CHEMISTRY OF POLYFLUOROCARBANIONS.

1. NUCLEOPHILIC IODOFLUORINATION OF PERFLUOROALKYL VINYL ETHERS

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Nucleophilic iodofluorination of perfluorovinyl methyl (I) and perfluorovinyl propyl (II) ethers by iodine chloride in nitrobenzene or sulfolan afforded 1iodoperfluoro-1-methoxyethane (III) and 1-iodoperfluoro-1-propoxyethane in yields of 65 and 77%, respectively. In addition to compound (III), the reaction of perfluorovinyl methyl ether afforded two side products: 1-iodo-2chloroperfluoro-1-methoxyethane and 2-iodo-1-chloroperfluoro-1-methoxyethane. The latter products are formed via a radical reaction, which takes place under drastic conditions. On the basis of quantum chemical calculations of (I), (II), and the two anions formed from (I), $CF_3O\bar{C}FCF_3$ (VI) and $CF_3OCF_2\bar{C}F_2$ (VII), it is proposed that nucleophilic iodofluorination of perfluoroalkyl vinyl ethers involves the formation of thermodynamically more stable anions. The higher reactivity of (I) compared with (II) is in accord with the energy of the lowest unoccupied molecular orbitals and the charge density on the CF_2 carbon atoms. ¹⁹F NMR spectra of the synthesized products are shown.

Nucleophilic iodofluorination (NIF) of perfluorovinyl methyl ether (I) in SO_2 yields a negligible amount of the appropriate iodine derivative; the reaction does not proceed at all in N-methylpyrrolidone, which the authors ascribe to the low reactivity of the carbanion formed at the first stage [1]. The latter is not evident, and it could be assumed that the low yield of iodoperfluoro ether under the given conditions is due to complex formation between iodine and SO_2 , which sharply decreases the activity of iodine as an iodinating agent.

This hypothesis is in complete accord with the results of our quantum chemical calculations, which show that the reactivity of perfluoroalkyl vinyl ethers with respect to NIF lies between tetrafluoroethylene and hexafluoropropylene (Table 1). Thus, in the NIF reaction of (I) or (II) we would expect iodoperfluoro ether yields commensurate with those of 2-iodoperfluoropropane and iodoperfluoroethane (61 and 7%, respectively [2]).

In the present work we investigated nucleophilic iodofluorination of perfluorovinyl methyl ether (I) and perfluorovinyl propyl ether (II) by iodine chloride in nitrobenzene or sulfolan with the aim of eliminating or reducing complex formation as well as increasing the electrophilicity of iodine.

Under these conditions, NIF of perfluorovinyl methyl ether took place much more readily than in the system SO_2 -I₂ (Table 2); however, in addition to the NIF product - 1-iodoper-fluoro-1-methoxyethane (III) - iodochlorination products were formed: 1-iodo-2-chloroper-fluoro-1-methoxyethane (IV) and 2-iodo-1-chloroperfluoro-1-methoxyethane (V):

 $\begin{array}{c} CF_{3}OCF = CF_{2} \xrightarrow{KF + ICl} CF_{3}OCFICF_{3} + CF_{3}OCFICF_{2}Cl + CF_{3}OCFClCF_{2}I \\ (1) & (III) & (IV) & (V) \end{array}$

The formation of products (IV) and (V) may be explained by parallel intramolecular radical iodochlorination of ether (I) according to the following scheme:*

*The degree of dissociation of IC1 (IC1 ≠ I' + C1') at 100°C is 1.1% [6].

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TABLE 1. Energies of Formation, Charges on Carbon Atoms, Enthalpies of Formation of Unsaturated Perfluorinated Compounds and Carbanions, and Reaction Enthalpies (MNDO method)

Molecule	-ΔH _{form} , kJ/mole	HOMO energy	LUMO energy	Charge on =CF ₂ ,	-AH of F addition,
		eV		units .	K.J**
$C_{3}F_{7}OCF = CF_{2} (II)$ $CF_{3}OCF = CF_{2} (I)$ $CF_{2} = CF_{2} **$ $CF_{3}CF = CF_{2} **$	2070 1353 735,8 1142	10,69 10,94 10,74 11,45	1,378 1,523 1,262 1,777	+0.319 +0.346 +0.288 +0.402	220 173 231
CF ₃ OCFCF ₃ (VI)	1833	-3,871	6,348	-	_
$CF_3OCF_2CF_2$ (VII)	1809	3,652	5,072	- 1	- 1

 $*\Delta H_{298}F = -260 \text{ kJ/mole [3]}.$

**The data are in good agreement with those published earlier [4, 5].

TABLE 2. Conversion of Perfluoroalkyl Vinyl Ethers and Yields of Iodoperfluoro Ethers

KF/ICÍ, moles/ mole	Reaction conditions	Original ether	Conver- sion, %	Yield,%		
				(III)	(IV)	(V)
1,32 4,16 5,17 5,17	C₅H₅NO₂ 150°. 6 h Sulfolan 100°, 6 h	(I) (I) (I) (II)	95 94 80 62	12,6 49,5 65 77	27,9 6,29 Trac 0,66	12,1 1,64 ces (in sum)

$$CI' + CF_{3}OCF = CF_{2} \longrightarrow CF_{3}OCFCF_{2}CI \xrightarrow{1' \text{ or } IX} CF_{3}OCFICF_{2}CI \xrightarrow{(IV)} (IV)$$
$$\longrightarrow CF_{3}OCFCICF_{2} \xrightarrow{1' \text{ or } IX} CF_{3}OCFCICF_{2}I \xrightarrow{(V)} (V)$$

Indeed, the formation of products (IV) and (V) decreased significantly with an increase in the KF excess and a decrease in temperature (Table 2). Moreover, the product ratio - 27.9% (IV) and 12.1% (V) (Table 2) - also was in accord with a radical mechanism. Nevertheless, nucleophilic iodochlorination cannot be completely excluded.

Nucleophilic iodofluorination of perfluorovinyl propyl ether was similar to that of ether (I), except that the reactivity of ether (II) is lower than that of (I): the conversion of (I) and (II) to the NIF product in sulfolan was 80 and 62%, respectively (Table 2). This is in agreement with the results of our quantum chemical calculations for ethers (I) and (II) (Table 1). The lowest unoccupied molecular orbital (LUMO) energy for ether (II) is higher and the charge on the electrophilic (attacked by fluoride ion) carbon atom is lower than for ether (I), which also determines the lower reactivity of (II) toward fluoride ion (cf. [7, 8]). The quantum chemical calculations also show that, because of the higher "electronegativity" of the trifluoromethoxyl group compared with fluoride, carbanion (VI) is formed more readily than the isomeric carbanion (VII), which leads to the formation of 1-iodoperfluoro-1-methoxyethane. Thus, nucleophilic iodofluorination of perfluoroalkyl vinyl ethers by iodine chloride in nitrobenzene or sulfolan may be used as a preparative method for obtaining the appropriate iodine derivatives. The most thermodynamically stable carbanion participates in the reaction, which determines the position of iodine during nucleophilic iodofluorination.

EXPERIMENTAL

¹⁹F NMR spectra were recorded on a WP80SY spectrometer (75.4 MHz, hexafluorobenzene as internal standard). The chemical shifts of compounds (III)-(V) are shown in Table 3.

Compound 2 3 4 5 1 $CF_{3}OCFICF_{3}^{1}$ (III) 73,02 82.85 54,18 $clcF_2cFIOcF_3$ (IV) 67,66 64,61 53.03 $1CF_2CFCIOCF_3$ (V) 53,79 77.20 57.62CF₃CFIOCF₂CF₂CF₃ 84:4 (AB) 130.3 80,6 83.1 73,8

TABLE 3. ^{19}F NMR Spectra of the Synthesized Compounds (5, ppm, CCl_3F)

Gas absorption chromatography was carried out using a LKhM-72 chromatograph (column, 0.004×3 cm with hydroxylated Silochrome C-80); temperature 97°C; gel flow 2.5 liters/h). Starting materials and solvents were prepared and purified by standard methods.

<u>Nucleophilic Iodofluorination of Perfluorovinyl Methyl Ether (I).</u> a. A 200-cm³ stainless steel autoclave was charged with 50.4 g (0.31 mole) iodine chloride, 23.8 g (0.41 mole) potassium fluoride, 50 cm³ nitrobenzene, and 51.6 g (0.31 mole) of ether (I). Shaking for 6 h at 150°C afforded 54.7 g of raw material containing 6.6% of (I), 20.8% of (III), 21% of (IV), and 7.9% of (V); the yield of compound (III) with respect to the amount of reacted compound (I) was 12.6%.

<u>b.</u> When the synthesis was carried out under the same conditions but with a fourfold excess of potassium fluoride (75.1 g = 1.2 moles), 56.3 g of raw material was obtained containing 5.3% of (I), 80.1% of (III), 10.6% of (IV), and 2.8% of (V); the yield of compound (III) with respect to (I) was 49.5%.

<u>Nucleophilic Iodofluorination of Compounds (I) and (II).</u> Two identical autoclaves 30 cm³ in volume were charged with 10 cm³ sulfolan, 3 g (51.7 mmoles) potassium fluoride, and 1.62 g (10 mmoles) iodine chloride. Then 1.66 g (10 mmoles) of compound (I) was added to one of them, and 2.66 g (10 mmoles) of compound (II) was added to the other. Reaction for 6 h (with shaking) at 100°C afforded, in the first case, 1.96 g of raw material containing 27% of (I) and 71% of compound (III); conversion of (I) was 80%; yield of compound (III) with respect to reacted compound (I) was 65%. In the second case 3 g of raw material was obtained containing 44% of (II) and 55% NIF product; conversion of (II) was 62%; yield of 1-iodoperfluoro-1-propoxyethane was 77% with respect to converted compound (II).

LITERATURE CITED

- É. P. Lur'e, I. L. Knunyants, and B. L. Dyatkin, Zh. Org. Khim., <u>7</u>, No. 9, 1835 (1971).
 C. D. Krespan, J. Org. Chem., <u>27</u>, No. 5, 1813 (1962).
- 3. R. A. Lidin, L. L. Andreeva, and V. M. Molochko, Manual of Inorganic Chemistry [in Russian], Khimiya, Moscow (1987), pp. 170-174.
- 4. I. N. Rozhkov and Yu. A. Borisov, "Electronic structure of fluoroolefins based on quantum chemical calculations," in: 5th All-Union Conference on the Chemistry of Fluoroorganic Compounds, Moscow (1986), p. 149.
- 5. V. A. Gubanov, A. V. Tumanova, and I. M. Dolgopol'skii, Zh. Obshch. Khim., <u>35</u>, No. 3, 588 (1965).
- 6. G. Brauer (ed.), Handbook of Inorganic Synthesis, Ferdinand Enke Verlag, Stuttgart (1981).
- 7. M. A. Landau and S. S. Dubov, Zh. Vses. Khim. Ova, <u>14</u>, No. 4, 460 (1969).
- 8. V. P. Zhukov and V. A. Gubanov, Zh. Strukt. Khim., 16, No. 2, 322 (1975).