-12 (^1H , 60 MHz) and Hitachi (^{19}F , 56.46 MHz) spectrometers in CCl_4 solution. The external standards were TMS and CF_3COOH . The IR spectra were recorded on a UR-20 instrument. The GLC analysis was run on an LKM-8MD instrument, using a column packed with Silicone DS-550 deposited on Chromosorb. The properties of the obtained compounds are given in Table 1.

Reaction of Perfluoroisobutylene with Sulfenyl Chlorides in the Presence of KF or CsF. With stirring and cooling in ice water, 0.05 mole of perfluoroisobutylene was passed into a suspension of 0.05 mole of freshly ignited CsF in 30 ml of abs. monoglyme, and then a solution of 0.045 mole of the sulfenyl chloride in 10 ml of monoglyme was added in drops. The mixture was warmed up to $\sim 20^{\circ}\text{C}$, and after 0.5-1 h the unreacted perfluoroisobutylene was vacuum distilled, while the residue was poured into water, and the obtained oil was extracted with ether, dried over MgSO_4 , and distilled. The yields and constants of the obtained sulfides (IIa, b) and sulfenamide (Vc) are given in Table 1. Sulfenamide (Vb) was obtained in a similar manner in abs. DMF in the presence of KF.

Perfluoro-tert-butyl o-Nitrophenyl Sulfide (IIc) and Di(o-nitrophenyl) Disulfide. Similar to the preceding, from 7 g of CsF, 11 g of perfluoroisobutylene, and 9 g of o-nitrobenzenesulfenyl chloride in 70 ml of monoglyme, after distilling off the perfluoroisobutylene and chloride (III), separation of the precipitate by filtration, and evaporation of the solution we isolated 14.4 g of a solid residue, the extraction of which with hot CCl_4 gave 2.7 g (36%) of di(o-nitrophenyl) disulfide, mp $189-192^{\circ}$. The mixed melting point with an authentic sample was not depressed. After evaporation of the CCl_4 , the extract was vacuum sublimed (2 mm), followed by recrystallization from heptane, to give 7.9 g of sulfide (IIc).

Perfluoro-tert-butyl Chloride (III). To a suspension of 10 g of CsF in 30 ml of monoglyme were added 9 g of perfluoroisobutylene and 8.3 g of trichloromethanesulfenyl chloride in 20 ml of monoglyme. After 2 h the fraction with bp $28-80^{\circ}$ was distilled from the reaction mixture, followed by redistillation over conc. H_2SO_4 to give 8.8 g (77%) of chloride (III), bp $26-28^{\circ}$. ^{19}F NMR spectrum: -6.5 s, cf. [4].

N,N-Diethylperfluoroisopropanesulfenamide (Va). To a stirred suspension of 7 g of CsF in 25 ml of abs. DMF was added 6.65 g of diethylaminosulfenyl chloride, and then 8.7 g of perfluoropropylene was bubbled in over 6 h. The reaction mixture was poured into water, and the organic layer was extracted with ether, washed with water, and dried over MgSO_4 . Sulfenamide (Va) was isolated by distillation.

Methyl Ester of α -Diethylaminosulfenylhexafluoroisobutyric Acid (Vd). A mixture of 5.5 g of CsF, 3.2 g of diethylaminosulfenyl chloride, and 3.5 g of ester (IV) in 20 ml of monoglyme was stirred at $45-50^{\circ}$ for 3.5 h. Then it was poured into water, extracted with ether, and the sulfenamide (Vd) was distilled. Infrared spectrum: 1760 cm^{-1} ($\text{C}=\text{O}$).

α -Phenylthiohexafluoroisobutyryl Chloride (VIII). With cooling in ice, into a solution of 3.1 g of benzenesulfenyl chloride and 0.1 g of $\text{C}_2\text{H}_5\text{N}$ in 10 ml of monoglyme was passed 3.9 g of bis(trifluoromethyl)ketene. The mixture was warmed up to $\sim 20^{\circ}$. At the end of reaction (checked by GLC) the acid chloride (VIII) was isolated by distillation. Infrared spectrum: 1780 cm^{-1} ($\text{C}=\text{O}$).

Reaction of Methyl Perfluoromethacrylate with Benzenesulfenyl Chloride in Presence of KF or CsF. To a suspension of 2.2 g of freshly ignited KF in 20 ml of abs. MeCN were added 3.2 g of benzenesulfenyl chloride and 4.2 g of ester (IV). The mixture was stirred for 12 h at $\sim 20^{\circ}$, poured into water, and the obtained oil was extracted with ether, dried, and distilled. We obtained 7 g of a fraction with bp $88-103^{\circ}$ (3 mm), which contained (GLC) 65% of sulfide (VI) and 35% of chloro sulfide (VII). An analogous experiment with CsF in monoglyme gave a mixture of 20% of (VI) and 80% of (VII). The pure sulfide (VI) was obtained in 60% yield by treating acid chloride (VIII) with methanol. Infrared spectrum: 1765 cm^{-1} ($\text{C}=\text{O}$).

Perfluoro-tert-butanesulfenyl Chloride (IXa). With cooling in ice water, a solution of 5 g of N,N-diethylperfluoro-tert-butanesulfenamide in 15 ml of abs. diglyme was saturated with dry HCl. The mixture was kept for 24 h at $\sim 20^{\circ}$, and then the volatile products were vacuum distilled (10 mm) into a trap (-78°). Distillation of the condensate gave 2.8 g (63%) of sulfenyl chloride (IXa), bp $74-76^{\circ}$. ^{19}F NMR spectrum: -11.5 s, cf. [5].

Methyl Ester of α -Chlorosulfenylhexafluoroisobutyric Acid (IXb). With cooling in ice, a solution of 4.6 g of sulfenamide (IVd) in 25 ml of abs. ether was saturated with dry HCl. The precipitate was filtered, while the filtrate was distilled to give sulfenyl chloride (IXb). Infrared spectrum: 1780 cm^{-1} ($\text{C}=\text{O}$).

CONCLUSIONS

1. Fluorocarbanions, generated by the addition of fluoride anion to the multiple bond of perfluoropropylene, perfluoroisobutylene, and methyl perfluoromethacrylate, are sulfenylated by ethane-, benzene-, and dialkylaminosulfenyl chlorides to give polyfluoroalkyl sulfides and sulfenamides.

2. Sulfenyl chlorides with electron-acceptor substituents chlorinate fluorocarbanions.

3. A method was proposed for the synthesis of perfluoroalkanesulfenyl chlorides by reacting fluorocarbanions with dialkylaminosulfenyl chlorides and subsequent replacement of the dialkylamino group by chlorine.

LITERATURE CITED

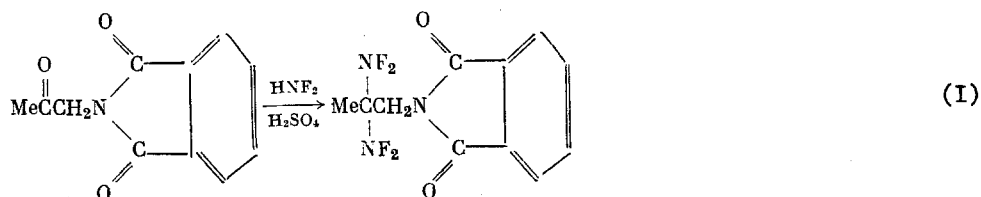
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DIFLUOROAMINATION OF N-ACETONYLPHTHALIMIDE

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While trying to synthesize the previously unknown N-difluoroaminoalkylphthalimides we established that 2,2-bis(difluoroamino)propyl bromide does not react with potassium phthalimide even at high temperature. This is apparently explained by the substantial decrease in the activity of the C-Br bond due to the strong -I effect of the difluoroamino group. Alkyl halides with more distant difluoroamino groups are difficultly accessible. Consequently, we studied the possibility of using difluoroamine to difluoroaminate N-acetylphthalimide [1-3]. It was found that treatment with HNF_2 under mild conditions in CH_2Cl_2 , in the presence of protonating agents (weak oleum), leads to replacement of the carbonyl oxygen of the acetyl moiety by two difluoroamino groups. The thus-formed N-[2,2-bis(difluoroamino)propyl]phthalimide (I) is a pale yellow crystalline powder (mp 53-54°) that is soluble in organic solvents and insoluble in water.



Phthalimide (I) proved to be exceedingly stable toward electrophilic reagents. Thus, if the acid hydrolysis of ordinary N-alkylphthalimides gives the corresponding salts of primary amines in good yield [4], then (I) is recovered practically unchanged after long (more than 30 h) heating with a large excess of conc. HCl in a sealed ampul at 160°C. The high stability of (I) under these conditions is probably due to the -I effect of the difluoroamino group.

At the same time, the high C-H acidity of the methylene fragment favors attack by nucleophilic reagents: When (I) is heated with a 1.5% methanol solution of hydrazine hydrate the difluoroamino groups are destroyed completely to fluoride ions. Here only phthalylhydrazide could be isolated from the organic reaction products.

EXPERIMENTAL

N-[2,2-Bis(difluoroamino)propyl]phthalimide (I). Using the method given in [2], into a stirred solution of 4.6 g (0.027 mole) of N-acetylphthalimide in 25 ml of dry CH_2Cl_2 , cooled

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