V. F. Cherstkov, M. V. Galakhov,
 UDC 542.91:547.413.5:546.16:546.

 S. R. Sterlin, L. S. German,
 226-31

 and I. L. Knunyants
 226-31

Fluoroethylene derivatives react with SO_3 to give β -sultones according to an electrophilic mechanism [1]. Higher homologs, such as other perfluoro- α -olefins, also react in uncatalyzed reactions to give cycloaddition products. In the presence of a catalyst, B derivatives in particular, these compounds react with SO_3 to give both cycloaddition products as well as insertion of SO_3 into an allylic C-F bond [2, 3].



Perfluorocyclobutene reacts in an analogous manner with SO_3 to give mono- and perfluorosulfates [4].

In contrast, linear aliphatic internal olefins do not react with SO_3 even in the presence of BF₃, apparently because neither SO_3 nor $SO_3/[BF_3]$ is sufficiently electrophilic with respect to this class of compounds. For this reason, we have proposed examining the reactions of internal perfluoroolefins with SO_3 in the presence of a more powerful Lewis acid catalyst, namely, SbF₅.

It was found that treatment of perfluoro-2-alkenes in the presence of 1-2% SbF₅ results in insertion of SO₃ into the C-F bond of a CF₃ group to give the corresponding fluorosulfates (I).*

$$R_{F}CF = CFCF_{3} \xrightarrow{SO_{3}/(SbF_{3}]} R_{F}CF = CFCF_{2}OSO_{2}F$$
(Ia - e)
$$R_{F} = C_{3}F_{7}(a); i-C_{3}F_{7}(b); t-C_{4}F_{9}(c); C_{5}F_{11}(d); C_{2}F_{5}(e).$$

The first step of the mechanism of this reaction presumably involves reaction of SbF_5 with SO_3 to form Sb fluorosulfate derivatives. It has been demonstrated previously that heating SbF_5 with SO_3 (in a 1:7 molar ratio) leads to the formation of pyrosulfuryl difluoride [6]. Later it was also found that tetrafluorofluorosulfate antimony was formed upon treatment of SbF_5 with SO_3 in a molar ratio of $SbF_5:SO_3$ of 1:2.1 [7]. Higher fluorosulfateantimony fluorides ($FSO_2O_1nSbF_5-n$ (II) (n = 1-3) are obtained upon reaction of SbF_5 with SO_3 (1:1-3 molar ratio) in HSO_3F [8]. Fluorosulfatefluorides (II) with n > 3 have not been successfully prepared; according to the authors, these compounds should be unstable, decomposing with elimination of SO_3 .

We have now demonstrated by means of ¹⁹F NMR that solutions of SbF_5 in SO₃ in the concentration range 0.004-0.04 mole % contain only fluorosulfonyl groups; the spectra exhibit several signals in the -124 to -126 ppm region, and do not contain any signals characteristic of Sb-F bonded atoms. It is assumed, therefore, that when SbF₅ is dissolved in the presence of excess SO₃, either Sb(OSO₂F)₅ or other mixed anhydrides of fluorosulfonic and antimony acids are formed.

*For preliminary communication, see reference [5].

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1864-1868, August, 1985. Original article submitted April 16, 1984.

Compound	δ, ppm, J, Hz			
$CF_{3}F_{2}CF_{2}CF_{2}CF = CFCF_{2}OSO_{2}F$ (Ia)	$\begin{cases} 4.6 \text{ br. s } (F^1), 51.1 \text{ t } (F^2), 42.7 \text{ d.d.t } (F^3), \\ 75.5 \text{ d.d.t } (F^4), 79.2 \text{ d.t.t } (F^5), -4.5 \text{ d.d.d} \\ (F^6), -126.2 (F^7), J_{2-3}=10, J_{3-4}=10, \\ J_{4-5}=132, J_{4-6}=26.5, J_{5-6}=9.8, J_{6-7}=9.4 \end{cases}$			
$(CF_3)_2 CFCF = CFCF_2 OSO_2^6 (Ib)$	$\begin{bmatrix} -1,33 \text{ d.d.} (F^1), 111 \text{ d.d.hept} (F^2), \\ 76,4 \text{ d.m} (F^3), 81,6 \text{ d.d.t.hept} (F^4), \\ -4,66 \text{ d.d.} (F^5), 125,91 (F^6), J_{1-2}=7,5, \\ J_{1-4}=5,5, J_{1-3}=8,5, J_{2-4}=44,2, J_{2-3}=8,5, \\ J_{4-4}=144, J_{4-4}=26, J_{4-4}=28, J_{4-4}=8-5 \end{bmatrix}$			
$(CF_{3}^{1})_{3}CCF = CFCF_{2}^{3}OSO_{2}F^{5}$ (Ic)	$\begin{array}{c} -14.2 \text{ m}(\text{F}^{1}), \ 68.9 \text{ m} \ (\text{F}^{2}+\text{F}^{3}), \ 5.7 \text{ m}(\text{F}^{4}), \\ -126.4 \text{ m} \ (\text{F}^{5}), \ \text{F}^{1}: \ (\text{F}^{2}+\text{F}^{3}): \ \text{F}^{4}: \ \text{F}^{5}=\\ =9:2:2:4 \end{array}$			
$CF_{3}CF_{2}CF_{$	trans-isomer: 5.3m (F ¹), 49.5 m (F ²) 47 m (F ³), 46,1m (F ⁴), 41,7m (F ⁵), 75.3 d.t.m (F ⁶), 79d.t.m (F ⁷), -4,4 d.d.d (F ³) -126,4 t (F ⁹); J_{e-7} =139, J_{e-8} =25,4, J_{7-8} =8, J_{5-9} =8 cis-isomer: 5.8 m (F ¹), 49.5 m (F ²), 47m (F ³), 46,3m (F ⁴), 39,3m (F ⁵), 58m (F ^e), 59,3m (F ⁷), -6,7m (F ⁸), -126,1 (F ⁹)			
$CF_{3}CF_{2}CF = CFCF_{2}OSO_{2}F^{6}$ (Je)	8,3d.d.t (F ¹), 45,3 d.d.q (\vec{F}), 76.4 d.t.t.q (F ³), 79,8d.t.t (F ⁴), -4,3 d.d.d (F ⁵), -125 t (F ⁶), $J_{1-2}=2$, $J_{1-3}=J_{1-4}=5$, $J_{2-3}=7,5$, $J_{2-4}=34,5$, $J_{3-4}=147$, $J_{3-5}=34,5$, $J_{4-5}=7,5$, $J_{5-6}=7,5$			
$^{1}_{CF_{3}CF_{2}CF_{2}CF_{2}CF} = ^{5}_{CFCOF} ^{6}_{(III a)}$	4.9 t (F ¹), 51.8d.d. (F ²), 42.9 d.d.q (F ³), 63.7d.d.m (F ⁴), 78.8 d.d.t.t (F ⁵), $-103.6 d.d$ (F ⁶), $J_{1-2}=8.5$, $J_{2-4}=5.6$, $J_{2-5}=8$, $J_{3-4}=8.5$, $J_{3-5}=27.3$, $J_{4-5}=135.6$, $J_{4-6}=56.5$, $J_{5-6}=20.7$			
$(CF_3)_2 CFCF = CFCOF$ (IIIb)	-161d.d.d (F^1), 110,7 d.d. hept (F^2), 62,4 d.d.d hept (F^3), 77,4 d.d.d. hept (F^4). -103,3 d.d.(F^5), $J_{1-2}=6$, $J_{1-3}=8,4$, $J_{1-4}=5,6$, $J_{2-3}=10,3$, $J_{2-4}=48$, $J_{3-4}=139$, $J_{3-5}=56,5$, $J_{4-3}=22,6$			
$(CF_3)_3CCF = CFCOF^4$ (IIIc)	-14.22d.d (F ¹), 55,5 d.d.dec (F^2), 68,2 d.d.dec (F^3), -104,4 d.d (F^4), $J_{1-2}=12$, $J_{1-3}=17,9, J_{2-3}=135,4, J_{2-4}=54,1, J_{3-4}=21,6$			
$CF_{2}CF_{2}CF_{2}CF_{2}CF_{2}CF_{2}CF$ (IIId)	trans-isomer: $-5,3 \text{ m}(F^4)$, $50,1 \text{ m}(F^2)$, $47 \text{ m}(F^3)$, $46 \text{m}(F^4)$, $42,1 \text{m}(F^5)$, $64 \text{ d.m}(F^5)$, $77,3 \text{ d.m}(F^7)$, $-103,4 \text{ d.d}(F^8)$, $J_{6-7}=125$, $J_{6-8}=56$, $J_{7-8}=49,5$ cis-isomer: $5,3 \text{m}(F^4)$, $50,1 \text{m}(F^2)$, $47 \text{ m}(F^3)$, $45,7 \text{m}(F^4)$, $38,5 \text{m}(F^5)$, $49 \text{m}(F^6)$, $57 \text{m}(F^7) - 105,5 \text{m}(F^8)$			
$(CF_3)_2 CFCF = CFCOOSO_2F$ (IVa)	$-1.9d$, d, d (f^{i}), 110,2 d, d, hept (F^{2}), 59,5 d, d, hept (F^{3}), 76,9 d, d, hept (F^{4}), $-124.4s$ (F^{5}); $J_{1-2}=6.2$, $J_{1-3}=6.2$, $J_{1-4}=5.6$, $J_{2-3}=10.3$, $J_{2-4}=40.2$, $J_{3-4}=136$			
$(CF_3)_3CCF = CFCOOSO_2F$ (IVb)	-13.9d.d (F ¹), 53.5 d. dec (f^2), 69.1 d. dec (f^3), -124.1s (F ⁴), J_{1-3} =18.8, J_{1-2} =12.2, J_{2-3} =137.4			
$^{1}_{CF_{3}CF_{2}CF} = ^{3}_{CFCOOH} (Va)$	8,5 d.d.t (F ¹), 45,3 d.d.q (f^2), 67.3 d.t.q (F ³), 77,1 d.t.q (F ⁴), $J_{1-2}=3$, $J_{1-3}=$ = $J_{2-3}=4,5$, $J_{1-4}=6,5$, $J_{2-4}=27,5$, $J_{3-4}=124$			
$CF_{3}CF_{2}CF_{$	4.4m (F ¹), 50m (F ²), 41m (F ³), 65d.m (\mathbf{F}^{4}), 73,5d.m (F ⁵), J_{4-5} =125			
$(CF_3)_2 CFCF = CFCOOH (Vc)$	-1.1 \dot{m} (F ⁴), 110d.m (F ²), 65 d.m (F ³), 76d.d.m (F ⁴); $J_{2-4}=26,5, J_{3-4}=70$			
$(CF_3)_3CCF = CFCOOH (Vd)$	$-14,5 \text{ m} (\text{F}^{1}), 79 (\text{F}^{2}+\text{F}^{3}), \text{F}^{1}: (\text{F}^{2}+\text{F}^{3})=9:2$			

Compound	δ, ppm, J, Hz
$^{1}_{CF_{3}CF_{2}CF_{2}CF_{2}CF_{2}CF_{2}CF_{2}CF=CFCOOH}^{7}$ (Ve) (obtained by washing fluoroanhydride (IIId))	trans-isomer: $4,4 \text{ m}$ (F ¹), $49,5 \text{ m}$ (F ²), 46,9 m (F ³), $45,9 m$ (F ⁴), $41 m$ (F ⁵), $72,3 m(F6+F7)cis-isomer: 4,4 \text{ m} (F1), 49,5 \text{ m} (F2), 45,9 \text{ m}(F3), 45,2 \text{ m} (F4), 37 \text{ m} (F5), 51,2 \text{ m} (F6),64,5 m$ (F ⁷)

Compound	Yield, %	b p, Շ (p, mm Hg)	Found/Calculated, %			
			С	н	F	S
(Ia)	93	115-116				8,22
(Ib)	93	107-110	<u>18,75</u> 18 94		<u>60,38</u> 60.00	8,66
(Ic)	89	128-129	<u>19,92</u> <u>19,55</u>		00,00	7,62
(Id)	87	78-80(50)	<u>19,54</u> 20.00		$\tfrac{63,34}{63,33}$	
(Ie)	65	87	<u>18,85</u> <u>18,18</u>		58,35 57,57	
(1112)	78	79-80	$\frac{25,90}{25,89}$		$\tfrac{68,25}{68,34}$	
(Шь)	83	74-76	$\frac{25,83}{25,89}$		$\frac{68,39}{68,34}$	
(IIIc)	80	85-86	$\frac{25,95}{25,61}$		$\begin{array}{r} 69,63\\ \hline 69,51 \end{array}$	
(IIId)	54	124-123	$\frac{25,35}{25,39}$		$\frac{70,28}{70,39}$	
(IVa)	84	60(20)	<u>8,91</u> 8,93		<u>52,92</u> 53,08	
(IVb)	97	65 (20)	$\tfrac{20,35}{20,58}$		$\tfrac{54,62}{55,88}$	
(Va)	73	152	$\frac{26,11}{26,15}$	$\frac{0,37}{0,44}$	58,88 58,84	
(Vb)	73	89-90(20)	$\frac{26.09}{26.08}$	0,33	$\tfrac{61,97}{62,14}$	
(Vc)	70	173–174 98–100(40)	$\frac{26,02}{26,08}$	$\frac{-0,36}{-0,37}$	$\frac{61,96}{62,14}$	
(Vd)	72	183186 110115 (40)	$\frac{26,14}{25,77}$	$\frac{-0.42}{-0.31}$		
(Ve)	92	93-95(7) (crystallizes upon standing, mp 54-55°C)	$\frac{25,27}{25,53}$	<u>0,36</u> 0,27	$\frac{65,68}{65,69}$	

TABLE 2. Properties of the Fluorosulfates (I)

The mechanism for the formation of the fluorosulfates (I) involves nonclassical carbonium ion intermediates and is analogous to a mechanism which has been proposed earlier [2, 4]; it is assumed that the stereoisomeric composition of the intermediate(s) is independent of the stereoisomeric composition of the fluoroolefinic precursors. However, separate experiments revealed that a change in the ratio of the cis and trans isomers in the fluoroolefin was accompanied by a symbatic change in the streoisomeric composition of the reaction product. This fact indicates that a purely carbonium ion mechanism is not realized in this reaction. The formation of the fluorosulfates (I) apparently occurs via a cyclic transition state involving a Sb(V) fluorosulfate derivative

$$SbF_{5} + SO_{3} \rightarrow FSO_{2}OSb = R_{F}CF = CFCF_{2} \qquad Sb = R_{F}CF = CFCF_{2}OSO_{2}F + (I)$$

$$(I)$$

$$SbF_{5} + SO_{3} \rightarrow FSO_{2}OSb = (I)$$

Treatment of the perfluoroalkenylfluorosulfates with excess SO_3 results in insertion of a second molecule of SO_3 into a C-F bond.

The resulting geminal bis(fluorosulfates) are unstable and eliminate pyrosulfuryl difluoride to generate fluoroanhydrides of perfluorinated α,β -unsaturated acids (III), which, under the reaction conditions, react with a third molecule of SO₃ to yield the perfluoroacylfluorosulfates (IV).

$$R_{F}CF = CFCF_{3} \xrightarrow{SO_{3}/[SbF_{5}]} (I) \xrightarrow{SO_{3}/[SbF_{5}]} [R_{F}CF = CFCF(OSO_{2}F)_{2}] \xrightarrow{-(FSO_{2})_{2}O} [R_{F}CF = CFCOF] \rightarrow R_{F}CF = CFCOOSO_{2}F (III) (IVa-d)$$

$$R_{F} = C_{2}F_{5}(a); C_{3}F_{7}(b); i-C_{3}F_{7}(c); t-C_{4}F_{9}(d).$$

It is not possible to separate the perfluoroacylfluorosulfates (IV) from the mixture of inorganic fluorosulfates by distillation of the reaction mixture. Analytically pure samples of (IV) were obtained according to [9] via reaction of the fluoroanhydrides (III)* with SO_3 .

Washing the acylfluorosulfates (IV) with aqueous base followed by workup of the resulting salts with concentrated H_2SO_4 gives excellent yields of the α,β -unsaturated acids (V).

$$(IVa-d) \xrightarrow{\text{NaOH}} \text{R}_{F}CF = CFCOONa \xrightarrow{\text{H}_{s}\text{SO}_{4}} \text{R}_{F}CF = CFCOOH \qquad \text{R}_{F} = C_{2}F_{5}(a); C_{3}F_{7}(b); i-C_{3}F_{7}(c); t-C_{4}F_{9}(d).$$

EXPERIMENTAL

¹⁹F NMR spectra were recorded on a Perkin-Elmer R-32 spectrometer at 84.6 MHz versus CF₃COOH as internal standard.

<u>Solutions of SbF₅ in SO₃</u>. A weighed, freshly prepared sample of SO₃ was treated dropwise with stirring with freshly prepared SbF₅ (1-10%) and stirred for 2-2.5 h until all of the SbF₅ had dissolved. A ¹⁹F NMR spectrum of a 8% solution of SbF₅ in SO₃ was recorded on a Bruker WP-200 SY spectrometer at 188.3 MHz versus CF₃COOH as internal standard: δ_1 (ppm) -125.35 br s; δ_2 -125.82 br s; δ_3 -125.97 br s; δ_4 -126.05 br.s; intensity ratio $\delta_1:\delta_2:\delta_3:\delta_4 =$ 14.3:7:3.27:1.

Solutions of Fluorosulfates (I). a) Typical Experiment. A mixture of fluoroolefin (cis:trans ratio = 5:95) and 1-2% of a solution of SbF_5 in SO_3 (molar ratio of perfluoro-olefin to $SO_3 = 2:1$) was heated in a sealed glass ampoule for 2 h at 75-80°C. The mixture was worked up with a small portion of concentrated H_2SO_4 and concentrated at 25-40 mm Hg pressure. Repeated distillation gave the fluorosulfates (I) (see Tables 1 and 2).

b) Under the experimental conditions described in a) above, 15 g of perfluorooct-2-ene (cis:trans = 52:48) and 1.4 g of a 1% solution of SbF_5 in SO_3 yielded 2.5 g of (Id) (cis:trans = 34:66); 12.7 g of the starting material perfluorooct-2-ene (cis:trans = 55:45) was recovered. The ratio of the stereoisomeric products (Id) reflects the ratio of the stereoisomers entering into reaction (cis:trans = 35:65), which apparently reflects the differing rates of reaction of the stereoisomers.

Synthetic Acids (V). A mixture of perfluoroolefin and a 1-2% solution of SbF_5 in SO_3 (perfluoroolefin: SO_3 molar ratio = 1:3.1) was heated in a sealed glass ampoule for 2 h at 80°C, for 4 h at 100°C, and then was distilled *in vacuo* over conc. H_2SO_4 . The resulting mixture contained, according to GLC and ¹⁹F NMR analysis, the acylsulfate (IV) and a mixture of polysulfuryl difluorides. The product mixture was cooled and neutralized, with vigorous stirring, with a 15% aqueous NaOH solution, and then evaporated on a steam bath; the residue was extracted with EtOH. After removal of the alcohol solvent the residue was acidified by treatment with a 2-3 fold excess of conc. H_2SO_4 and distilled under vacuum to give the acid (V).

The individual acylsulfates (IV) were prepared by heating equimolar mixtures of the fluoroanhydrides (III) and SO₃ in a sealed glass ampoule (2 h at 100°C), followed by vacuum distillation of the product mixtures.

Synthetic Fluoroanhydrides (III). A weighed portion of fluorosulfate (I) was treated with a small amount of fused KF until all traces of SO_3 had been removed; the mixture was vacuum distilled, and the distillate was treated with 10-20 mole % of freshly fused CsF and maintained at 20-60°C until all gas evolution had ceased. The resulting fluoroanhydride was condensed *in vacuo* in a trap cooled to -78°C. The fluoroanhydrides (III) were then obtained via distillation of the trapped condensate.

*The fluoroanhydrides (III) were prepared by cleavage of the fluorosulfates (I) upon treatment with alkali metals [10].

CONCLUSIONS

In the presence of SbF₅ sulfur trioxide undergoes insertion reactions into the allylic C-F bonds of perfluoro-2-alkenes to give perfluoroalk-2-enyl fluorosulfates.

LITERATURE CITED

- 1. I. L. Knunyants and G. A. Sokolski, Angew. Chem. Inter. Ed., 11, 583 (1972).
- 2. C. G. Krespan and D. C. England, J. Am. Chem. Soc., 103, 5598 (1981).
- 3. V. F. Cherstkov, S. R. Sterlin, L. S. German, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 2791 (1982).
- 4. B. E. Smart, J. Org. Chem., <u>41</u>, 2353 (1976).
- 5. V. F. Cherstkov, S. R. Sterlin, L. S. German, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 1917 (1982).
- 6. E. Hayek and W. Koller, Monats., 82, 942 (1951).
- 7. R. I. Gillespie and R. A. Rothenburg, Can. J. Chem., 42, 416 (1964).
- 8. R. C. Thompson, J. Barr, R. J. Gillespie, J. B. Milne, and R. A. Rothenburg, Inorg. Chem., 4, 1641 (1965).
- 9. C. G. Krespan and D. C. England, J. Org. Chem., 40, 2937 (1975).
- V. F. Cherstkov, S. R. Sterlin, L. S. German, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 1872 (1983).

SYNTHESIS AND STRUCTURE OF N-ETHYL-N-PROPARGYLPHOSPHONAMIDIC CHLORIDES

UDC 542.91:541.6:547. 1'118

A. A. Shtyrlina, K. M. Enikeev,
E. V. Bayandina, I. É. Ismaev,
A. V. Il'yasov, and I. A. Nuretdinov

Acetylenic organophosphorus compounds present interest as biologically active substances [1] and intermediate products in organic synthesis [2, 3]. Acid halides of N-propargylamidoacids of phosphorus are important initial compounds in the production of various organophosphorus compounds since the halogen atom is readily substituted on interacting with nucleophilic reagents. The synthesis of the acid dichlorides of some N-alkylpropargylamidophosphoric and thiophosphoric acids was described in the brief communication [4].

The present work describes the production of N-ethyl-N-propargylphosphonamidic, phosphonamidothioic, and phosphonamidoselenoic chlorides by reaction of the corresponding phosphonic dichloride (I) with N-ethyl-N-propargylamine (II) in the presence of base

 $\begin{array}{c} X & X \\ RPCl_2 + HN(Et)CH_2C \equiv CH & +B \\ (I) & (II) \end{array} \begin{array}{c} H \\ R = Et, X = O \ (a); R = Et, X = S \ (b); R = Et, X = Se \ (c); R = Ph, X = O \ (d); \\ R = Ph, X = S \ (e); R = Ph, X = Se \ (f); B = Et_3N. \end{array}$

The compounds (IIIa-f) were obtained in an inert atmosphere in dry solvent. Compounds (IIIa-e) are liquids which are distilled *in vacuo*; but (IIIf) is a crystalline substance. It should be noted that the derivatives of selenophosphonic acids (IIIc) and (IIIf) are unstable in the presence of moisture in the air. The structure and the purity of the compounds obtained are confirmed by spectra methods and elemental analysis. The constants and some spectral characteristics of (IIIa-f) are presented in Table 1. A doublet characteristic of vibrations of the $\Xi C-H$ bond is observed in the IR spectra of (IIIa) and (IIId) in the region of 3200-3300 cm⁻¹, whereas one absorption band is observed in the spectra of the thio

A. E. Arbuzov Institute of Organic and Physical Chemistry, Każan Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1869-1872, August, 1985. Original article submitted February 20, 1984.