CHLORINE FLUOROSULFATE

7. MECHANISM OF THE SUBSTITUTION OF HALOGEN ATOMS BY CHLORINE FLUOROSULFATE

A. V. Fokin, Yu. N. Studnev,
I. N. Krotovich, L. D. Kuznetsova,
and O. V. Verenikin

UDC 541.124:542.91:546.226'16'131

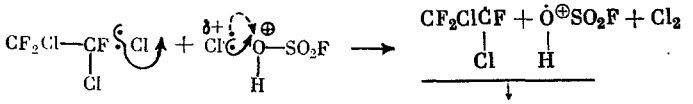
Chlorine fluorosulfate comparatively smoothly substutes chlorine atoms in freons on the fluorosulfate group in the presence of HSO_3F [1, 2]; moreover, an increase in the amount of the latter activates the $ClOSO_2F$ [2].

Further study of the indicated reaction, with the goal of making its mechanism and the possible limits of its application more precise, showed that the process is catalyzed only by strong acids of the type HSO_3F, whereas even CF_3COOH is practically not active. As was established HSO_3Cl theoretically could be used as a catalyst, but in this case it easily reacts with $ClOSO_2F$ with the formation of chlorine and poorly stable HS_2O_6F [3]. Therefore, the catalytic action can be explained by the appearance of HSO_3F

$$ClOSO_2F + HSO_3Cl \rightarrow \underset{\downarrow}{FSO_2OSO_3H} + Cl_2$$
$$HSO_3F + SO_3$$

A more detailed study of the ^{19}F NMR spectra of the HSO_3F—$ClOSO_2F$ system shoed that upon mixing equivalent amounts, the individual signals of $ClOSO_2F$ (δ—112.2) and HSO_3F (δ—119.0) disappear and a single signal with δ—116.1 appears. In addition, solutions of $BrOSO_2F$ in HSO_3F have a rather low electric conductivity [4]. To a certain degree, this data confirms the assumption earlier expressed by us that HSO_3F contributes a stronger polarization of the Cl atom in $ClOSO_2F$ [2]. Therefore, the development of the process according to the following scheme of a one-electron transfer becomes possible:

$$ClOSO_2F + H^{\oplus} + SO_3F^{\ominus} \rightarrow \underset{\underset{H\,(I)}{|}}{Cl\overset{\oplus}{O}SO_2F} + SO_3F^{\ominus}$$



$$CF_2ClCFClOSO_2F \xleftarrow[-HSO_3F]{SO_3F^{\ominus}} CF_2ClCFCl\overset{\oplus}{O}SO_2F \quad (H)$$

Moreover, compound (I) evidently has a limited stability, since it is possible to almost quantitatively separate an equimolar mixture of $ClOSO_2F$ and HSO_3F into its component parts by fractional distillation.

Subsequently it was established that $ClOSO_2F$, just as easily as in Freons, substitutes Cl atoms in acid chlorides of perfluorocarboxylic acids (already at ~20°C with a slight exothermic effect) with the formation of mixed anhydrides of perfluorocarboxylic and fluorosulfonic acids

$$RCOCl + ClOSO_2F \longrightarrow RC(=O)OSO_2F + Cl_2$$

(IIa-c)

R = CF_3 (IIa), C_3F_7 (IIb), C_8F_{17} (IIc)

Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 806-809, April, 1979. Original article submitted October 25, 1977.

 0568-5230/79/2804-0748$07.50

The reaction is also catalyzed by HSO_3F and, as a rule, brief heating to 60-70°C is necessary for its completion. The reaction of $ClOSO_2F$ with CF_3COCl is accomplished by heating in a steel autoclave with a glass lining (4 h at 70°C). Fluoroanhydrides of perfluorocarboxylic acids are significantly less active. For example, after heating the fluoroanhydride of perfluoropelargonic acid and $ClOSO_2F$ (28 h at 80°C), mixed anhydrides (IIc) are obtained in an insignificant yield.

Earlier reactions of $(OSO_2F)_2$ with derivatives of polyfluorocarboxylic acids [5-7] and with bis(trifluoromethyl) ketene [8], N,N-difluorohydroxylamine-O-fluorosulfate with bis-(trifluoromethyl) ketene [8], treatment of fluoroanhydrides of carboxylic acids with SO_3 [9, 10], and also the addition of $ClOSO_2F$ to bis(trifluoromethyl ketene [11] were used for the synthesis of mixed anhydrides of fluorocarboxylic and fluorosulfonic acids.

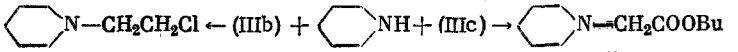
In the course of the subsequent research it was established that by means of $ClOSO_2F$ the selective substitution of a Cl atom in chloroalkanes and even in complex molecules, for example in esters of monochloroacetic acid, on the fluorosulfiate group is completely feasible

$$RCH_2Cl + ClOSO_2F \rightarrow \underset{\text{(IIIa–d)}}{RCH_2OSO_2F} + Cl_2$$

R = Cl(IIIa), CH_2Cl(III b, COOBu (III c, COOEt (IIId)

The reaction is easily accomplished at minus temperatures, better in a solvent [excess of chloroalkane for compounds (IIIa) and (IIIb) or in Freons]. Upon the addition of $ClOSO_2F$ to a solution of (IIIc) in Freon-113 at −35°C an intense violet coloration, which disappears in time, is observed at the spot of the addition and in the gaseous phase.

Alkylfluorosulfates (IIIa) and (IIIb) (the latter was described earlier [11, 12]) are sufficiently stable and their isolation does not encounter any difficulty. The esters of fluorosulfatoacetic acids (IIIc) and (IIId) quickly darken at 20°C, and decompose upon distillation in vacuum. They are by far more active than alkylfluorosulfates and already at −35°C alkylate not only amines but also benzene



(IV) (V)

$$(IIId) + C_6H_6 \rightarrow \underset{\text{(VI)}}{C_6H_5CH_2COOEt}$$

The high alkylation capacity of alkylfluorosulfates is widely known; however, earlier benzene was alkylated without a catalyst only by isopropylfluorosulfate at ~25°C [13].

Thus, on the basis of $ClOSO_2F$, rather broad possibilities of synthesis of diverse and earlier inaccessible alkylating agents are made available. The limited stability of some of the products does not lessen their value since, after removal of Cl_2 in vacuum, they can be successfully used for various synthetic goals.

EXPERIMENTAL

^{19}F and ^1H NMR spectra are taken on a Hitachi R-20 (56.45; 60.0 MHz) instrument. Chemical shifts are presented in ppm relative to CF_3COOH and HMDS. IR spectra are taken on a Perkin–Elmer 225 spectrophotometer.

Mixed Anhydride of Perfluoropelargonic and Fluorosulfonic Acids (IIc). The dropwise addition is made of 3.48 g of $ClOSO_2F$ at 20°C to a mixture of 8.3 g of the chloroanhydride of perfluoropelargonic acid and 0.2 ml HSO_3F. After completion of the exothermic reaction (~0.7 ml of Cl_2 is evolved), the mixture is heated for 1 h at 60°C. By fractionation 7.5 g (80%) of a colorless liquid is separated: bp 52°C (5 mm); n_D^{20} 1.3073; d_4^{20} 1.817. Found: 19.72% C, 62.49% F, 5.88% S. $C_9F_{19}O_4S$. Calculated: 19.78% C, 62.63% F, 5.86% S. IR spectrum (ν, cm^{-1}): 1870 (C=O), 1480 (S=O), and 832 (S–F). ^{19}F NMR spectrum: 4.6 t (CF_3), 40.3 m ($CF_2C(O)$), 44.7 m, 49.3 m (CF_2), −124.3 s (S–F) (corresponding intensities 3:2:10:2:1).

The mixed anhydride of perfluorobutyric and fluorosulfonic acids (IIb) is prepared in an analogous manner: bp 78-79°C, n_D^{20} 1.2960; d_4^{20} 1.685. ^{19}F NMR spectrum: 4.7 t (CF_3), 50.1 s (CF_2), 41.7 t [$CF_2C(O)$], −124.0 s (S–F), J_{F-F} = 9.0 Hz, see [5]. The mixed anhydride of trifluoroacetic and fluorosulfonic acids (IIa): bp 46-47°C. ^{19}F NMR spectrum: −3.2 s (CF_3), −124.2 s (S–F), see [5, 6, 10].

2-Chloroethylfluorosulfate (IIIb). The dropwise addition with stirring of 13 g of $ClOSO_2F$ is made to 14.4 g CH_2ClCH_2Cl at −35° to −30°C. The mixture is held for 30 min at −30°C, slowly brought to ~20°C and heated for 1 h at 35°C. The total amount of Cl_2 evolved is ~3.5 ml. By fractionation, 13 g (83%) of a colorless liquid is obtained: bp 60°C (17 mm); n_D^{20} 1.3981; d_4^{20} 1.532. IR spectrum (ν, cm^{-1}): 1440, 1222 (S=O), 822 (S—F). ^{19}F NMR spectrum: −114.4 s (S—F). PMR spectrum: 3.82 t (CH_2Cl), 4.74 t (CH_2OSO_2F), J_{H-H} = 5.5 Hz, see [11, 12].

Chloromethylfluorosulfate (IIIa) is prepared by an analogous method: bp 60°C (125 mm); n_D^{20} 1.3781; d_4^{20} 1.589. Found: 7.82% C, 1.34 % H, 12.00% F, 21.32% S. CH_2ClFO_3S. Calculated: 8.08% C, 1.35% H, 12.79% F, 21.55% S. ^{19}F NMR spectrum: −121.5 t (S—F). PMR spectrum: 5.95 d (CH_2), J_{H-F} = 1.5 Hz. Mass spectrum: 113 [$CH_2OSO_2F^+$, 100], 83 [SO_2F^+, 25], 67 [SOF^+, 13.5], 65 [HSO_2^+, 3.1], 64 [SO_2^+, 4.5], 49 [CH_2Cl^+, 75], 48 [SO^+, 8], 30 [CH_2O^+, 4.8], 29 [HCO^+, 18] and 28 [CO^+, 6.2].

Butyl Ester of Fluorosulfatoacetic Acid (IIIc). A solution of 10.8 g $ClOSO_2F$ in 20 ml of Freon-113 is slowly added dropwise to a solution of 12.1 g butyl chloroacetate in 40 ml of Freon-113 at −30°C. An intense violet coloration, which disappeared in time, was observed at the spot of the falling drops and also in the gaseous phase. The mixture is held at −30°C for 30 min, slowly brought to 0°C, and concentrated at 0°C for 15 min in the vacuum of an aspirator for the evolution of Cl_2. To the residue, 10 ml abs. chloroform are added and the product is used for further syntheses without isolation.

The ethyl ester of fluorosulfatoacetic acid (IIIc) is prepared by an analogous method.

N-(β-Chloroethyl)piperidine (IV). Piperidine (8.46 g) is added dropwise with stirring to a solution of 8.1 g of 2-chloroethylfluorosulfate in 20 ml of Freon-113 and 10 ml of $CHCl_3$ at −35 to −40°C. The mixture is slowly warmed to 20°C. The precipitate is filtered, washed with 40 ml of Freon-113 and the solvent is evaporated in the vacuum of an aspirator. By fractionation, 5.3 g (72%) of a colorless liquid is obtained: bp 69°C (13 mm); n_D^{20} 1.4749; d_4^{20} 1.009; chlorohydrate, mp 196°C, see [13].

Obtained by analogous methods: 1) butyl ester of N-piperidineacetic acid (V), bp 85-86°C (1 mm); n_D^{20} 1.4583; see [14]. PMR spectrum: 1.09 m [$(CH_2)_3$], 2.11 m [$N(CH_2)_2$], 2.71 s [$CH_2C(O)$], 3.64 t (OCH_2), 1.09 m [$(CH_2)_3$], and 0.53 t (CH_3). 2) Ethyl ester of phenylacetic acid (VI), bp 63°C (1 mm); n_D^{20} 1.4993; d_4^{20} 1.033; see [15].

The authors express sincere gratefulness to I. L. Knunyants for his help in the interpretation of the substitution mechanism of halogen atoms by chlorine fluorosulfate.

CONCLUSIONS

1. The hypothesis is expressed that substitution of halogen atoms on the fluorosulfate group of chlorine fluorosulfate is accomplished by a one-electron exchange scheme, which is indirectly indicated by ^{19}F NMR spectral data.

2. A method of preparing mixed anhydrides of perfluorocarboxylic and fluorosulfonic acids from the chloroanhydrides of perfluorocarboxylic acids and chlorine fluorosulfate is worked out.

3. The possibility of the synthesis is of highly active alkylating agents is shown, i.e., esters of fluorosulfonic acids by selective substitution of a chlorine atom in the corresponding chloro derivatives under the action of chlorine fluorosulfate.

LITERATURE CITED

1. A. V. Fokin, Yu. N. Studnev, A. I. Rapkin, and L. D. Kuznetsova, Izv. Akad. Nauk SSSR, Ser. Khim., 1892 (1974).
2. A. V. Fokin, Yu. N. Studnev, A. I. Rapkin, L. D. Kuznetsova, O. V. Verenikin, and I. N. Krotovich, Izv. Akad. Nauk SSSR, Ser. Khim., 2422 (1976).
3. W. L. Jolly (editor), Syntheses of Inorganic Compounds [Russian translation], Vol. 3, Mir, Moscow (1970), p. 65.
4. F. Aubke and R. J. Gillespie, Inorg. Chem., 3, 599 (1968).
5. D. D. DesMarteau and G. H. Cady, Inorg. Chem., 5, 169 (1966).
6. J. J. Delfino and J. M. Shreeve, Inorg. Chem., 5, 308 (1966).
7. R. L. Kirshmeier and J. M. Shreeve, Inorg. Chem., 12, 2886 (1973).

8. D. T. Meshri, J. Am. Chem. Soc., 90, 1711 (1968).
9. M. A. Belaventsev, V. A. Pashinin, L. I. Ragulin, and G. A. Sokol'skii, Zh. Org. Khim., 9, 256 (1973).
10. C. G. Krespan and D. C. England, J. Org. Chem., 40, 2937 (1975).
11. A. V. Fokin, Yu. N. Studnev, L. D. Kuznetsova, and I. N. Krotovich, Izv. Akad. Nauk SSSR, Ser. Khim., 649 (1978).
12. M. M. Boudakian, G. A. Hyde, and S. Kongpricha, J. Org. Chem., 36, 940 (1971).
13. W. Marckwald and O. Frobenins, Chem. Ber., 34, 3544 (1901).
14. B. Matkovics, S. Foldeak, J. Pórszdsz, and G. Sipos, Acta Pharm. Hung., 31, 113 (1961).
15. Dictionary of Organic Compounds [in Russian], Vol. 3, IL, Leningrad (1949), p. 376.

RADICAL COTELOMERIZATION OF HEXAFLUOROPROPENE AND ETHYLENE WITH SULFURYL CHLORIDE FLUORIDE

N. A. Grigor'ev, L. S. German, and R. Kh. Freidlina

UDC 541.515:66.095.2:547.313.2:547.413.5

Hexafluoropropene (HFP) enters into a radical chain reaction with difficulty. The radical polymerization of HFP occurs only at pressures of 4500-15,000 atm, temperatures of 100-230°C, and under initiation by γ radiation [1]. Thus, each new example of the involvement of HFP in free-radical reactions is quite interesting.

In the present work, the potential of conducting the radical telomerization of HFP by sulfuryl chloride fluoride in the presence of benzoyl peroxide (BP) or a $Fe(CO)_5$-based initiating system, and also the cotelomerization of HFP and ethylene with FSO_2Cl by peroxidic initiation, are studied.

EXPERIMENTAL

The GLC analyses were carried out on an LKhM-8MD apparatus, in a stream of He (3.5 liters/h) with a thermal conductivity detector (TCD), and a glass column 1000 × 3 mm with 5% SE-30 on an N-AW support at 135 and 170°C. Preparative GLC was on a "Khrom-3" apparatus with a preparative attachment, a steel column 2400 × 6 mm with 5% SE-30 on an N-AW support in a stream of He (8 liters/h), TCD, 140°C. PMR and ^{19}F NMR spectra were recorded on a Hitachi–Perkin–Elmer R-20 spectrometer at 60 MHz and on a Perkin–Elmer R-20 at 90 MHz. Mass spectra were obtained on an AEJ MS-30 mass spectrometer with a DS-50 data handling system (accuracy of mass determination ±0.015 amu), with an ionization chamber temperature of 200°C, 150°C in the glass inlet system, and an ionization voltage of 70 eV.

The reactions were carried out in 10-ml stainless-steel autoclaves. The method of conducting the experiments was identical to that described earlier [2]. The reaction mixture was fractionated by vacuum distillation, and the reaction products were isolated from the corresponding fractions by preparative GLC. The initial amounts of reagents, reaction conditions, and results of the GLC analysis of the reaction mixtures are given in Table 1.

DISCUSSION OF RESULTS

An attempt to carry out the telomerization of HFP with sulfuryl chloride fluoride (90°C, 4 h, 20 mmole HFP, 30 mmole FSO_2Cl, and 2 mole % BP) did not lead to positive results; no reaction products whatsoever were detected. This might be due either to the inability of the electrophilic radical $F\dot{S}O_2$ formed in the initiation stage to combine with the electrophilic HFP, or to the inability of the growing radical $FSO_2[CF_2CF(CF_3)]_n^{\cdot}$, because of its high electrophilicity, to transfer the chain to FSO_2Cl. To verify this hypothesis, we applied the initiating system $Fe(CO)_5$–DMF, the use of which increases the effectiveness of chain transfer in the telomerization of vinylic monomers with CCl_4 [3] and FSO_2Cl [2]. But even in the presence of 2.1 mmole $Fe(CO)_5$ and 5.6 mmole DMF no reaction took place. Thus, it follows that the decisive obstacle to the telomerization of HFP with FSO_2Cl is evidently

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 809-813, April, 1979. Original article submitted November 3, 1977.

0568-5230/79/2804-0751$07.50