CONCLUSIONS

We accomplished the electrophilic alkylation of some fluorinated olefins using dihaloethanes in the presence of SbF_5.

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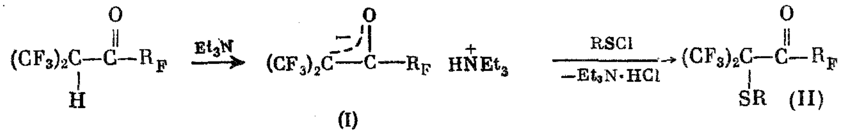
SULFENYLATION OF FLUORINATED CH ACIDS

Yu. V. Zeifman and L. T. Lantseva

UDC 542.545.22:547.464

Polyfluoroalkyl carbanions, which are generated by the addition of either Cl^- [1] or F^- [2, 3] to the multiple bond of fluoroolefins in aprotic dipolar solvents, react smoothly with sulfene chlorides to give the sulfenylation products.

In the present paper* we studied the reaction of sulfene chlorides RSCl (R = Et, Ph, Et_2N) with fluoro carbanions, formed by the deprotonation of fluorinated CH acids using tertiary amines. This reaction is a convenient method for the synthesis of a number of fluorinated sulfides and sulfenamides. Thus, the reaction of the mesomeric carbanions (I) with EtSCl or PhSCl under mild conditions (ether, 0-20°C) gave sulfides (II), the C-sulfenylation products, in high yield.

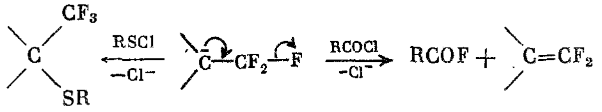


$R_F = F$, $R = Et$ (a); $R_F = C_2F_5$, $R = Ph$ (b).

Under analogous conditions, using Et_3N and RSCl, we accomplished the sulfenylation of monohydroperfluoroisobutane, the ester and nitrile of hexafluoroisobutyric acid, the diester of trifluoromethylmalonic acid, and phenyl hexafluoroisopropyl ketone. The characteristics of the obtained compounds are given in Table 1.

The methyl ester of 2,2,2-trifluoropropionic acid does not react with sulfene chlorides (PhSCl or Et_2NSCl) in the presence of Et_3N, and here only the reaction products of the sulfene chlorides with the amine were isolated. As a result, it is obvious that a quite high protic lability of the CH acid is necessary for successful sulfenylation.

An analysis of the composition of the reaction mixtures employing GLC and NMR reveals that in none of the studied reactions do the fluorinated CH acids undergo dehydrofluorination. In contrast to this, the reaction of fluorinated CH acids with acyl chlorides in the presence of Et_3N gives exclusively the dehydrofluorination products, while C-acylation fails to occur [5, 6].



The indicated facts are explained within the framework of the theory of hard and soft acids and bases (HSAB): a soft electrophile RSCl attacks a soft carbanion, whereas the hard

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*See [4] for preliminary communication.

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1102-1106, May, 1980. Original article submitted April 17, 1979.

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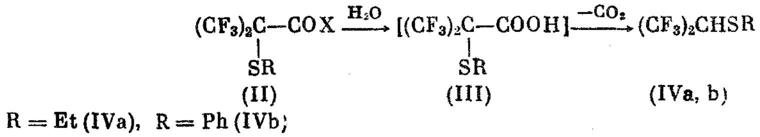
TABLE 1. Physicochemical Properties and IR and NMR Spectra of Obtained Compounds

Compound	Yield, %	mp, °C (p, mm Hg)	n_D^{20}	Found, %			Empirical formula	Calc., %			IR spectrum, ν_{max}, cm^{-1}	^{19}F NMR spectrum (δ, ppm); J, Hz
				C	H	F		C	H	F		
$(CF_3)_3CSPh$ [2]	19,5	46 (5)	1,4190									
$(CF_3)_3CSNMe_2$ [2]	53	65–67 (100)	1,3540									
$(CF_3)_2C(SEt)COF$	67,5	49–50 (70)	1,3536	28,08	1,78	51,54	$C_6H_5F_7OS$	27,90	1,93	51,55	1860	−11,6 d (CF_3), −122 h (CF), $J=12$
$(CF_3)_2C(SPh)COOMe$ [2]	90	80–82 (2)	1,4545									
$(CF_3)_2C(SNEt_2)COOMe$ [2]	82,5	54–55 (4)	1,4071									
$(CF_3)_2C(SPh)CN$	73	53–55 (4)	1,4408	42,21	1,91	39,92	$C_{10}H_5F_6NS$	42,15	1,75	40,02		−10 s
$CF_3(SEt)(COOMe)_2$	72	84–86 (2)	1,4283	36,69	4,22	21,95	$C_8H_{11}F_3O_4S$	36,92	4,23	21,92	1755	−10,5 s
$(CF_3)_2C(SPh)COC_2F_5$	85	63–65 (3)	1,4148	35,62	1,37	51,01	$C_{12}H_5F_{11}OS$	35,48	1,23	51,48	1750	−16,0 t [(CF_3)]$_2$, 3,0 s (CF_2), 36,0 h (CF_3), $J=13$
$(CF_3)_2C(SEt)COPh$	76	103–108 (3)	1,4704	45,84	3,34	35,62	$C_{12}H_{10}F_6OS$	45,56	3,16	36,13	1700	−12,5 s
$(CF_3)_2CHSEt$	74,5	99–100	1,3480	28,16	2,80	53,53	$C_5H_6F_6S$	28,25	2,82	53,77		−11,0 d $J=8$
$(CF_3)_2CHSPh$	66	60–62 (18)	1,4311	41,52	2,35	43,77	$C_9H_6F_6S$	41,53	2,30	43,84		−11,0 d, $J=8$
$CF_2{=}C(SEt)CF_3$	58	83–86	1,3670	31,75	2,67	49,17	$C_5H_5F_5S$	31,25	2,60	49,10	1710	−15,8 dd (CF_3), −12,4 and −8,7 d.q (CF_2); $J_{CF_3-F}=21,4$ and 10,5, $J_{F-F}=4,2$
$(CF_3)_2C{=}C{=}C(SEt)CF_3$		114–116	1,3609	31,21	1,73	55,81	$C_8H_5F_9S$	31,58	1,64	56,22	1990	−14,8 s [$(CF_3)_2$], −13,7 s (CF_3)
$(CF_3)_2(SEt)_2$		58–59 (10)	1,4177	31,05	3,90	41,87	$C_7H_{10}F_6S_2$	30,88	3,67	41,97		−11,0 s
$(CF_3)_2C(SEt)CF{=}C(SEt)CF_3$		57–58 (2)	1,4097	31,31	2,67	49,50	$C_{10}H_{10}F_{10}S_2$	31,25	2,60	49,48	1620	−18,0 d (CF_3), −13,7 d [$(CF_3)_2$], −0,1 m (CF), $J_{CF_3-F}=24$, $J_{(CF_3)_2C-F}=15$

RCOCl preferentially reacts with the hard F$^-$ anion. A similar difference exists in the directions of the reactions of RSCl and RCOCl with the N-anions of trifluoromethylamines [7].

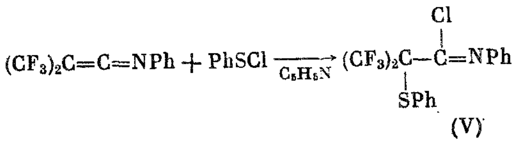
In studying the sulfenylation products of the fluorinated CH acids we found reactions that testify that the $C(CF_3)_2SR$ grouping is effectively leaving as the anion. This is manifested, for example, in the spontaneous decarboxylation of the acids (III), which are formed by the hydrolysis of the acid fluoride of α-ethylthiohexafluoroisobutyric acid (IIa) and the acid chloride of α-phenylthiohexafluoroisobutyric acid (IIc).



$$\underset{\text{(II)}}{(CF_3)_2\underset{SR}{C}-COX} \xrightarrow{H_2O} \underset{\text{(III)}}{[(CF_3)_2\underset{SR}{C}-COOH]} \xrightarrow{-CO_2} \underset{\text{(IVa, b)}}{(CF_3)_2CHSR}$$

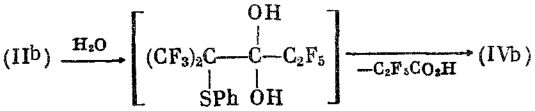
$$R = Et\,(IVa),\ R = Ph\,(IVb)$$

Acid chloride (IIc) was obtained previously [2] by the addition of PhSCl to bis(trifluoromethyl)ketene when catalyzed by pyridine. The analogous addition of PhSCl to N-phenylbis-(trifluoromethyl)ketenimine gives imidoyl chloride (V).



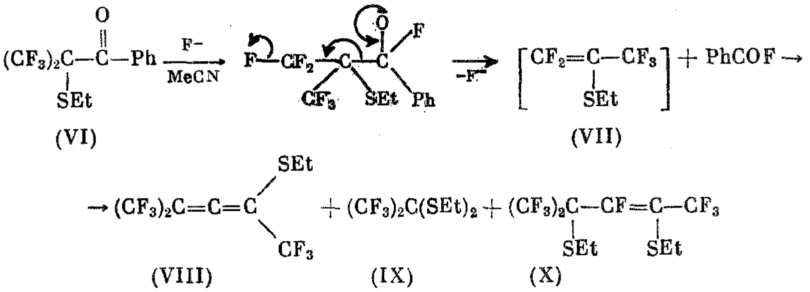
$$(CF_3)_2C{=}C{=}NPh + PhSCl \xrightarrow[C_5H_5N]{} \underset{\text{(V)}}{(CF_3)_2\underset{SPh}{C}-\overset{Cl}{C}{=}NPh}$$

Another example is the exceedingly easy "haloform" decomposition of ketone (IIb) even when it is dissolved in moist ether.



$$(IIb) \xrightarrow{H_2O} \left[(CF_3)_2\underset{SPh}{C}-\overset{OH}{\underset{OH}{C}}-C_2F_5\right] \xrightarrow[-C_2F_5CO_2H]{} (IVb)$$

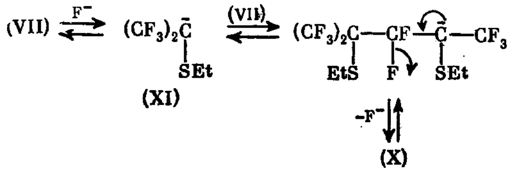
Phenyl 2-ethylthiohexafluoroisopropyl ketone (VI) does not react with water even under drastic conditions (100°, diglyme), but it decomposes completely in several hours when treated with catalytic amounts of CsF in acetonitrile at 20°. The formation of 2-ethylthiopentafluoropropylene (VII) and PhCOF could be expected here:



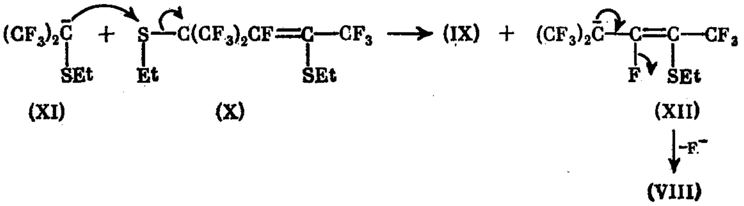
$$\underset{\text{(VI)}}{(CF_3)_2\underset{SEt}{C}-\overset{O}{\overset{\|}{C}}-Ph} \xrightarrow[MeCN]{F^-} F-CF_2-\underset{CF_3\ \ SEt}{C}-\overset{O^-}{\underset{Ph}{C}}-F \xrightarrow{-F^-} \underset{\text{(VII)}}{\left[CF_2{=}\underset{SEt}{C}-CF_3\right]} + PhCOF \rightarrow$$

$$\rightarrow \underset{\text{(VIII)}}{(CF_3)_2C{=}C{=}C\begin{matrix}SEt\\CF_3\end{matrix}} + \underset{\text{(IX)}}{(CF_3)_2C(SEt)_2} + \underset{\text{(X)}}{(CF_3)_2\underset{SEt}{C}-CF{=}\underset{SEt}{C}-CF_3}$$

However, together with PhCOF, 1,1,3-tris(trifluoromethyl)-3-ethylthioallene (VIII) and 2,2-diethylthiohexafluoropropane (IX) were isolated, and also the dimer of olefin (VII), namely 2,4-diethylthioperfluoro-(4-methyl-2-pentene) (X). The formation of these products is related to the transformations of olefin (VII) when treated with F$^-$ (a convenient method for the preparation of olefin (VII) is the dehydrofluorination of ethyl hexafluoroisopropyl sulfide (IVa) by KOH powder in ether). Actually, when (VII) in MeCN is treated with catalytic amounts of CsF at 20° the olefin is gradually converted to (VIII)-(X), in which connection it was established by GLC that in the initial reaction period, which is ended in 4-5 h, the amount of dimer (X) in the reaction mixture reaches a maximum and then it decreases, with a gradual increase in the amount of allene (VIII) and dithio ketal (IX). The formation of dimer (X) does not evoke astonishment, since dimerization during F$^-$ catalysis is very characteristic for many fluoroolefins [8]. The formation of allene (VIII) and dithio ketal (IX) is evidently related to the fact that the dimerization of (VII) is a reversible reaction and a certain concentration of carbanions (XI) is retained in the reaction medium.



Carbanion (XI) is capable of being sulfenylated by dimer (X), which leads to dithio ketal (IX) and the intermediate allyl anion (XII). The latter is stabilized by the elimination of F^-, giving allene (VIII).



In conclusion, it should be mentioned that the sulfenylation of fluorinated CH acids expands the gamut of the reactions of this type of compounds, which have been studied up to now, with electrophilic reagents (see, for example, [5, 9]).

EXPERIMENTAL

The ^{19}F NMR spectra were recorded on a Hitachi spectrometer (56.46 MHz, external standard = CF_3COOH), and the IR spectra were recorded on a UR-20 instrument. The GLC analysis was run on an LKhM-8MD instrument, using a column packed with Silicone DS-550 deposited on Chromosorb.

Sulfenylation of Fluorinated CH Acids (typical method). With stirring and cooling with ice, to a solution of 0.05 mole of the CH acid in 50 ml of abs. ether were added in drops 0.05 mole of Et_3N and then a solution of 0.05 mole of RSCl in 25 ml of ether. The mixture was stirred for 2-3 h at 20°, the precipitate of $Et_3N \cdot HCl$ was separated, and the filtrate was distilled. The yields and constants of the products are given in Table 1.

Ethyl Hexafluoroisopropyl Sulfide (IVa). With stirring and cooling with ice, to 3 ml of water in 40 ml of diglyme was added in drops 17.5 g of the acid fluoride of α-ethylthiohexafluoroisobutyric acid (IIa) in 1 h. After the gas evolution had ceased the fraction with bp up to 160° was distilled from the reaction mixture, which was poured into water, and the organic layer was separated and vacuum distilled over conc. H_2SO_4 to give 10.7 g of sulfide (IVa) with bp 45-50° (90 mm).

Phenyl Hexafluoroisopropyl Sulfide (IVb). To a solution of 9.6 g of ketone (IIb) in 30 ml of ether was added 5 ml of water, and the mixture was stirred for 3 h at 20°. At the end of reaction (checked by GLC) the ether layer was washed with water, dried over $MgSO_4$, and distilled to give 4.1 g of sulfide (IVb).

2-Ethylthiopentafluoropropylene (VII). With stirring and cooling with ice, to a suspension of 12.4 g of KOH powder in 15 ml of abs. ether was added in drops 9.4 g of ethyl hexafluoroisopropyl sulfide (IVa) in 10 ml of ether. The mixture was stirred for 2 h at 20° until all of the sulfide was converted (GLC), and the volatile products were distilled at 10 mm into a trap (−78°). From the trap contents was distilled 15 ml of ether through a column, while the residue was treated under cooling with conc. H_2SO_4. Olefin (VII) was isolated by distillation.

Reaction of 2-Ethylthiopentafluoropropylene (VII) with CsF. A mixture of 0.6 g of freshly ignited CsF, 6 g of olefin (VII), and 13 ml of abs. MeCN was stirred for 5 h at 20°, poured into water, and the obtained oil was extracted with ether, dried, and distilled. We obtained 1 g of a fraction with bp 56-60° (85 mm), which contained (GLC) 90% of allene (VIII), and 3.1 g of a fraction with bp 50-93° (12 mm), which contained 5% of allene (VIII), 56% of dithio ketal (IX), and 39% of dimer (X). The pure (VIII)-(X) were isolated by preparative GLC (QF-1 deposited on Chromosorb).

Reaction of N-Phenyl-bis(trifluoromethyl)ketenimine with Benzenesulfenyl Chloride. To a solution of 2.45 g of the ketenimine and 1.4 g of the sulfenyl chloride in 10 ml of abs. monoglyme was added 0.05 g of pyridine. After 24 h the solvent was vacuum distilled, and distillation of the residue gave 3.2 g (83%) of (V) with bp 140-142.5° (2 mm), n_D^{20} 1.5208. Found: C 48.59; H 2.58%. $C_{16}H_{10}ClF_6NS$. Calculated: C 48.30; H 2.51%. ^{19}F NMR spectrum (in CCl_4): −15.5 s. Infrared spectrum: 1670 cm^{-1} (C=N).

CONCLUSIONS

1. Fluorinated CH acids smoothly react with sulfenyl chlorides in the presence of Et_3N to give either alkyl or aryl polyfluoroalkyl sulfides and polyfluoroalkyl sulfenamides.

2. In a number of reactions the bis(trifluoromethyl)alkyl(aryl)thiomethyl group is effectively leaving as the anion.

3. 2-Ethylthiopentafluoropropylene was synthesized and its transformations during catalysis by fluorine anion were studied.

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ORGANOBORON COMPOUNDS.

376. BROMINATION OF 1-BORAADAMANTANE AND SYNTHESIS OF HETEROBORAHOMOADAMANTANES

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and V. V. Veselovskii

UDC 542.944:546.14:547.1'127

Organoboron compounds easily react with bromine to give brominated organoboranes, which are used successfully in organic synthesis [1].

The bromination of organoboron compounds proceeds by the radical chain mechanism [2, 3]. When the ethylene glycol ester of 1-phenylethylboric acid is brominated in CCl_4, the α-hydrogen is replaced by bromine to give the stable ethylene glycol ester of 1-bromo-1-phenylethylboric acid and HBr [2]. The bromination of triethylborane in the gas phase proceeds in two directions, in which connection $k_1 > k_2$ [3]:

$$\left.\begin{array}{l}(CH_3CH_2)_3B + Br^{\cdot} \xrightarrow{k_1} (CH_3CH_2)_2B\dot{C}HCH_3 + HBr \\ (CH_3CH_2)_2B\dot{C}HCH_3 + Br_2 \rightarrow (CH_3CH_2)_2BCHBrCH_3 + Br^{\cdot}\end{array}\right\} \quad (1)$$

$$\left.\begin{array}{l}(CH_3CH_2)_3B + Br^{\cdot} \xrightarrow{k_2} (CH_3CH_2)_2BBr + C_2H_5^{\cdot} \\ C_2H_5^{\cdot} + Br_2 \rightarrow C_2H_5Br + Br^{\cdot}\end{array}\right\} \quad (2)$$

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, 1106-1113, May, 1980. Original article submitted March 27, 1979.

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