Found: C 12.41; H 0.89; F 46.04; Cl 20.08%. $C_2H_2ClF_5$. Calculated: C 13.02; H 1.08; F 51.50; Cl 19.25%. ^{19}F NMR spectrum (δ, ppm): −103.5 s (NF_2), 65.5 t (C–F, J = 5 Hz); and compounds with T_R 1.15 and 1.40, which proved to be the anti- and syn-isomers of N,N,N'-trifluoromonochloroacetamidine (amount in fluorination products 41%, and yield 27%), bp 80-84° (Sivolobov); d_4^{20} 1.454; n_D^{20} 1.3836. Found: C 14.63; H 1.18; F 38.38; Cl 23.95%. $C_2H_2N_2ClF_3$. Calculated: C 16.38; H 1.36; F 38.90; Cl 24.10%. ^{19}F NMR spectrum (δ, ppm): anti-isomer −102.5 s (C=NF), −128.0 s (NF_2); syn-isomer −108.0 s (C=NF), −125.6 s (NF_2).

Reaction of F_2 with Hydroxyacetamidine Hydrochloride. A mixture of 5 g (0.046 mole) of hydroxyacetamidine, 40 g of NaF, and 50 g of nickel turnings was fluorinated the same as described above. The products were extracted by vacuum-distillation at 100° (1 mm) and then fractionally distilled. We obtained 2.3 g (31%) of 2,2-bis(difluoroamino)-2-fluoroethanol, bp 60° (93 mm); d_4^{20} 1.594; n_D^{20} 1.3495. Found: C 14.41; H 1.45; N 19.37; F 55.02%. $C_2H_3N_2F_5O$. Calculated: C 14.47; H 1.20; N 16.86; F 57.23%. ^{19}F NMR spectrum (δ, ppm): −99.7 s (NF_2), 72.7 t (C–F, J = 10 Hz); PMR spectrum (30% tetrachloroethane solution) (τ, ppm): 4.17 s (OH), 4.30 m (CH_2, $^3J_{H-F}$ = 10, $^4J_{H-F}$ = 2 Hz);

Reaction of F_2 with Carbethoxyacetamidine Hydrochloride. A mixture of 8 g (0.048 mole) of carbethoxyacetamidine hydrochloride, 50 g of NaF, and 100 g of nickel turnings was fluorinated the same as above. The reaction mass was extracted with CH_2Cl_2 (2 × 100), dried over $MgSO_4$, the solvent was removed, and the residue was vacuum-distilled. We obtained 4.0 g (38%) of ethyl β,β-bis(difluoroamino)-β-fluoropropionate, bp 72-74° (40 mm); d_4^{20} 1.439; n_D^{20} 1.3591. Found: C 26.85; N 12.92; F 42.72%. $C_5H_7N_2F_5O_2$. Calculated: C 27.27; N 12.72; F 42.70%. ^{19}F NMR spectrum (δ, ppm): −101.3 s (NF_2), 62.7 t (C–F, J = 14 Hz). Infrared spectrum (ν, cm^{-1}): 2960, 1760, 1436, 1392, 1362, 1326, 1248, 1220, 1190, 1080, 1010, 930, 896, 850.

CONCLUSIONS

Conditions were found for selectively fluorinating the guanyl group of alkyl-substituted amidines with elemental fluorine without touching the alkyl radical.

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REACTION OF POLYFLUORINATED ALCOHOLS WITH FLUOROOLEFINS

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Unfluorinated alcohols easily add to fluoroolefins [1, 2]. At the same time, the reaction of polyfluorinated alcohols, which have an acidity that is comparable or substantially greater than that of phenol, has not been investigated systematically. Only the preparation of the addition products of trifluoroethanol and 3,3,3-trifluoropropanol to tetrafluoroethylene, using sodium catalysis and long heating (180-200°C) in an autoclave, has been described [3]. Together with vinyl ethers, the corresponding addition products were isolated in low yield from the alcoholates of certain polyfluorinated alcohols and tetrafluoroethylene when reacted under drastic conditions [4]. Besides this, addition products were obtained when equimolar amounts of fluoroolefins and KOH were reacted with an excess of the lower polyfluorinated alcohols under pressure in an autoclave [5].

We established that 2,2,3,3-tetrafluoropropanol and 2-nitro-2,2-difluoroethanol, in the presence of either KOH or Et_3N, react with perfluoropropylene at room temperature:

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$$RCH_2OH + CF_3CF{=}CF_2 \xrightarrow{KOH} RCH_2OCF_2CFHCF_3$$
$$R = HCF_2CF_2\ (I),\ O_2NCF_2\ (II)$$

At the same time, the indicated alcohols do not react with the tetrafluoro- and trifluorochloroethylenes under similar conditions.

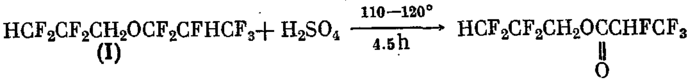
1,1,5-Trihydroperfluoropentanol, 1,1,7-trihydroperfluoroheptanol, and 1-nitro-1,1-difluoro-2-propanol are even less active, and their reaction even with perfluoropropylene is extremely slow. In view of the close boiling points of the formed ethers and starting alcohols, and also the low solubility of the latter in water, in this case we were able to isolate only the 2-nitro-2,2-difluoroisopropyl 2'-monohydroperfluoropropyl ether in the pure state.

$$O_2NCF_2CH(CH_3)OH + CF_3CF{=}CF_2 \xrightarrow{KOH} \underset{(III)}{O_2NCF_2CH(CH_3)OCF_2CFHCF_3}$$

Further studies disclosed that the addition of the discussed alcohols to fluoroolefins can be accomplished under mild conditions (∿20°, atmospheric pressure) in the presence of catalytic amounts of KOH in DMF solution, in which connection the isolation of the end products does not present any special difficulties.

$$RR'CHOH + XCF{=}CF_2 \xrightarrow[DMF]{KOH} RR'CHOCF_2CFHX$$
$$R = O_2NCF_2,\ R' = CH_3,\ X = CF_3\ (III);\ R = HCF_2CF_2CF_2CF_2,$$
$$R' = H,\ X = CF_3\ (IV);\ R = HCF_2CF_2CF_2CF_2CF_2CF_2,$$
$$R' = H,\ X = CF_3 (V);\ R = HCF_2CF_2,\ R' = H,\ X = F\ (VI);$$
$$R' = HCF_2CF_2,\ R' {=} H,\ X = Cl\ (VII);\ R = HCF_2CF_2CF_2CF_2,$$
$$R' = H, X = Cl\ (VIII); R = HCF_2CF_2CF_2CF_2CF_2CF_2, R' {=} H, X = Cl\ (IX);$$
$$R = O_2NCF_2,\ \ R' = H,\ \ X = Cl\ \ (X);\ \ R = O_2NCF_2,\ \ R' = CH_3,$$
$$X = Cl\ (XI)$$

The obtained ethers are much more resistant to acid hydrolysis than the addition products of unfluorinated alcohols to fluoroolefins, which are easily hydrolyzed to the corresponding polyfluorocarboxylic acid esters [6]. Thus, the 2,2,3,3-tetrafluoropropyl ester of α-monohydroperfluoropropionic acid (XII) could be obtained only by heating (I) with conc. H_2SO_4 above 100°.

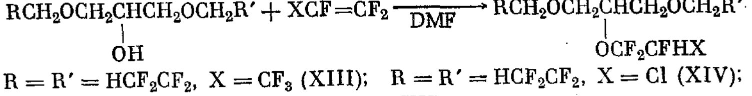


$$\underset{(I)}{HCF_2CF_2CH_2OCF_2CFHCF_3} + H_2SO_4 \xrightarrow[4.5h]{110-120°} HCF_2CF_2CH_2O\overset{}{\underset{\|\atop O}{C}}CHFCF_3$$

(XII)

The low yield of (XII) is apparently explained by its quite low stability in strongly acid media. At the same time (II) is recovered practically unchanged under these conditions, and is contaminated with a small amount (up to 8% when based on the GLC data) of the corresponding carbonyl compound, as is evidenced by the appearance of an absorption band at 1797 cm^{-1} [1790 cm^{-1} for (XII)] in the IR spectrum.

The developed method also made it possible to add the glycerol 1,3-diethers obtained from polyfluorinated alcohols to fluoroolefins, in which connection the reaction in this case is accompanied by the formation of appreciable amounts of the vinyl substitution products, which can be removed only by their prior bromination before fractional distillation of the reactions mixtures.



$$RCH_2OCH_2\underset{\overset{|}{OH}}{C}HCH_2OCH_2R' + XCF{=}CF_2 \xrightarrow[DMF]{KOH} RCH_2OCH_2\underset{\overset{|}{OCF_2CFHX}}{C}HCH_2OCH_2R'$$

$$R = R' = HCF_2CF_2,\ X = CF_3\ (XIII);\ \ R = R' = HCF_2CF_2,\ X = Cl\ (XIV);$$
$$R = HCF_2CF_2,\ R' = O_2NCF_2,\ X = CF_3\ (XV)$$

The role of DMF in the discussed process is probably more than just improving the conditions for forming the alcoholates and their better solubility in the reaction mass. Apparently, DMF activates the fluoroolefins to a certain degree. This assumption is supported

TABLE 1

Compound	Formula	Chemical shifts, ppm												J, Hz
		δ_1	δ_2	δ_3	δ_4	δ_5	δ_6	δ_7	δ_8	δ_9	δ_{10}	δ_{11}	δ_{12}	
(I)	$\overset{1}{H}\overset{2}{C}F_2\overset{3}{C}F_2\overset{4}{C}H_2O\overset{5}{C}F_2C\overset{6}{H}\overset{7}{F}\overset{8}{C}F_3$	6,04	61,08	47,80	4,50	5,07 5,77	4,90	136,10	—1,84					$J_{12} = 52{,}5$; $J_{13} = 4{,}5$; $J_{24} = 1{,}2$; $J_{34} = 12{,}5$; $J_{56} = 5{,}0$; $J_{67} = 48{,}8$; $J_{68} = 6{,}0$
(II)	$O_2N\overset{1}{C}F_2C\overset{2}{H}_2O\overset{3}{C}F_2C\overset{4}{F}\overset{5}{H}\overset{6}{C}F_3$	16,51	4,73	5,01 5,61	136,50	4,95	—1,82							$J_{12} = 9{,}0$; $J_{56} = 6{,}2$; $J_{45} = 48{,}2$
(III)	$O_2N\overset{1}{C}F_2C\overset{2}{H}(C\overset{3}{H}_3)O\overset{4}{C}F_2C\overset{5}{F}\overset{6}{H}\overset{7}{C}F_3$	18,56 22,50	5,25	1,62	2,71 3,36	135,90	4,86	—1,74						$J_{23} = 6{,}0$; $J_{56} = 48{,}2$; $J_{67} = 6{,}2$
(IV)	$\overset{1}{H}\overset{2}{C}F_2\overset{3}{C}F_2\overset{4}{C}F_2\overset{5}{C}F_2\overset{6}{C}H_2O\overset{7}{C}F_2C\overset{8}{F}\overset{9}{H}\overset{10}{C}F_3$	6,08	60,71	53,05	43,42	48,11	4,50	5,91 6,81	137,10	4,78	—1,15			$J_{12} = 52{,}5$; $J_{13} = 5{,}2$; $J_{56} = 12{,}2$; $J_{46} = 1{,}2$; $J_{89} = 48{,}6$; $J_{8\,10}\,6{,}0$
(V)	$\overset{1}{H}\overset{2}{C}F_2\overset{3}{C}F_2\overset{4}{C}F_2\overset{5}{C}F_2\overset{6}{C}F_2\overset{7}{C}F_2C\overset{8}{H}_2O\overset{9}{C}F_2C\overset{10}{F}\overset{11}{H}\overset{12}{C}F_3$	6,04	60,71	52,47	43,85	45,50	46,91		4,46	5,77 6,77	134,40	4,65	—1,33	$J_{12} = 52{,}5$; $J_{13} = 5{,}2$; $J_{78} = 12{,}0$; $J_{10\,11} = 48{,}6$; $J_{10\,12} = 6{,}2$
(VI)	$\overset{1}{H}\overset{2}{C}F_2\overset{3}{C}F_2\overset{4}{C}H_2O\overset{5}{C}F_2\overset{6}{C}F_2\overset{7}{H}$	5,83	62,70	48,54	4,35	16,12	60,53	4,35						$J_{12} = 52{,}5$; $J_{13} = 4{,}2$; $J_{24} = 1{,}2$; $J_{34} = 12{,}2$; $J_{56} = 5{,}0$; $J_{57} = 2{,}8$; $J_{67} = 53{,}5$
(VII)	$\overset{1}{H}\overset{2}{C}F_2\overset{3}{C}F_2\overset{4}{C}H_2O\overset{5}{C}F_2C\overset{6}{F}Cl\overset{7}{H}$	5,94	61,22	48,08	4,40	11,69 11,91	76,56	6,17						$J_{12} = 52{,}5$; $J_{13} = 4{,}6$; $J_{24} = 1{,}5$; $J_{34} = 12{,}2$; $J_{56} = 11{,}3$; $J_{57} = 4{,}2$; $J_{67} = 48{,}8$

TABLE 1 (contd.)

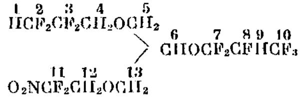
Compound	Formula	Chemical shifts, ppm												J, Hz
		δ_1	δ_2	δ_3	δ_4	δ_5	δ_6	δ_7	δ_8	δ_9	δ_{10}	δ_{11}	δ_{12}	
(VIII)	$\overset{1}{H}C\overset{2}{F}_2C\overset{3}{F}_2C\overset{4}{F}_2C\overset{5}{F}_2C\overset{6}{H}_2OC\overset{7}{F}_2C\overset{8}{F}Cl\overset{9}{H}$	6,09	60,48	52,82	43,17	47,94	4,49	11,76 11,96	77,09	6,17				$J_{12} = 52,5$; $J_{56} = 12,4$; $J_{46} = 1,2$; $J_{89} = 48,2$; $J_{79} = 4,2$
(IX)	$\overset{1}{H}C\overset{2}{F}_2C\overset{3}{F}_2C\overset{4}{F}_2C\overset{5}{F}_2C\overset{6}{F}_2C\overset{7}{F}_2C\overset{8}{F}_2OC\overset{9}{F}_2C\overset{10}{F}Cl\overset{11}{H}$	6,07	60,65	52,26	42,82	44,57	45,81		4,46	11,67 11,87	77,41	6,17		$J_{12} = 53,5$; $J_{13} = 5,4$; $J_{68} = 0,8$; $J_{78} = 13,0$; $J_{9\,10} = 11,3$; $J_{9\,11} = 5,2$; $J_{10\,11} = 48,2$
(X)	$O_2NC\overset{1}{F}_2C\overset{2}{H}_2OC\overset{3}{F}_2C\overset{4}{F}Cl\overset{5}{H}$	16,65	4,73	11,04 11,24	77,20	6,14								$J_{12} = 9,0$; $J_{34} = 11,3$; $J_{35} = 4,2$; $J_{45} = 47,5$
(XI)	$O_2NC\overset{1}{F}_2C\overset{2}{H}(C\overset{3}{H}_3)OC\overset{4}{F}_2C\overset{5}{F}Cl\overset{6}{H}$	18,21 22,67	5,22	1,58	8,72 8,92	76,87	6,11							$J_{23} = 6,2$; $J_{46} = 4,5$; $J_{56} = 47,5$
(XII)	$C\overset{1}{F}_3C\overset{2}{F}\overset{3}{H}C(O)OC\overset{4}{H}_2C\overset{5}{F}_2C\overset{6}{F}_2\overset{7}{H}$	—0,78	127,90	5,25	4,71	46,85	60,53	5,92						$J_{13} = 6,5$; $J_{23} = 48,2$; $J_{45} = 13,5$; $J_{46} = 1,4$; $J_{67} = 52,5$; $J_{12} = 11,8$; $J_{57} = 4,2$; $J_{65} = 1,2$
(XIII)	$(\overset{1}{H}C\overset{2}{F}_2C\overset{3}{F}_2C\overset{4}{H}_2OC\overset{5}{H}_2)_2C\overset{6}{H}OC\overset{7}{F}_2C\overset{8}{F}\overset{9}{H}C\overset{10}{F}_3$	5,94	62,07	47,69	4,17			2,56 3,75	135,60	4,82	—2,41			$J_{12} = 52,5$; $J_{13} = 5,4$; $J_{89} = 48,4$
(XIV)	$(\overset{1}{H}C\overset{2}{F}_2C\overset{3}{F}_2C\overset{4}{H}_2OC\overset{5}{H}_2)_2C\overset{6}{H}OC\overset{7}{F}_2C\overset{8}{F}Cl\overset{9}{H}$	5,94	61,60	47,24	4,13			7,02 7,32	75,28	6,13				$J_{12} = 52,5$; $J_{13} = 4,8$; $J_{78} = 11,3$; $J_{79} = 4,2$; $J_{89} = 48,2$
(XV)	 $\left.\begin{array}{l}\overset{1}{H}C\overset{2}{F}_2C\overset{3}{F}_2C\overset{4}{H}_2OC\overset{5}{H}_2\\O_2NC\overset{11}{F}_2C\overset{12}{H}_2OC\overset{13}{H}_2\end{array}\right\rangle C\overset{6}{H}OC\overset{7}{F}_2C\overset{8}{F}\overset{9}{H}C\overset{10}{F}_3$	5,92	62,44	47,99				1,22 2,48	134,70	4,72	—2,21	16,49	4,25	$J_{12} = 52,5$; $J_{13} = 5,4$; $J_{89} = 48,2$; $J_{11\,12} = 9,4$

TABLE 2

Compound	Yield, %	bp, °C (p, mm of Hg)	d_4^{20}	n_D^{20}	Found, %				Empirical formula	Calculated, %			
					C	H	F	H		C	H	F	N
(I)	85,3	102–103	1,578	~1,293	25,80	1,43	66,98	–	$C_6H_5F_{10}NO_3$	25,53	1,42	67,38	–
(II)	77,1	60 (58)	1,621	1,3198	21,56	1,42	54,43	5,44	$C_5H_3F_8NO_3$	21,66	1,08	54,87	5,05
(III)	39,3	62–63 (40)	1,532	1,3312	25,21	1,80	51,93	5,25	$C_6H_5F_8NO_3$	24,74	1,72	52,23	5,39
(IV)	47,4	146	1,662	1,3020	24,88	1,10	69,33	–	$C_8H_4F_{14}O$	25,[illegible]	1,05	69,63	–
(V)	31,8	79–80 (20)	1,735	1,3031	24,78	0,78	70,87	–	$C_{10}H_4F_{18}O$	24,90	0,83	70,95	–
(VI) *	20,5	93–95	1,531	~1,292	25,64	1,97	65,14	–	$C_5H_4F_8O$	25,86	1,72	65,52	–
(VII)	86,8	115–117	1,551	1,3240	24,24	1,71	53,09	–	$C_5H_4ClF_7O$	24,15	1,61	53,52	–
(VIII)	57,5	85 (75)	1,653	1,3250	24,31	1,15	59,53	–	$C_7H_4ClF_{11}O$	24,10	1,15	59,97	–
(IX)	50,4	58 (70)	1,711	1,3230	24,18	0,80	63,15	–	$C_9H_4ClF_{15}O$	24,08	0,89	63,55	–
(X)	41,6	66 (85)	1,592	1,3600	19,82	1,26	38,71	5,69	$C_4H_3ClF_5NO_3$	19,71	1,23	39,01	5,75
(XI)	30,5	85 (75)	1,504	1,3660	23,50	2,07	36,43	5,28	$C_5H_5ClF_5NO_3$	23,30	1,94	36,89	5,44
(XII)	22,4	127	1,582	1,3196	27,99	1,49	58,87	–	$C_6H_4F_8O_2$	27,71	1,54	58,51	–
(XIII)	43,1	101 (1)	1,554	1,3440	30,67	2,57	56,93	–	$C_{12}H_{12}F_{14}O_3$	30,64	2,55	56,60	–
(XIV)	54,3	125 (2,5)	1,537	1,3660	29,81	2,58	47,39	–	$C_{11}H_{12}ClF_{11}O_3$	30,24	2,75	47,88	–
(XV)	35,5	108 (1)	1,590	1,3600	28,45	2,35	49,53	3,28	$C_{11}H_{11}F_{12}NO_5$	28,40	2,37	49,09	3,01

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*Data from [4]: bp 92°, d_4^{20} 1.5356, n_D^{20} 1.2910.

by the fact that DMF substantially facilitates the dimerization and oligomerization of fluoroolefins by the ionic mechanism [7].

The ^1H and ^{19}F NMR spectra of the obtained compounds have definite interest. From Table 1 it can be seen that the ^{19}F NMR spectra of the synthesized compounds exhibit an anisochronicity of the diastereotopic OCF_2 and O_2NCF_2 groups, in which connection the difference in the values of the chemical shifts for the fluorine atoms depends both on the size of the substituents at the chiral center and on the length of the fluorohydrocarbon chain. Thus, replacing the chlorine atom by the bulky CF_3 group at the chiral center leads to an increased difference in the chemical shifts of the fluorine atoms in the OCF_2 group [compounds (VII) and (I), (VIII) and (IV), (IX) and (V), (X) and (II), (XI) and (III), (XIV) and (XIII)]. For compounds (I), (IV), and (V) the anisochronicity of the fluorine atoms increases with increase in the length of the fluorohydrocarbon chain, whereas for the compounds with a chlorine atom at the chiral center it is practically independent of the length of the fluorohydrocarbon chain. In addition, replacement of the hydrogen atom in the OCH_2 group by a more bulky substituent leads to an increase in the anisochronicity of the fluorine atoms in the OCF_2 group.

EXPERIMENTAL

The NMR spectra were taken on a Hitachi R-20 instrument (60 and 56.45 MHz). The chemical shifts were determined relative to HMDS and CF_3COOH.

The GLC analysis was run on an LKhM-8MD chromatograph, using a 3 m × 3 mm column packed with 5% SE-30 deposited on Chromaton N-AW-DMCS (particle size 0.200-0.250 mm), and a 2 m × 3 mm column packed with 15% polymethylphenylsiloxane oil deposited on Chromaton N-AW-DMCS; helium was used as the carrier gas at a flow rate of 18.7 ml/min.

Typical Experiment. Excess fluoroolefin was bubbled through a solution of 10 g of the alcohol and 1 g of KOH in 10 ml of DMF. The reaction mass was poured into 150 ml of water, and the organic layer was washed five times with equal volumes of water, dried over $CaCl_2$, and fractionally distilled.

2,2,3,3-Tetrafluoropropyl Ester of α-Monohydroperfluoropropionic Acid (XII). A mixture of 15 g (0.0532 mole) of (I) and 10 ml of conc. H_2SO_4 was stirred vigorously for 4.5 h at 110-120°, after which it was cooled and poured on 40 g of cracked ice. The organic layer was separated, washed with ice water (3 × 30 ml), dried over $MgSO_4$, and fractionally distilled. We obtained 3.1 g (22.4%) of (XII) as a colorless mobile liquid.

The structure and properties of the obtained compounds are given in Table 2.

CONCLUSIONS

1. The addition of polyfluorinated alcohols to trifluorochloroethylene, tetrafluoroethylene, and perfluoropropylene, with the formation of the corresponding ethers, can be accomplished under mild conditions in the presence of bases in DMF solution.

2. The ^{19}F NMR spectra of the synthesized compounds exhibit an anisochronicity of the diastereotopic OCF_2 and O_2NCF_2 groups, which depends both on the size of the substituent at the chiral center and on the length of the fluorohydrocarbon chain.

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