α-FLUOROALKYLAMINES, A NEW SOURCE OF NONHYDRATED FLUORIDE IONS. COMMUNICATION 5.* N,N-DIMETHYLMETHYLENIMMONIUM PERFLUOROALCOHOLATES AND THEIR REACTIONS WITH PERFLUOROOLEFINS

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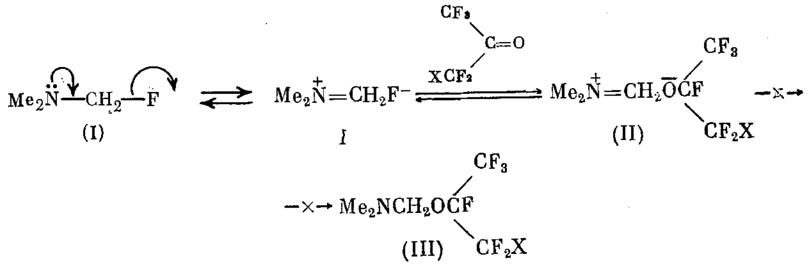
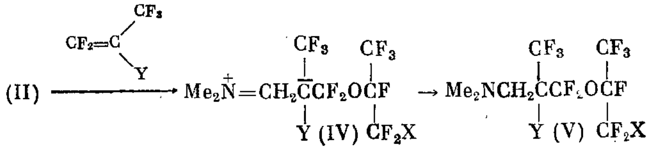
In our previous work [2], we showed that fluoromethyldimethylamine (I) readily adds to electrophilic unsaturated compounds including perfluoroolefins, bis(trifluoromethyl)ketene, and perfluoroazapropene with the formation of fluoromethylaminomethylation products. In the present work, we studied the reactions of (I) with polyfluoroketones. Amine (I) readily reacts with these ketones but N,N-dimethylmethylenimmonium perfluoroalcoholates (II) are formed instead of the covalent addition products (III). The structure of perfluoroalcoholates (II) was confirmed by their physical properties and spectral data. Thus, salts (II) are highly soluble in polar solvents such as DMF and acetonitrile but, similar to $[Me_2N=CH_2]^+Cl^-$, does not dissolve in ether. The IR spectrum of salt (IIa) has bands at 1700 and 3040 cm^{-1} which are characteristic for dimethylmethylenimmonium salts and correspond to the C=N and =C—H bonds, while the PMR spectrum has singlets at 3.3 and 8.2 ppm, which correspond to the CH_3 and CH_2 groups of the $Me_2\overset{+}{N}=CH_2$ cation [3]. The ^{19}F NMR spectrum of salt (IIa) taken at −40°C has signals corresponding to the CF_3 and CF_2 groups of the heptafluoroisopropoxy anion. Fluorine atom signals are not seen above −20°C, which indicates exchange processes apparently related to reversibility of the addition of fluorotrimethylamine to polyfluoroketones. These results support our previous hypothesis transfer of a fluoride ion from (I) to the electrophilic double bond with the formation of the corresponding anion and immonium cation



X = F (a), Cl (b).

The chemical properties of salts (II) proved interesting. Thus, these salts readily react with perfluoropropylene (PFP) and perfluoroisobutylene (PFIB) to form the products of the addition (V) of the perfluoroalkoxy anion and methylenimmonium cation at the fluoroolefin double bond. We should note that PFP reacts with (IIa) under more vigorous conditions than PFIB, while tetrafluoroethylene does not undergo this reaction at all. The order of fluoroolefin activity indicates that the reaction proceeds by a nucleophilic mechanism with initial attack of the perfluoroalkoxy anion on the fluoroolefin to form β-perfluoroalkoxy carbanion (IV) and its subsequent covalent bonding with the methylenimmonium cation



X = Y = F (a), X = F, Y = CF_3 (b), X = Cl, Y = CF_3 (c).

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*For communication 4, see [1].

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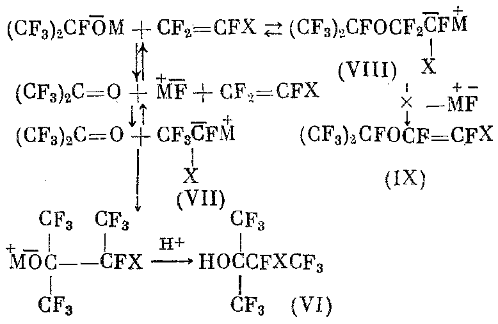
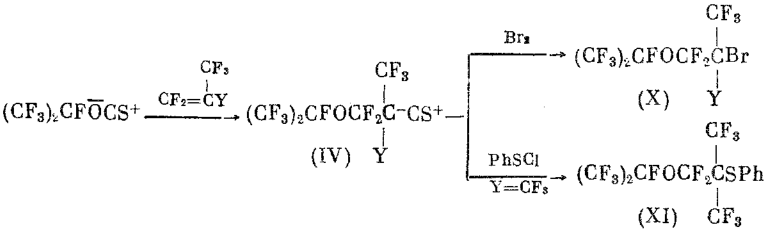
The reaction of PFIB with (IIa) below –20°C gives only alkoxyalkylamine (Vb). Above –10°C, this reaction also gives the product of the addition of (I) to PFIB, namely, $Me_2NCH_2C(CF_3)_3$ in addition to (Vb). This finding is in accord with the reversible nature of the addition of (I) to polyfluoroketones.

We should note that the reaction of perfluoroalcoholates of alkali metals with fluoroolefins leads to completely different results, namely, the exclusive formation of tertiary alcohols (VI) by a mechanism involving the generation of perfluoroalkyl carbanion (VII) and its addition to the carbonyl group of the starting ketone [4-6]:



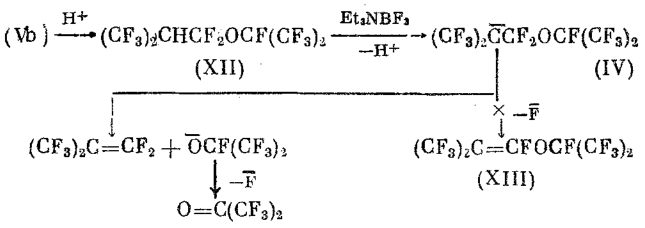
X = F, CF_3

In this case, no products are detected indicating the formation of β-perfluoroalkoxy carbanions (VIII) such as perfluorovinyl ethers (IX).* Thus, the question of the capacity of perfluoroalkoxy anions to add to fluoroolefins remained open prior to the onset of this study. Nevertheless, the results of the reactions of salts (II) with fluoroolefins indicated that alkali metal perfluoroalcoholates are also capable of adding to fluoroolefins with the formation of anions (IV). However, this addition, in contrast to that examined above, is reversible and the equilibrium is virtually entirely shifted toward the starting materials. Indeed, while the reaction of cesium perfluoroisopropylate with fluoroolefins occurs in the presence of strong electrophiles such as Br_2 or PhSCl, β-perfluoroalkoxy carbanion (IV) is detected as products of the conjugated perfluoroalkoxybromination or perfluoroalkoxysulfenylation of fluoroolefins



Y = F (a), CF_3 (b).

Thus, perfluoroalkoxy anions are capable of adding to fluoroolefins with the formation of β-perfluoroalkoxy carbanions. The reversibility of this reaction in the absence of electrophilic reagents which are capable of fixing these carbanions indicates that the perfluoroalkoxy anion is a better leaving group than the F^- anion. Furthermore, an attempt to dehydrofluorinate ether (XII) by the action of the Et_3NBF_3 complex, i.e., under conditions most favorable for the elimination of F^- anions, β-perfluoroalkoxy carbanion does not eliminate F^- but rather a perfluoroisopropoxy anion and gives PFIB and HFA rather than vinyl ether (XIII). Ether (XII) was obtained by the acid hydrolysis of alkoxyalkylamine (Vb) [2, 8]



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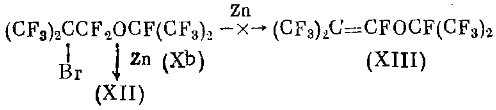
*However, the reaction of perfluorocyclobutene with hexafluoroacetone (HFA) in the presence of KF yields a mixture of mono- and diperfluoroisopropylcyclobutenyl ethers [7].

Vinyl ether (XIII) also could not be obtained in the reaction of bromide (Xb) with zinc. This reaction only gives hydride (XII)



$$\underset{\substack{|\\ Br}}{(CF_3)_2C}CF_2OCF(CF_3)_2 \xrightarrow[\times]{Zn} \underset{(XIII)}{(CF_3)_2C{=}CFOCF(CF_3)_2}$$
$$\Big\downarrow Zn\ (Xb)$$
$$(XII)$$

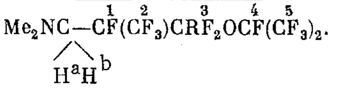
In conclusion, we note that conjugated perfluoroalkoxyhalogenation has been reported for a series of fluoroolefins. Until now, these reactions have been considered to proceed by an electrophilic mechanism through an intermediate halonium ion [9]. Our results indicate that this is true largely for ethylenic olefins. However, the perfluoroalkoxyhalogenation of higher fluoroolefins including perfluoropropylene [9] may occur by a nucleophilic mechanism. Thus, a characteristic change in the reaction mechanism from electrophilic to nucleophilic in going from lower to higher fluoroolefins occurs in the conjugated addition to fluoroolefins [10].

EXPERIMENTAL

The ^{19}F and ^1H NMR spectra (δ, ppm) were taken on a Perkin-Elmer R-32 spectrometer at 84.6 and 90 MHz relative to CF_3CO_2H and HMDS, respectively. The IR spectra were taken on a UR-20 spectrometer.

N,N-Dimethylmethylenimmonium Perfluoroisopropylate (IIa). A sample of 16 g HFA was added gradually to a solution of 7 g (I) in 10 ml abs. ether. At the end of the exothermal reaction, the ether was removed by decantation. Distillation of the residue gave 16.6 g (75%) salt (IIa) with bp 38°C (13 mm) which crystallizes upon cooling. Found: C 29.96; H 3.36; F 54.61; N 6.02%. Calculated for $C_6H_8F_7ON$: C 29.63; H 3.29; F 54.73; N 5.76%. PMR spectrum (DMF): 3.3 s (Me), 8.2 s (CH_2). ^{19}F NMR spectrum (–40°C, DMF): –1.2 m (CF), 5.3 d (CF_3), J_{CF_3-CF} = 2.0 Hz. At 20°C, the ^{19}F NMR spectrum shows only a broad singlet at 3.1 ppm. IR spectrum (ν, cm^{-1}, diglyme): 1695 (C=N), 3040 (=C–H).

N, N-Dimethyl-2,3,3-trifluoro-2-trifluoromethyl-3-heptafluoroisopropoxypropylamine (Va),



$$Me_2N\underset{H^aH^b}{C}{-}C\overset{1}{F}(\overset{2}{C}F_3)C\overset{3}{R}F_2OC\overset{4}{F}(\overset{5}{C}F_3)_2.$$

A mixture of 7.7 g amine (I), 32 g HFA, 15 g PFP, and 20 ml abs. diglyme was maintained in a steel autoclave for 76 h at about 20°C. The volatile products were removed. Distillation of the lower layer gave 12.1 g (31.5%) (Va), bp 70-73°C (95 mm). Found: C 27.46; H 1.98%. Calculated for $C_9H_8F_{13}ON$: C 27.50; H 2.02%. PMR spectrum: 2.2 s (Me), 2.2 and 2.6 br. signals (H^a and H^b). ^{19}F NMR spectrum: –1.8 m (F^2), –1.7 m (F^3), 3.8 m (F^5), 6.9 t (F^4), 107 m (F^1), $J_{F^2-F^3}$ = 20.6 Hz.

N,N-Dimethyl-2,2-bis(trifluoromethyl)-3,3-difluoro-3-heptafluoroisopropoxypropylamine (Vb), $Me_2NCH_2C(C\overset{1}{F_3})_2C\overset{2}{F_2}O\overset{3}{C}F(\overset{4}{C}F_3)_2$. A sample of 18 g HFA was added to a solution of 7.7 g (I) in 20 ml abs. ether and then 22 g PFIB was added over 1 h with stirring at –20°C. The homogeneous solution obtained was stirred for 1 h at –15°C and then warmed to about 20°C. Distillation gave 34.2 g (77.5%) (Vb), bp 84-87°C (100 mm). Found: C 27.25; H 1.86; F 64.88; N 3.75%. Calculated for $C_{10}H_8F_{15}ON$: C 27.10; H 1.80; F 64.00; N 3.16%. ^{19}F NMR spectrum: –12.2 t (F^1), –11.2 m (F^2), –3.6 m (F^4), 69 t (F^3), $J_{F^1-F^2}$ = 9.4, $J_{F^2-F^3}$ = 22.6 Hz.

The analogous reaction at 10°C gave a 1:3 mixture containing $(CF_3)_3CCH_2NMe_2$ (bp 34-35°C (95 mm)) and (Vb) as indicated by gas-liquid chromatography.

N,N-Dimethyl-2,2-bis(trifluoromethyl)-3,3-difluoro-3-β-chlorohexafluoroisopropoxypropylamine (Vc), $Me_2NCH_2C(C\overset{1}{F_3})_2C\overset{2}{F_2}O\overset{3}{C}\overset{4}{F}(CF_2Cl)\overset{5}{C}F_3$. A sample of 9 g chloropentafluoroacetone was added gradually with stirring and ice-water cooling to a solution of 4 g (I) in 20 ml abs. ether. Then, 15 g PFIB was added with stirring and ice-water cooling over 2 h and stirring was continued for an additional 30 min. Distillation yielded 9.4 g $(CF_3)_2CCH_2NMe_2$ and 7.3 g (31.7%) (Vc), bp 54-56°C (10 mm). Found: C 26.37; H 1.84; F 58.10; N 3.21%. Calculated for $C_{10}H_8ClF_{14}ON$: C 26.20; H 1.75; F 58.00; N 3.04%. PMR spectrum: 2.1 s (Me), 2.9 s (CH_2). ^{19}F NMR spectrum: –12.0 m (F^1), –10.0 m (F^4), 1.1 m (F^5), 65.0 t (F^3), $J_{F^2-F^3}$ = 22.6 Hz.

2-Bromo-2-trifluoromethylpentafluoropropyl Heptafluoroisopropyl Ether (Xa), $(\overset{1}{CF_3})_2\cdot\overset{2}{C}Br\overset{3}{CF_2}\overset{4}{O}CF(CF_3)_2$. A sample of 42 g HFA was added to a suspension of freshly roasted CsF in

50 ml abs. diglyme and then 10 g Br_2 and 10 PFIB were added consecutively at −40°C. Stirring was continued for an additional 30 min at from −30° to −40°C. The excess HFA was distilled off. The reaction mass was poured into a mixture of hydrochloric acid with ice. The lower layer was washed with aq. Na_2CO_3 until its color disappeared and then dried over $MgSO_4$. Distillation yielded 20 g (87%) (Xa), bp 113-115°C. Found: C 18.28; Br 16.78; F 60.68%. Calculated for $C_7BrF_{15}O$: C 18.10; Br 17.20; F 61.30%. ^{19}F NMR spectrum: −11.0 m (F^2), −10.0 t (F^1), 4.5 br signal (F^4), 69.5 t (F^3), $J_{F^1-F^2}$ = 9.4, $J_{F^2-F^3}$ = 22.3 Hz.

<u>2-Bromohexafluoropropyl Heptafluoroisopropyl Ether (Xb)</u> $\overset{1}{CF_3}\overset{2}{CF}Br\overset{3}{CF_2}O\overset{4}{CF}\overset{5}{(CF_3)_2}$. This ether was obtained similarly to (Xa) in 41% yield, bp 74-77°C. Found: C 17.57; Br 19.03; F 59.43%. Calculated for $C_6BrF_{12}O$: C 17.30; Br 19.30; F 59.60%. ^{19}F NMR spectrum: −0.8 m (F^3), −0.5 d.t (F^1), 4.2 t (F^5), 64.4 t.q (F^2), 68.0 t (F^4), $J_{F^3-F^5}$ = 5.7, $J_{F^1-F^2}$ = $J_{F^1-F^3}$ = $J_{F^2-F^3}$ = 9.4, $J_{F^3-F^4}$ 22.6 Hz.

<u>[1,1-Bis(trifluoromethyl)-2,2-difluoro-2-perfluoroisopropoxy]ethyl Phenyl Sulfide (XI),</u> $PhSC\overset{1}{(CF_3)_2}\overset{2}{CF_2}O\overset{3}{CF}\overset{4}{(CF_3)_2}$. A sample of 22 g HFA and 8 g PFIB was added gradually to a mixture of 6 g CsF and 20 ml abs. diglyme with stirring and cooling to −40°C. Stirring was continued for 30 min at −40°C and then, 5.6 g benzenesulfenyl chloride in 5 ml abs. diglyme was added at this temperature. Stirring was continued for 1 h at −40°C. The mixture was warmed to −10°C and excess HFA was distilled off. The residue was poured into water and the precipitated oil was distilled over concentrated sulfuric acid to yield 8.5 g of a mixture consisting of 28% $(CF_3)_3CSPh$ and 72% sulfide (XI) as determined by gas-liquid chromatography. Redistillation gave pure (XI), bp 89-90°C (8 mm). Found: C 31.72; H 1.09; F 57.39%. Calculated for $C_{13}H_5F_{15}S$: C 31.59; H 1.02; F 57.69%. ^{19}F NMR spectrum: −13.7 t (F^1), −13.1 m (F^2), 3.0 broad signal (F^4), 67.8 t (F^3), $J_{F^1-F^2}$ = 9.4, $J_{F^2-F^3}$ = 22.3 Hz.

<u>2-Hydro-2-trifluoromethylpentafluoropropyl Heptafluoroisopropyl ether (XII),</u> $\overset{1}{(CF_3)_2}\cdot CH\overset{2}{CF_2}O\overset{3}{CF}\overset{4}{(CF_3)_2}$. a) A sample of 30 ml conc. hydrochloric acid was added dropwise with stirring to 22.5 g (Vb) and then stirred for about 3 h at 90-100°C until the precipitate disappeared. The lower layer was distilled over concentrated sulfuric acid to yield 13.7 g (70%) (XII), bp 80-81°C. Found: C 21.67; H 0.27; F 73.75%. Calculated for $C_7HF_{15}O$: C 21.76; H 0.26; F 73.83%. PMR spectrum: 3.4 m (CH). ^{19}F NMR spectrum: −12.9 d (F^1), −12.9 broad signal (F^2), 4.4 broad signal (F^4), 69.5 m (F^3), J_{F^1-H} = 7.5 Hz.

b) A sample of 5 g (Xb) was added gradually with stirring to 3 g zinc powder and a catalytic amount of $ZnCl_2$ in 15 ml diglyme and the mixture was stirred for 3 h at 20°C. Distillation of the reaction mixture gave 3.5 g (80%) (XII).

<u>Reaction of 2-Hydro-2-trifluoromethylpentafluoropropyl Heptafluoroiscpropyl Ether with $Et_3N\cdot BF_3$.</u> A mixture of 7.7 g ether (XII) and 5 g $Et_3N\cdot BF_3$ was heated at 90°C until no further gas was liberated. The volatile components were collected in a trap at −78°C. The yield was 3.8 ml of a mixture of PFIB and HFA (as indicated by ^{19}F NMR spectroscopy).

CONCLUSIONS

1. The reaction of fluoromethyldimethylamine with polyfluoroketones leads to N,N-dimethylmethylenimmonium polyfluoroalcoholates which are capable of adding to perfluoroolefins to form polyfluoro-substituted alkoxyalkyldimethylamines.

2. Alkali metal perfluoroalcoholates add reversibly to perfluoroolefins to give β-perfluoroalkoxy carbanions which may be trapped by reaction with electrophilic reagents.

3. These results indicate that the perfluoroalkoxyhalogenation of higher perfluoroolefins proceeds by a nucleophilic mechanism.

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REACTION OF CHLORINE FLUOROSULFATE AND PEROXYDISULFURYL DIFLUORIDE WITH PERFLUORONITROSOALKANES

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It is known that highly electrophilic chlorine fluorosulfate ($ClOSO_2F$) easily replaces with fluorosulfate groups the halogen atoms in haloalkanes [1, 2] and even the Cl atoms in Freons [3, 4]. Unlike $ClOSO_2F$, under mild conditions peroxydisulfuryl difluoride ($S_2O_6F_2$) which is a radical agent, replaces with the fluorosulfate group only the Br [5] and I [6] atoms in Freons, i.e., the comparatively easily oxidizable halogens.

Therefore, the study of the reaction of perfluoronitroso compounds with such strong oxidizing agents as $ClOSO_2F$ and $S_2O_6F_2$ seemed of definite interest. Previously we noted that 1-chloro-2-nitrotetrafluoroethane (II) is formed in the reaction of $ClOSO_2F$ with 1-nitroso-2-nitrotetrafluoroethane (I) [7]. In the present paper, we have determined that (II) is formed only under very mild conditions (<−50°C, dilution with an inert solvent) with obligatory addition of $ClOSO_2F$ to a large molar excess of (I). In the absence of a solvent or in sufficiently concentrated solutions, even at low temperature (≤−50°C), the main direction of the reaction is replacement of the nitroso group not by Cl, but by the fluorosulfate group with the formation of 2-nitrotetrafluoroethyl fluorosulfate (III), nitrosyl fluorosulfate, and Cl_2. 1,2-Dinitrotetrafluoroethane (IV) and pyrosulfuryl difluoride ($S_2O_5F_2$) were also isolated as byproducts.

$$ClOSO_2F + \underset{(I)}{O_2NCF_2CF_2NO} \rightarrow \underset{(III)}{O_2NCF_2CF_2OSO_2F} + ONSO_3F + Cl_2 + \underset{(IV)}{O_2NCF_2CF_2NO_2} + S_2O_5F_2$$

In the considered process, about 2 moles of $ClOSO_2F$ is consumed per 1 mole of (I). Increasing the temperature to between −30 and −20°C leads to some decrease of the yield of (III) and $ONSO_3SF$ and to a simultaneous increase of the yield of (IV) and $S_2O_5F_2$.

At −60°C, $ClOSO_2F$ also reacts easily with trifluoronitrosomethane (CF_3NO)

$$ClOSO_2F + CF_3NO \rightarrow CF_3OSO_2F + CF_3Cl + ONSO_3F + Cl_2 + CF_3NO_2 + S_2O_5F_2$$

Unlike in the case of the reaction involving (I), in this case, despite the reverse order of mixing of the reagents, not only the product of replacement of the nitroso group by fluorosulfate, trifluoromethyl fluorosulfate (CF_3OSO_2F), is formed, but also the product of its replacement by Cl—CF_3Cl.

The reaction of $ClOSO_2F$ with perfluoro-tert-nitrosobutane $(CF_3)_3CNO$ does not afford perfluoro-tert-butyl fluorosulfate. The formation of perfluoro-tert-butyl chloride, perfluoro-tert-nitrobutane, and $S_2O_5F_2$ was determined by spectral methods and GLC:

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