ELECTROPHILIC ADDITION TO INTERNAL PERFLUOROOLEFINS

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The reaction of fluoroolefins with electrophilic reagents is usually difficult, although it proceeds very readily even below 0°C with hypohalites [1, 2]. The regiospecificity and stereospecificity of this reaction have been studied only for the lowest members of the series, namely, fluoroethylenes [3].

In the present work, we studied the reactions of chlorine fluorosulfate (I) with internal perfluoroolefins.

Bromine fluorosulfate adds readily to perfluoro-2-butene (IIa) [4]

$$CF_3CF{=}CFCF_3 \xrightarrow{FSO_2OBr} CF_3CFBrCF(OSO_2F)CF_3$$

The symmetrical nature of the starting olefin naturally does not permit us to establish the orientation of the electrophilic addition.

In the previously studied reactions of perfluoro-2-pentene (IIb) and perfluoro-2-hexene (IIc) with secondary amines, the nucleophilic attack is directed exclusively towards C-2 of the starting olefins [5]. This is attributed to the concurrent effect of electronic and steric factors. The reduced −I effect and smaller volume of the CF_3 group relative to C_2F_5 and C_3F_7 determine this course. In the case of electrophilic attack, the electronic and steric factors do not act in the same direction: the electronic effect directs the attack to C-3, while C-2 is more available sterically.

Chlorine fluorosulfate (I) adds to trans-(IIa-d) under mild conditions. Mixtures of regioisomers were obtained from unsymmetrical olefins (IIb-d): (IIIb):(IVb) ∿ 1:2, (IIIc):(IVc) ∿ 1:3, and (IIId):(IVd) ∿ 3:2.

$$CF_3CF{=}CFR_F \xrightarrow{FSO_2OCl} CF_3CFClCFR_F + CF_3CFCFClR_F$$

(II) (III) OSO_2F OSO_2F (IV)

$\downarrow$ CsF $\downarrow$ CsF

$R_F = CF_3$ (a), C_2F_5 (b); n-C_3F_7 (c), i-C_3F_7 (d)

$$CF_3CFClCR_F + CF_3CCFClR_F$$

(V) O O (VI)

Thus, the amount of the "electronic" product isomer (IV) decreases sharply, and the amount of the "steric" product isomer (III) increases accordingly, in going from normal perfluoroalkyl groups C_2F_5 and n-C_3F_7 to iso-C_3F_7.

The ratio of the isomeric adducts was found chromatographically. Unfortunately, the similar adsorption coefficients of the regioisomers did not in all cases permit separation into pure products by preparative gas–liquid chromatography, and the chemical shifts in the ^{19}F NMR spectra of the mixtures could not be completely assigned. However, the structures of isomeric adducts (III) and (IV) were proven by their conversion into the corresponding ketones (V) and (VI) by the action of dry CsF. Separation of the pure ketone products also could be achieved only in some cases. However, the structures of (V) and (VI) were established unequivocally using ^{19}F NMR, IR, and mass spectroscopy.

Study of the stereochemistry of the addition of (I) to (IIa-d) was more difficult. The presence of two regioisomers in the addition products of (I) to (IIb-d) significantly complicated the interpretation of the ^{19}F NMR spectra. Thus, we studied only the structure of the adducts of (I) to trans-(IIa) and to a mixture of 30:70 cis-trans-(IIa). Chroma-

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TABLE 1. The Addition of (I) to (IIb-d)

Compound	Reaction products							
	(III):(IV) ratio	bp, °C (p, mm Hg)	Yield, %	found/calc., %				ν(S=O), cm^{-1}
				C	F	Cl	S	
(IIb)	~1 : 2	117–119	71,5	15,6 / 15,6	54,3 / 54,4	–	–	1490
(IIc)	~1 : 3	62–63 (46)	71,4	16,6 / 16,6	58,1 / 56,9	8,1 / 8,1	7,4 / 7,4	1495
(IId)	~3 : 2	68–69 (63)	83,3	16,7 / 16,6	56,6 / 56,9	8,1 / 8,1	7,1 / 7,4	1495

TABLE 2. Mass Spectra of Polyfluoroalkyl Fluorosulfates (IIIa-d) and (IVa-d): $CF_3CFClCF(OSO_2F)R_F$ (III) and $CF_3CF(OSO_2F)CFClR_F$ (IV)

Compound	R_F	Relative intensity, %									
		M^+	$M^+ - CF_3$	$M^+ - R_F$	R_FCFCl^+	$C_2F_4Cl^+$	$R_FCFSO_3F^+$	$C_2F_4SO_3F^+$	R_F^+	CF_3^+	SO_2F^+
(IIIa)	CF_3	0	5		40		30		100		75
(IIIb)	C_2F_5	0	0	<1	<1	20	8	<1	50	100	90
(IVb)	C_2F_5	0	2	<1	17	6	<1	29	15	100	71
(IIIc)	n-C_3F_7	0	<1	7	<1	50	17	<1	63	100	90
(IVc)	n-C_3F_7	0	<1	1	7	10	<1	35	12	100	88
(IIId)	i-C_3F_7	0	<1	1	<1	40	17	4	37	100	93
(IVd)	i-C_3F_7	0	3	<1	10	10	<1	38	<1	100	90

TABLE 3. Action of CsF on (IIIb-d) and (IVb-d)

Starting mixture	Reaction products						
	(V):(VI) ratio	bp, °C	Yield, %	found/calc., %			ν(C=O), cm^{-1}
				C	F	Cl	
(IIIb)+(IVb)	~1:2	56–57	86,4	21,2 / 21,3	60,9 / 60,6	12,3 / 12,4	1785, 1795
(IIIc)+(IVc)	~1:3	80	90,6	21,5 / 21,7	62,8 / 62,9	10,6 / 10,7	1795
(IIId)+(IVd)	~3:2	78–80	75,1	21,7 / 21,7	62,7 / 62,9	10,7 / 10,7	1779, 1798

TABLE 4. Mass Spectra of Chloroperfluoroalkanones (Va-d) and (VIa-d) $CF_3CFClC(O)R_F$ (V) and $CF_3C(O)CFClR_F$ (VI)

Compound	R_F	Relative intensity, %									
		M+	M+ —CF_3	M+ – R_F	R_FCFCl^+	$C_2F_4Cl^+$	R_FCO^+	CF_3CO^+	R_F^+	CF_3^+	CF_2Cl^+
(Va)	CF_3	1	<1		29		50		100		21
(Vb)	C_2F_5	0	0	5	0	53	30	2	95	100	80
(VIb)	C_2F_5	0	0	0	7	<1	2	20	2	100	12
(Vc)	n-C_3F_7	0	0	6	*	98	*	<1	95	100	40
(VIc)	n-C_3F_7	0	0	0	20	10	10	95	2	100	25
(Vd)	i-C_3F_7	0	0	12	0	97	98	<1	50	100	31
(VId)	i-C_3F_7	0	<1	0	13	10	10	67	0	100	43

*Signal intensity not determined.

TABLE 5. ^{19}F NMR Spectra of Chloroperfluoroalkanones (Va-d) and (VIa-d)

$\overset{a}{CF_3}\overset{b}{CFCl}\overset{c}{C}(=O)\overset{d}{CFX}(\overset{e}{CF_2})_n-\overset{f}{Z}$ (V), $\overset{a}{CF_3}\overset{b}{C}(=O)\overset{c}{CFCl}\overset{d}{CFX}(\overset{e}{CF_2})_n\overset{f}{Z}$ (VI)

Compound	X	Z	n	Chemical shift, ppm						J, Hz											
				a	b	c	d	e	f	ab	ac	ad	bc	bd	be	bf	cd	ce	cf	de	df
(Va)	F	F	0	3,4	65,0	−2,8				6,7	<1	<1	17,1				–	–	–	–	–
(Vb)	F	F	1	2,5	65,4	42,1	42,4	5,7		5,4	*	*	19,7	21,6	5,4		307	*		*	
(VIb)	F	F	1	−3,0	63,4	43,1	43,6	2,5		16,0	2,6	2,3	5,6	5,6	12,6		284	<1		<1	
(Vc)	F	CF_3	1	3,6	65,5	39,1	39,5	49,8	5,2	5,5	<1	<1	*	*	11,3	<1	301	<1	9,4	<1	9,4
(VIc)	F	CF_3	1	−2,3	63,6	39,8	40,6	46,9	5,6	15,1	2,0	2,0	*	*	16,0	2,0	300	3,8	10,8	2,0	10,8
(Vd)	CF_3	CF_3	0	2,6	69,5	115,6	−2,9	–	−2,9	5,4	2,0	<1	44,0	*	–	*	6,9	–	6,9	–	–
(VId)	CF_3	CF_3	0	−4,0	63,1	106,0	−6,2	–	−6,2	16,0	6,0	<1	<1	*	–	*	6,0	–	6,0	–	–

*Constants not determined.

tographically pure adducts (IIIa) were obtained in both cases. The mass spectra and elemental analysis data of these adducts were identical. The ^{19}F NMR spectrum of the adduct obtained from trans-(IIa) shows five signals in accord with the presence of five different types of fluorine atoms in (IIIa). The spectrum of the adducts of (I) to a mixture of (IIa) stereoisomers has two sets of signals with 3:7 overall signal intensity ratio, i.e., there is a mixture of diastereomers in this cases, while (IIIa) obtained from pure trans-(IIa) is a pure compound.

It was impossible to assign diastereomers (IIIa) to the threo or erythro series using the available data. However, the steric specificity of the addition of (I) to internal perfluoroolefins may be considered to have been established.

EXPERIMENTAL

The ^{19}F NMR spectra were taken on a Perkin–Elmer R-32 spectrometer at 84.6 MHz relative to CF_3COOH external standard. The IR spectra were taken neat on a UR-20 spectrophotometer. The chromato-mass spectra were taken on a Varian MAT CH-8 spectrometer with 70-eV ionizing electron energy. The preparative separation and gas–liquid chromatographic analysis were carried out on a column packed with 20% FS-1265 stationary phase on Chromosorb W.

3-Chloroperfluoro-2-butyl Fluorosulfate (IIIa) (typical experiment). A sample of 15.2 g (0.11 mole) (I) was added dropwise to 22.5 g (0.11 mole) trans-(IIa) at –60 to –65°C. The mixture was maintained overnight at ∿20°C and then washed with four 50-ml portions of water and dried with $MgSO_4$. Distillation yielded 33.8 g (89.7%) (IIIa), bp 98°C. ^{19}F NMR spectrum (δ, ppm): –127.9 (1F), –0.5 (3F), 0.0 (3F), 54.2 (1F), 59.3 (1F). IR spectrum: 1495 cm^{-1} (S=O). Found: C 14.7; F 51.0; Cl 10.7; S 9.5%. Calculated for $C_4F_9ClO_3S$: C 14.4; F 51.5; Cl 10.6; S 9.6%.

Similarly, 20.7 g (82.5%) (IIIa) with bp 95–99°C was obtained from 15.0 g (75 mmoles) 30:70 cis-trans-(IIa) (ratio found by gas–liquid chromatography) and 10.1 g (75 mmoles) (I). ^{19}F NMR spectrum (δ, ppm): –127.9 (1F), –1.0 (0.9F), –0.5 (2.1F), 0.0 (3F), 54.2 (0.7F), 54.8 (0.3F), 59.3 (1F).

Similarly, mixtures of adducts (Table 1) whose mass spectra are given in Table 2 were obtained from (I) and (IIb-d). Pure (IIId), (IVb), and (IVd) were obtained by preparative gas–liquid chromatography.

3-Chloroperfluoro-2-butanone (Va) (typical experiment). A sample of 16.5 g (50 mmoles) (IIIa) was added dropwise to 2.0 g (13 mmoles) dry CsF at ∿20°C. When the separation of SO_2F_2 was complete, the liquid portion of the reaction mass was distilled to yield 9.8 g (85.5%) (Va) with bp 32°C. ^{19}F NMR spectrum of $CF_3^a–C(O)–CFCl^b–CF_3^c$ (δ, ppm, J, Hz): –2.8 d (F^a), 3.4 d (F^c), 65.0 q.q (F^b); J_{ab} = 17.1, J_{bc} = 6.7. IR spectrum: 1800 cm^{-1} (C=O). Found: C 20.6; F 57.1; Cl 15.3%. Calculated for C_4F_7ClO: C 20.7; F 57.2; Cl 14.6%.

Similarly, mixtures of ketones (Vb-d) and (VIb-d) (Table 3) were obtained from mixtures of regioisomeric adducts (IIIb-d) and (IVb-d). The mass spectra of these ketone products were given in Table 4 and their ^{19}F NMR spectra were given in Table 5. Pure (Vd) and (VId) were separated by preparative gas–liquid chromatography.

CONCLUSIONS

Chlorine fluorosulfate adds nonregiospecifically to fluoroolefins having a C(2)=C(3) double bond. This reaction is probably stereospecific independently of the order of addition.

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REACTIONS OF FLUOROOLEFINS WITH HYDROGEN SULFIDE AND MERCAPTANS

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One of the main differences between perfluoroolefins and their hydrocarbon analogs is the unusual ease of reactions with nucleophiles. This is generally attributed to the strong inductive effect of fluorine, the most electronegative element, which is only partially compensated by the reverse mesomeric effect due to the p electrons. As a result, the loss of a considerable portion of the electron density by the sp^2-hybridized C atom promotes nucleophilic attack, and the small size of the F atom, which facilitates the p—π interaction, and the large inductive effect make it possible to easily realize a biradical state in fluoroolefins (especially tetrafluoroethylene), which favors the attack of radicals and polymerization according to a radical mechanism.

In reactions with nucleophiles, fluoroolefins, especially the higher ones, are also characterized by vinyl and allyl substitution of the F atom.

The foundations for these presently fairly widely accepted theories were laid at the end of the forties and the beginning of the fifties.

The first investigations of that period include the work of Knunyants and Fokin (1948-1949) [1] on the addition of alkyl mercaptans and thiophenol to tetrafluoroethylene, trifluorochloroethylene, and 1,2-difluoro-1,2-dichloroethylene:

$$CF_2=CF_2+HSR\rightarrow HCF_2CF_2SR$$
$$CClF=CF_2+HSR\rightarrow HCClFCF_2SR$$
$$CClF=CClF+HSR\rightarrow HCClFCClFSR$$
$$R=Me,\ Et,\ i\text{-}Pr,\ Ph$$

In contrast to the ordinary olefins [2], the reaction under consideration of fluoroolefins is considerably more vigorous and is catalyzed by KOH or NaOH, in whose absence or in the case of catalysis by peroxides positive results could not be obtained [1].

Subsequently, the addition of alkyl mercaptans and 2-hydroxyethyl mercaptan to perfluoropropylene was realized with equal success also in the presence of bases [3]:

$$CF_3CF=CF_2 \xrightarrow[HSCH_2CH_2OH]{HSR} \begin{cases} CF_3CHFCF_2SR \\ CF_3CHFCF_2SCH_2CH_2OH \end{cases}$$

The anionoid attack in the case of asymmetric fluoroolefins is always directed at the terminal difluoromethylene group, i.e., to the most positively polarized C atom, in complete conformance to the electronic aspects of Markovnikov's rule. In addition, it was shown for the first time that the less symmetric fluoroolefins, viz., trifluorochloroethylene [1] and perfluoropropylene [3], react more vigorously with nucleophiles than does tetrafluoroethylene, products of the replacement of an F atom by an alkylthio group and the addition of two thioalkyl groups being formed simultaneously from perfluoropropylene [3].

The possibility of the initial addition of mercaptans to perfluoropropylene followed by the splitting off of HF under the conditions of the reaction was ruled out on the basis of direct experiments in [1, 3].

Ar attempt to alkylate alkyl mercaptides with 1,2-dibromotetrafluoroethane and symmetric dibromodichlorodifluoroethane resulted only in the oxidation of the latter to the disulfides

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