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SOME REACTIONS OF CHLORINE AND IODINE FLUOROSULFATES*

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SUMMARY

The behaviour of $ClOSO_2F$ towards acetylene and the C≡N bond of perfluorocarbon acid nitriles as well as a possibility of C-N bond cleavage in perfluoronitroso compounds were studied. Investigation of the chlorinating activity of $ClOSO_2F$ was continued. The addition reactions of $IOSO_2F$ to double bonds of fluoroolefines as well as the reactions of $S_2O_6F_2$ with ethylnitrobenzenes were realized.

INTRODUCTION

Not long ago $ClOSO_2F$ and $S_2O_6F_2$ attracted chemists' attention as highly reactive substances, that provide new reaction paths to compounds that were inaccessible earlier. Heretofore, reactions of $IOSO_2F$ with organic compounds practically have not been studied.

$ClOSO_2F$ extremely readily adds to double bonds of different compounds. Independently of their structure the reaction with perchloro- and perfluoroolefines occurs readily already at -65° to -75°C [2-6]. $ClOSO_2F$ forms addition products with bis(trifluoromethyl)ketene [6] and perfluorobenzene [7]. Addition of $ClOSO_2F$ to double [8-11] and triple [12] nitrogen -carbon bonds proceeds as well.

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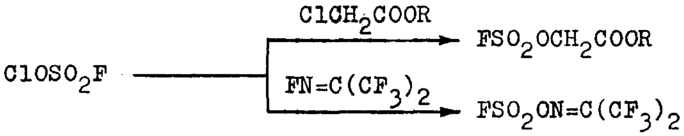
The halogen atom substitution in halogenalkanes and even in freons [13-15] by the fluorosulfate group as well as the chlorine and fluorine substitution in perfluorocarbon acid chlorides and fluorides [15] is characteristic for $ClOSO_2F$.

In spite of the extremely high reactivity of $ClOSO_2F$ towards organic compounds, in some cases the use of this compound leads to selective transformations. This can be exemplified by substitution of chlorine atoms in monochloracetic acid esters [15] and of fluorine atom in hexafluoroacetone N-fluoroimine [16] by fluorosulfate group.



In several cases the chlorinating activity of $ClOSO_2F$ is observed [5,12] . This allows to consider $ClOSO_2F$ as one of the most powerful chlorinating agents with positively polarized chlorine. Reaction of $ClOSO_2F$ with an exess of benzene occuring even at -100°C and giving an 80% yield of hexachlorobenzene [17] is a striking example of this aspect.

$$ClOSO_2F + C_6H_6 \longrightarrow C_6Cl_6$$

The chlorination of fluorine containing alcohols by $ClOSO_2F$ at subambient temperatures produces hypochlorites non-explosive and stable in moisture-free atmosphere [18] .

$$ClOSO_2F + R_fCH_2OH \xrightarrow[-HSO_3F]{} R_fCH_2OCl$$

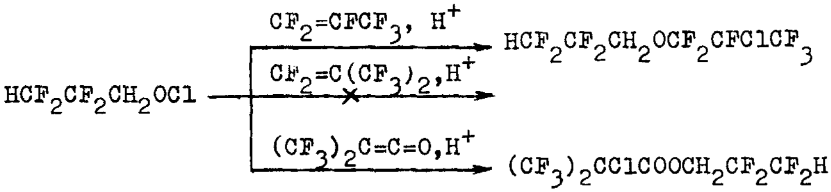
$$R_f = H(CF_2)_2,\ H(CF_2)_4,\ H(CF_2)_6 \text{ and } O_2NCF_2$$

Polyfluoroalkylhypochlorites are rather interesting and extremely powerful reagents, though they are less active than $ClOSO_2F$. These substances actively, exothermically add to tetrafluoroethylene, but do not interreact with the more electrophylic perfluoropropylene [18] .

$$R_fCH_2OCl + CF_2{=}CF_2 \longrightarrow R_fCH_2OCF_2CF_2Cl$$

$$R_f = H(CF_2)_4,\ H(CF_2)_6,\ O_2NCF_2$$

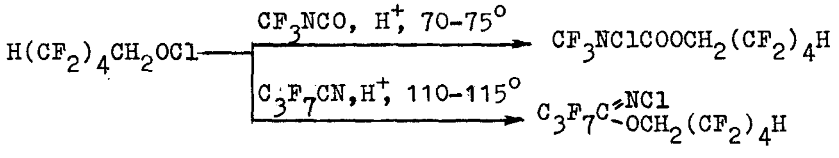
The addition of alkylhypochlorites to hexafluoropropylene and bis(trifluoromethyl)ketene was carried out only in the presence of acid catalyst (e.g. 1,1,3-trihydrotetrafluoropropylsulfate), but the reaction with perfluoroisobutylene was not realized at all [18] .



With unsubstituted olefines, as would be expected, polyfluoroalkylhypochlorites react extremely vigorously [18] .

$$H(CF_2)_4CH_2OCl + CH_2{=}CHC_5H_{11} \longrightarrow H(CF_2)_4CH_2OCH(CH_2Cl)C_5H_{11}$$

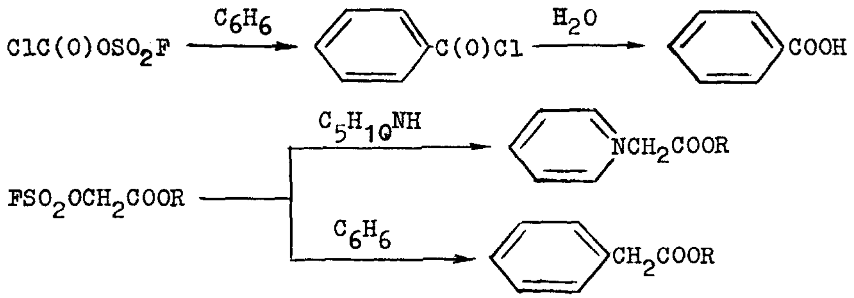
The addition of polyfluoroalkylhypochlorites to perfluoroisocyanates and perfluoronitriles proceeds in the presence of an acid catalyst and heating [19] .



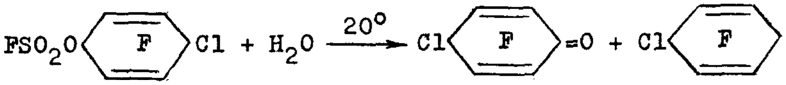
Contrary to $ClOSO_2F$, hypochlorites of fluorinated alcohols do not react at 20° with dichloro- and dibromoethanes; the chlorination of benzene leads only to monochlorobenzene[18].

Of no less interest are many fluorosulfonic acid derivatives obtained by the reactions with $ClOSO_2F$.

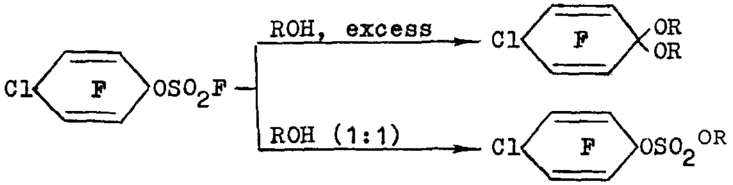
For instance, as a completely new processes can be mentioned the acylation of benzene at 20° with chlorocarbonylfluorosulfate (the adduct of $ClOSO_2F$ to carbon monooxide) [5] as well as the alkylation of not only amines but also benzene below 0°C without any catalyst with fluorosulfateacetic acid esters [15].



Rather unusual is also the reactivity of 4-chlorohexafluoro-2,5-cyclohexadienylfluorosulfate, obtained by the addition of $ClOSO_2F$ to hexafluorobenzene [7]. Its hydrolysis besides 4-chloropentafluoro-2,5-cyclohexadienone, leads also to 3-chlorohexafluoro-1,4-cyclohexadiene [20].



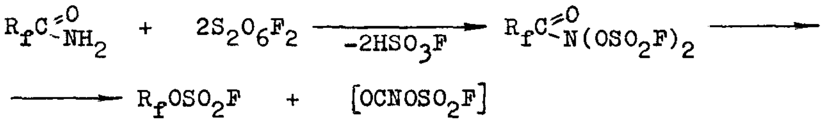
Fluoroalkane formation from fluorosulfate has not been known so far. Alcoholysis of the fluorosulfate in question leads to cyclohexadienone ketals [20]. In cases where an equimolar amount of alcohol is used, the substitution of fluorine atom in fluorosulfate group takes place.



The above facts allow to consider $ClOSO_2F$ as one of the most powerful electrophylic reagents, but in our mind some of its reactions proceed according to single-electron transfer scheme [15].

Though $S_2O_6F_2$ is usually considered as a reagent for free-radical processes, several reactions of this compound are not explicable from this point of view. Thus, $S_2O_6F_2$ easily adds to fluoroalkenes (though at temperatures higher than for $ClOSO_2F$) to give corresponding bis(fluorosulfate) derivatives [21-26] ; the analogous addition is also known for bis(trifluoromethyl)ketene [27] and hexafluorobenzene [7].

$S_2O_6F_2$ easily substitutes the hydrogen atoms in alkanes [28-31], polyfluoroalkanes [12,28,32,33], acids [24,28,29] and benzene [24] by the fluorosulfate group. Analogous formation of fluorosulfates in the reaction of $S_2O_6F_2$ with alcohols [28] and hexafluoroacetone imine is complicated by side reactions. Even below 0°C $S_2O_6F_2$ substitutes the hydrogen atoms of perfluorocarboxamides; the resulted N,N-bis(fluorosulfate)amides are, however, comparatively unstable and undergo a rearrangement into the corresponding perfluoroalkylfluorosulfates; the rearrangement apparently occurs in the course of reaction and isolation [34,35].



$$R_fC{\overset{O}{\lessgtr}}_{NH_2} + 2S_2O_6F_2 \xrightarrow[-2HSO_3F]{} R_fC{\overset{O}{\lessgtr}}_{N(OSO_2F)_2} \longrightarrow$$

$$\longrightarrow R_fOSO_2F + [OCNOSO_2F]$$

$IOSO_2F$ is known to undergo an easy transformation into iodine tris(fluorosulfate) [36]. Recently we have shown, that $S_2O_6F_2$ at -50°C actively adds to alkyl- and perfluoroalkyliodides resulting in solid (below) 0°C creme or white adducts, decomposing at -40 to -20°C to the corresponding alkylfluorosulfates and $IOSO_2F$ [37].

$$RI + S_2O_6F_2 \longrightarrow [RI(OSO_2F)_2] \longrightarrow ROSO_2F + IOSO_2F$$

$$R = CH_3,\ CF_3,\ C_3F_7$$

The formation of analogous adducts from perfluoroalkyliodides was also noted [38] .

To sum up, the reactions listed above characterize $S_2O_6F_2$ and $ClOSO_2F$ as very interesting reagents with wide synthetic abilities.

RESULTS AND DISCUSSION

Even with considerable excess of 1,3,5-trichlorobenzene the reaction of this compound with $ClOSO_2F$ at -25°C leads (as with C_6H_6 [17]) to hexachlorobenzene in quantitative yield.

$$1,3,5\text{-}Cl_3C_6H_3 \quad + \quad ClOSO_2F \longrightarrow C_6Cl_6$$

Introduction of a nitro group into the aromatic ring substantially retards chlorination with $ClOSO_2F$. For example, nitrobenzene, at -10 to 25°C giving up to 60% of pentachloronitrobenzene along with mono-, di-, tri-, and tetrachloronitrobenzenes.

$$O_2NC_6H_5 \quad + \quad ClOSO_2F \longrightarrow O_2NC_6Cl_5 \quad + \quad O_2NC_6HCl_4 \quad +$$

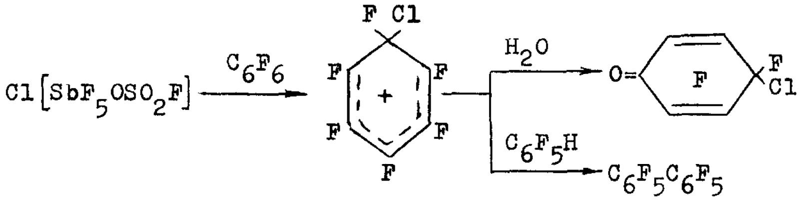
$$+ \; O_2NC_6H_2Cl_3 \quad + \quad O_2NC_6H_3Cl_2 \quad + \quad O_2NC_6H_4Cl$$

Further nitro groups in a benzene ring give rise to inhibition of chlorination under mild conditions (25°); 1,3,5-trinitrobenzene, for example, does not react even with a large excess of $ClOSO_2F$.

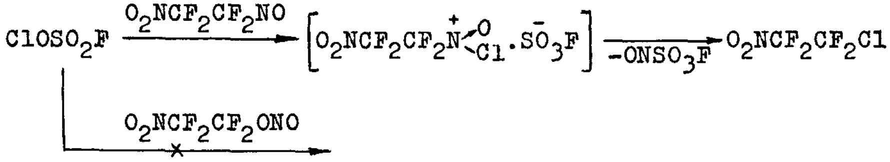
The complex of $ClOSO_2F$ with SbF_5 has more chlorinating activity than $ClOSO_2F$ alone. At 20°C this reagent chlorinates pentafluorobenzene and 4,4'-dihydroperfluorobiphenyl to pentafluorochlorobenzene and 4,4'-dichloroperfluo biphenyl in 95% and 60% yields, respectively.

$$\begin{tikzcd}
ClOSO_2F \;+\; SbF_5 \arrow[r] & Cl[SbF_5OSO_2F] \arrow[r, "C_6F_5H"] \arrow[d, "4\text{-}HC_6F_4C_6F_4H\text{-}4'"] & C_6F_5Cl \\
 & 4\text{-}ClC_6F_4C_6F_4Cl\text{-}4' &
\end{tikzcd}$$

Contrary to the reactions with $ClOSO_2F$ [7] this complex gives a benzolonium ion with hexafluorobenzene (cf. [39]), which after hydrolysis gives 4-chloropentafluorocyclohexa-2,5-dien-1-one; the reaction of the ion with pentafluorobenzene leads to perfluorobiphenyl.



The interreaction of $ClOSO_2F$ with perfluoronitrosoalkanes (1-nitroso-2-nitrotetrafluoroethane, for example) proceeds unde mild conditions and results in the substitution of the nitroso-group for chlorine, giving the corresponding chloroalkanes and nitrosolfluorosulfate. The first stage of the reaction apparently involves the formation of an unstable, presumably salt-like intermediate, which decomposes during the warming of reaction mixture. At the same time 2-nitrotetrafluoroethylnitrite does not react with $ClOSO_2F$ even under heating.



$$ClOSO_2F \xrightarrow{O_2NCF_2CF_2NO} \left[O_2NCF_2CF_2\overset{+}{N}{<}^{O}_{Cl}\cdot\overset{-}{SO_3}F\right] \xrightarrow[-ONSO_3F]{} O_2NCF_2CF_2Cl$$

$$ClOSO_2F \xrightarrow{O_2NCF_2CF_2ONO} \times$$

$ClOSO_2F$ is also highly reactive towards carbon-carbon triple bonds. It vigorously interreacts with acetylene in freon-113 at $-25^\circ C$. The reaction does not stop at the stage of monoadduct, but proceeds to the complete saturation of triple bond. This fact clearly suggests a higher nucleophility of the double bond of an intermediate comparing with triple bond of acetylene.

$$ClOSO_2F + HC{\equiv}CH \longrightarrow \underset{(I)}{Cl_2CHCH(OSO_2F)_2} + \underset{(II)}{(FSO_2OCHCl)_2}$$

The PMR data evidence that the main product of this reaction is 1,1-bis(fluorosulfate)-2,2-dichloroethane (I) $[\delta$ (ppm, HMDS) : 5,98 D ($CHCl_2$), 6,77 D $\{CH(OSO_2F)_2\}$; $J_{H-H} = 4,3$ Hz$]$ and yield of a minor isomer (II) does not exceed 5-7% $[\delta$ (ppm, HMDS) : 6,51 S ($CHClOSO_2F$)$]$. It is noticeable that (I) has comparatively high thermal and hydrolytic stability.

The formation of (II) in this reaction was independently confirmed by the reaction between $ClOSO_2F$ and symm.-tetrachloroethane.

$$HCCl_2CCl_2H \xrightarrow{ClSO_2F} \overset{V}{HCCl_2CClHOSO_2F} \xrightarrow{ClSO_2F} (I) + (II)$$

In this case, however, both isomers are also obtained with (I) being the main product [(I):(II) = 3:1 by GLC and PMR] . Attempts to isolate individual (II) by fractional distillation failed because of the small difference of boiling points.

Attempts to obtain $ClOSO_2F$ adducts with propyne and 2,2-dimethyl-3-pentyne also failed because of their instability. In the first case decomposition of a reaction product was observed during the warming of the reaction mixture up to room temperature; in the second case product decomposed already during the mixing the reagents at -50°÷ -40°C. Both reactions result in the formation of fluorosulfonic acid and tarry products. This fact is in a complete agreement with instability of secondary fluorosulfates previously observed [40] .

1,1,2,2-Tetrachloroethylfluorosulfate was synthesized for the PMR identification of (I) and (II); the compound eliminates fluorosulfonic acid at 20-25°C for several days.

$$CHCl{=}CCl_2 \xrightarrow{ClOSO_2F} \overset{VI}{CHCl_2CCl_2OSO_2F} \xrightarrow[-HSO_3F]{20\text{-}25^{\circ}C} CCl_2{=}CCl_2$$

$ClOSO_2F$ was found to be highly reactive towards C≡N bonds of perfluorocarbon acid nitriles, giving rise to equimolar adducts (corresponding N-chloroiminoperfluoroacylfluorosulfates) already at -45÷ -35°C.

$$R_fCN + ClOSO_2F \longrightarrow R_fC({=}NCl)OSO_2F$$

$$R_f = \underset{VII}{CF_3OCF_2},\ \underset{VIII}{n\text{-}C_3F_7},\ \underset{X}{n\text{-}C_4F_9},\ \underset{IX}{CF_2NO_2}$$

So, unlike the reactions of $S_2O_6F_2$ or ClF with perfluorocarbonitriles it is possible to obtain monoadducts of $ClOSO_2F$ to a triple bond [41,42].

Reaction of two moles of $ClOSO_2F$ with one mole of perfluorovalero- or butyronitrile gives mixtures of following products.

$$R_fCN + 2ClOSO_2F \longrightarrow \overset{XI}{R_fC(=NCl)OSO_2F} + \overset{XII}{R_fC(O)OSO_2F} + S_2O_5F_2$$

$$R_f = n\text{-}C_3F_7\ ,\ n\text{-}C_4F_9$$

An analogous mixture was obtained also in the reaction of $ClOSO_2F$ with one mole of N-chloroiminoperfluoroacylfluorosulfate; only half quantity of the latter come into this reaction. In accordance with it the reaction of N-chloroiminoperfluorovaleroylfluorosulfate with even more than two molar excess of $ClOSO_2F$ leads to the complete conversion of the latter.

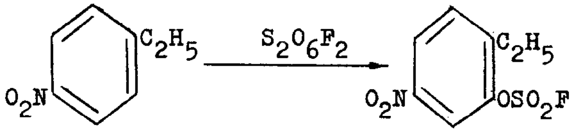
$$n\text{-}C_4F_9C(=NCl)OSO_2F + ClOSO_2F \longrightarrow \overset{XII}{n\text{-}C_4F_9C(O)OSO_2F} + S_2O_5F_2$$

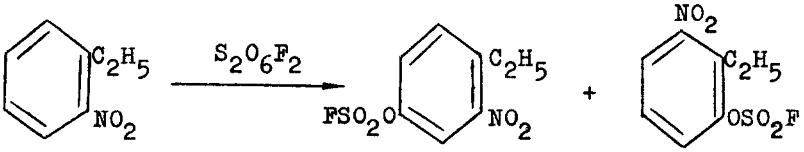
This results can be explained by the assumptions that dichloroamine (III) reacts mith $ClOSO_2F$ with elimination of pyrosulfuryldifluoride (and, possibly, nitrogen trichloride) and in this process (III) possesses higher reactivity, than N-chloroimine (IV).

$$R_fCN \xrightarrow{ClOSO_2F} \underset{(IV)}{R_fC(=NCl)OSO_2F} \xrightarrow{ClOSO_2F} \underset{(III)}{[R_fC(OSO_2F)_2NCl_2]} \longrightarrow$$

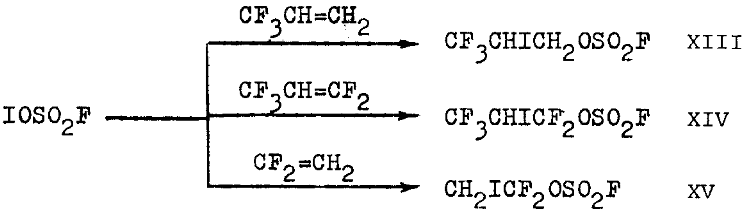
$$\xrightarrow{ClOSO_2F} R_fC(O)OSO_2F + S_2O_5F_2 + [NCl_3]$$

As was noted above, free radical substitutions of hydrogen atoms for fluorosulfate group are higly characteristic for reactivity of $S_2O_6F_2$. However, in the reaction of this compound with ethylnitrobenzenes at -40°C the aromatic ring substitution does occur; this fact is not in full concordance with free radical nature of the reagent.





As well as $ClOSO_2F$ $IOSO_2F$ is undoubtedly an ionic reagent; until recently, however, it had no use in organic synthesis. Lately reports of $IOSO_2F$ addition to tetrafluoroethylene and hexafluoropropene have appeared practically at the same time [1,37,43] . In the progress of our research [1,37] we have studied the addition of $IOSO_2F$ to various fluoroalkenes of ethylene and propylene series.



$IOSO_2F \xrightarrow{CF_3CH=CH_2} CF_3CHICH_2OSO_2F$ XIII

$IOSO_2F \xrightarrow{CF_3CH=CF_2} CF_3CHICF_2OSO_2F$ XIV

$IOSO_2F \xrightarrow{CF_2=CH_2} CH_2ICF_2OSO_2F$ XV

In the case of trifluorochloroethylene and trifluoroethylene the reaction leads to mixtures of isomers as well as analogous reaction of $ClOSO_2F$ [4,6] .

$$CFCl{=}CF_2 + IOSO_2F \longrightarrow \overset{XVI}{CFClICF_2OSO_2F} + \overset{XVII}{CF_2ICFClOSO_2F}$$

$$CHF{=}CF_2 + IOSO_2F \longrightarrow \overset{XIX}{CHFICF_2OSO_2F} + \overset{XVIII}{CF_2ICFHOSO_2F}$$

It is interesting to note that unlike the reaction of $ClOSO_2F$ with trifluorochloroethylene [4] , an isomer with $CFClOSO_2F$ - group predominates in the mixture possibly on account of steric factors.

The above mentioned reactions were carried out by bubbling fluoroolefines through stirred mixtures of $IOSO_2F$ and freon-113 at 20°C or at the freon boiling point. It is possible that poor solubility of $IOSO_2F$ in freon-113 is of rather importance, for these reactions, however it can develop the higher reactivity of $IOSO_2F$ towards less electrophylic fluoroolefines.

The adduct of $IOSO_2F$ with octafluoroisobutylene was obtained only after long standing (3 weeks) of a mixture at 20-25°.

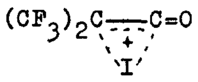
$$(CF_3)C{=}CF_2 + IOSO_2F \longrightarrow (CF_3)_2CICF_2OSO_2F \qquad XX$$

However, even in this case the conversion was relatively low and yield of product runs up only to 27,4%. In the same conditions $IOSO_2F$ does not add to hexafluorocyclobutene.

At the same time $IOSO_2F$ interreacts with such strongly electrophylic compound as bis(trifluoromethyl)ketene more easily than with perfluoroisobutylene or even some of fluorinated ethylenes and propylenes.

$$(CF_3)_2C{=}C{=}O + IOSO_2F \longrightarrow (CF_3)_2CIC(O)OSO_2F \qquad XXI$$

This fact seems to be explained by the ability of this ketene to form an intermediate complex.



So, $IOSO_2F$ seems to react with fluoroolefines and with bis(trifluoromethyl)ketene by an electrophylic mechanism. The character of this interaction evidences that $IOSO_2F$ is a weaker electrophyle than $ClOSO_2F$.

To sum up it is necessary to note that the reactivity of halogenofluorosulfates, usually considered as electrophylic reagents, and of $S_2O_6F_2$, a free radical reagent, leads to conclusion about the dependence of a reaction mechanism on the nature of organic partners.

EXPERIMENTAL

1,1-Bis(fluorosulfate)-2,2-dichloroethane (I)

An excess of acetylene-nitrogen mixture (1:10) was bubbled through a solution of 15g (0,112 moles) of $ClOSO_2F$ in 35 ml of freon-113 at -30÷ -25°C. The mixture was filtered through a paper filter and the solution was concentrated in vacuo. According to GLC and PMR data the remaining product (15g) consists of 1,1-bis(fluorosulfate)-2,2-dichloroethane (> 90%) and 1,2-bis(fluorosulfate)-1,2-dichloroethane (5-7%). Fractionation of this mixture gave 12,5g (75,7% yield) (I), b.p. 49--51°C (1 mm), n_D^{20} 1,4138; d_4^{20} 1,785. Anal. Calcd. for $C_2H_2Cl_2F_2O_6S_2$: C 8,14; H 0,68; Cl 24,07; F 12,88; S 21,70. Found: C 7,83; H 0,74; Cl 24,32; F 13,17; S 21,99.

N-Chloroiminotrifluoromethoxydifluoroacetylfluorosulfate

4,8g (0,0357 moles) of $ClOSO_2F$ was added dropwise (0,5hours) to 6,2g (0,0385 moles) of trifluoromethoxydifluoroacetonitrile at -50÷ -45°C. The mixture was stirred for 1 hour at -40°C and 2 hours at -30°C and allowed to warm to a room temperature for 2 hours. Fractionation gave 8,4g (79,3% yield) of N-chloroiminotrifluoromethoxydifluoroacetylfluorosulfate, b. p. 105-106°C; n_D^{20} 1,3330; d_4^{20} 1,679. Anal. Calcd. for $C_3ClF_6NO_4S$: C 12,18; Cl 12,01; F 38,58; N 4,74; S 10,83. Found: C 12,37; Cl 12,32; F 38,17; N 4,61; S 10,51.

2-Ethyl-5-nitrophenylfluorosulfate

To a stirred solution of 15,8g (0,105 moles) of p-nitroethylbenzene in 100 ml of freon-113 a solution of 8,85g (0,045 moles) of $S_2O_6F_2$ in 50 ml of freon-113 was added dropwise at -40°C. The mixture was cautiously warmed to 20°C , left at temperature for 16 hours, washed with water and dried with $MgSO_4$. After evaporation of solvent the resudue was fractionated to give 5,8g (64% yield) of 2-ethyl-5-nitrophenylfluorosulfate, b.p. 118°C (1 mm), n_D^{20} 1,5082; d_4^{20} 1,422. Anal. Calcd. for $C_8H_8FNO_5S$: C 38,61; H 3,21; F 7,63; N 5,62; S 12,85. Found: C 39,05; H 3,32; F 7,71; N 5,86; S 12,53. ^{19}F-NMR : -118,1 (S) ppm (CF_3COOH).

TABLE 1

Compound		Chemical shift (ppm) *				Coupling Constant (Hz)
		δ_1	δ_2	δ_3	δ_4	
(V)	$\overset{1}{H}CCl_2\overset{2}{C}HClOSO_2\overset{3}{F}$	5,95 D	6,48 D	-122,73 S		J_{12}=4,0
(VI)	$\overset{1}{H}CCl_2CCl_2OSO_2\overset{2}{F}$	6,14 S	-129,38 S			
(VII)	$\overset{1}{C}F_3O\overset{2}{C}F_2\underset{\underset{NCl}{\Vert}}{C}OSO_2\overset{3}{F}$	-21,18 T	-2,62 DQ	-125,92 T		J_{12}=10,2; J_{23}=5,6
(VIII)	$\overset{1}{C}F_3\overset{2}{C}F_2\overset{3}{C}F_2\underset{\underset{NCl}{\Vert}}{C}OSO_2\overset{4}{F}$	3,86 T	48,80 D	36,40 DQ	-125,82 TT	J_{13}=9,2; J_{24}=1,7; J_{34}=7,3
(IX)	$O_2N\overset{1}{C}F_2\underset{\underset{NCl}{\Vert}}{C}OSO_2\overset{2}{F}$	9,87 D	-128,33 T			J_{12}=6,8

* Relative to CF_3COOH and HMDS

(continued overleaf)

Table 1 (continued)

Compound		Chemical shift (ppm)					Coupling Constant (Hz)
		δ_1	δ_2	δ_3	δ_4	δ_5	
(X)	$\overset{1}{CF_3}\overset{2}{CF_2}\overset{3}{CF_2}\overset{4}{CF_2}\underset{\overset{\|}{NCl}}{C}OSO_2\overset{5}{F}$	4,89 TT	49,01 M	45,35 M	36,02 M	-125,73 TT	J_{13}=10,0; J_{14}=1,7; J_{35}=1,4; J_{45}=8,5
(XI)	$\overset{1}{CF_3}\overset{2}{CF_2}\overset{3}{CF_2}COSO_2\overset{4}{F}$	4,38 T	50,42 S	41,51 Q	-124,39 S		J_{13}=9,1
(XII)	$\overset{1}{CF_3}\overset{2}{CF_2}\overset{3}{CF_2}\overset{4}{CF_2}COSO_2\overset{5}{F}$	4,78 TT	49,14 M	46,15 M	40,73 M	-124,18 S	J_{13}=9,0; J_{14}=2,3
(XIII)	$\overset{1}{CF_3}\overset{2}{CHI}\overset{3}{CH_2}OSO_2\overset{4}{F}$	-11,41 D	4,65 TQ	4,80 D	-115,67 S		J_{12}=6,8
(XIV)	$\overset{1}{CF_3}\overset{2}{CHI}\overset{3}{CF_2}OSO_2\overset{4}{F}$	-13,87 M	4,98 M	-10,78M -11,38M	-126,69 T		J_{34}=8,5
(XV)	$\overset{1}{CH_2I}\overset{2}{CF_2}OSO_2\overset{3}{F}$	3,77 T	-11,71 DT	-126,12 T			J_{12}=11,2; J_{23}=9,6

(XVI)	$\mathrm{C\overset{1}{F}ClIC\overset{2}{F}_2OSO_2\overset{3}{F}}$	0,23 T	4,08 DD 4,28 DD	-127,38 T		J_{12}=11,3; J_{23}=8,5
(XVII)	$\mathrm{C\overset{1}{F}_2IC\overset{2}{F}ClOSO_2\overset{3}{F}}$	-18,95 D	-5,30 DT	-128,85 D		J_{12}=J_{23}=10,2
(XVIII)	$\mathrm{C\overset{1}{F}_2IC\overset{2}{F}\overset{3}{H}OSO_2\overset{4}{F}}$	7,52 DD 7,74 DD	65,80 DDT	6,43 DT	-123,93 D	J_{12}=J_{24}=6,8; J_{13}=2,8; J_{23}=51,8
(XIX)	$\mathrm{\overset{1}{F}C\overset{2}{H}IC\overset{3}{F}_2OSO_2\overset{4}{F}}$	90,92 DT	7,02 DDD	0,75 DD 0,90 DD	-126,63 DT	J_{12}=48,6; J_{13}=18,8; J_{23}=6,5 and 1,5; J_{34}=9,6
(XX)	$\mathrm{(C\overset{1}{F}_3)_2CIC\overset{2}{F}_2OSO_2\overset{3}{F}}$	-14,54 T	-12,38 DSept	-127,05 T		J_{12}=11,2; J_{23}=8,5
(XXI)	$\mathrm{(C\overset{1}{F}_3)_2CIOOSO_2\overset{2}{F}}$	-14,38 S	-125,94 S			

TABLE 2

Compound *	B.P. °C (mm Hg)	d_4^{20}	n_D^{20}	Formula	Anal. found (calculated)						Yield %
					C	H	Cl	F	N	S	
(V)	56-57(9)	1,698	1,4380	$C_2H_2Cl_3FO_3S$	10,59 (10,37)	0,93 (0,86)	45,81 (46,00)	7,92 (8,21)	-	13,61 (13,82)	88,7
(VI)	75-77(19)	1,769	1,4558	$C_2HCl_4FO_3S$	8,77 (9,02)	0,42 (0,38)	53,61 (53,38)	7,46 (7,14)	-	12,31 (12,03)	80,7
(VIII)	67(165)	1,697	1,3378	$C_4ClF_8NO_3S$	14,29 (14,57)	-	10,67 (10,77)	45,82 (46,13)	4,21 (4,25)	9,56 (9,71)	89,2
(IX)	70-71(95)	1,729	1,3938	$C_2ClF_3N_2O_5S$	9,59 (9,36)	-	14,17 (13,84)	21,88 (22,22)	11,13 (10,92)	12,73 (12,48)	89,9
(X)	135	1,701	1,3335	$C_5ClF_{10}NO_3S$	15,69 (15,81)	-	9,05 (9,35)	49,74 (50,07)	4,02 (3,69)	8,57 (8,43)	61,4

(XII)	104-105	1,720	≮1,29	$C_5F_{10}O_4S$	17,08 (17,34)	-	55,32 (54,91)	-	9,47 (9,25)	55,8
(XIV)	85-86(135)	2,163	1,3823	$C_3HF_9IO_3S$	9,96 (10,06)	0,17 (0,28)	32,15 (31,84)	35,73 (35,48)	8,78 (8,94)	74,8
(XV)	69-71(45)	2,130	1,4143	$C_2H_2F_3IO_3S$	8,39 (8,28)	0,72 (0,69)	19,40 (19,66)	43,56 (43,79)	11,12 (11,04)	65,9
(XIX)	77-78(175)	2,150	1,3930	$C_2HF_4IO_3S$	7,73 (7,79)	0,52 (0,33)	24,93 (24,68)	41,02 (41,23)	10,48 (10,39)	58,7
(XX)	84-85(130)	2,162	1,3622	$C_4F_9IO_3S$	11,08 (11,27)	-	39,82 (40,14)	30,13 (29,81)	7,76 (7,51)	27,4
(XXI)	68-70(47)	2,151	1,3835	$C_4F_7IO_4S$	11,98 (11,88)	-	32,60 (32,93)	31,79 (31,44)	8,18 (7,92)	78,6

*Structural formulas are listed in table 1

2-Iodo-3,3,3-trifluoropropylfluorosulfate

An excess of 1,1,1-trifluoropropene was bubbled at 20-30°C through a mixture of 13g (0,0575 moles) of $IOSO_2F$ and 20 ml of freon-113. The mixture was left at room temperature for 16 hours, filtered and evaporated. Fractionation of a residue gave 14g (75,3% yield) of 2-iodo-3,3,3-trifluoropropylfluorosulfate, b.p. 72-73°C (10 mm), n_D^{20} 1,4204, d_4^{20} 2,121. Anal. Calcd. for $C_3H_3F_4IO_3S$: C 11,18; H 0,93; F 23,60; I 39,44; S 9,94. Found: C 11,35; H 1,02; F 23,39; I 39,74; S 9,88.

Properties of some synthesized compounds are listed in Tables 1 and 2.

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