

PERFLUORO- $\omega$ -IODO- $\beta$ -OXAALKANESULFONYL FLUORIDES AS INTERMEDIATES FOR SURFACTANTS AND VINYL COMPOUNDS (\*)

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SUMMARY

Fluorosulfonyldifluoroacetyl fluoride (FOCCF<sub>2</sub>SO<sub>2</sub>F) quantitatively formed from sulfur trioxide and TFE through tetrafluoroethanesultone, has been converted into the octafluoro-5-iodo-3-oxapentanesulfonyl fluoride (ICF<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F) by the well known reaction involving MF, iodine and TFE in aprotic solvents. The iodo compound allowed us to obtain TFE telomers having both fluorosulfonyl and iodo terminal groups. These telomers were easily converted into the surfactants CF<sub>3</sub>CF<sub>2</sub>(CF<sub>2</sub>CF<sub>2</sub>)<sub>n</sub>OCF<sub>2</sub>CF<sub>2</sub>SO<sub>3</sub><sup>M</sup> by fluorination, and into the vinyl derivatives CF<sub>2</sub>=CF(CF<sub>2</sub>CF<sub>2</sub>)<sub>n</sub>OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F by dehalogenation.

The scope of this study was to illustrate new methods for the synthesis of perfluoroalkane and perfluoroalkene sulfonates.

INTRODUCTION

The fluorinated  $\beta$ -sultones (I) derived from sulfur trioxide and fluorinated olefins have been well known for some time. These compounds can be transformed by nucleophilic agents into related linear isomers, whose structures are fluorosulfonylfluoroacetyl fluorides.

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(\*) Paper presented at the 7th European Symposium on Fluorine Chemistry, Venice Lido, Italy, September 1980.

The compound (II) derived from  $C_2F_4$ , shows an interesting reaction with fluoride anion giving a stable intermediate (III) from which products with surface active properties (VI a) can be obtained; intermediate (III) can also be used to give fluorinated alkenes (VI b) which are able to copolymerize with common fluorinated olefins.

The complete series of compounds prepared from tetrafluoroethanesultone has been reported in Table 1.

TABLE 1  
Compounds prepared

I	$\begin{array}{c} \text{CF}_2-\text{CF}_2 \\   \quad   \\ \text{SO}_2-\text{O} \end{array}$	tetrafluoroethanesultone
II	$\begin{array}{c} \text{CF}_2-\text{COF} \\   \\ \text{SO}_2\text{F} \end{array}$	fluorosulfonyldifluoroacetyl fluoride
III	$\left[ \begin{array}{c} \text{CF}_2-\text{CF}_2\text{O} \\   \\ \text{SO}_2\text{F} \end{array} \right]^{-}\text{K}^{+}$	fluorosulfonyltetrafluoropotassium ethanolate
IV	$\begin{array}{c} \text{CF}_2-\text{CF}_2-\text{O}-\text{CF}_2-\text{CF}_2-\text{I} \\   \\ \text{SO}_2\text{F} \end{array}$	octafluoro-5-iodo-3-oxapentanesulfonyl fluoride
V	$\begin{array}{c} \text{CF}_2-\text{CF}_2-\text{O}-(\text{CF}_2-\text{CF}_2)_n-\text{CF}_2-\text{CF}_2-\text{I} \\   \\ \text{SO}_2\text{F} \end{array}$	perfluoro- $\omega$ -iodo-3-oxaalkanesulfonyl fluoride
VIa	$\begin{array}{c} \text{CF}_2-\text{CF}_2-\text{O}-(\text{CF}_2-\text{CF}_2)_n-\text{CF}_2-\text{CF}_3 \\   \\ \text{SO}_3\text{K} \end{array}$	perfluoro-3-oxaalkane potassium sulfonate
VIb	$\begin{array}{c} \text{CF}_2-\text{CF}_2-\text{O}-(\text{CF}_2-\text{CF}_2)_n-\text{CF}=\text{CF}_2 \\   \\ \text{SO}_2\text{F} \end{array}$	perfluoro-3-oxa-( $\omega$ -1)-alkenesulfonyl fluoride

## RESULTS AND DISCUSSION

Tetrafluoroethanesultone (I) and fluorosulfonyldifluoroacetyl fluoride (II) were obtained by a method already described [1].

Fluorosulfonyltetrafluoro potassium ethanolate (III)

Some alkaline perfluoroalkoxides  $R_f-OM$  have been isolated [2], but their stability is limited, especially when the cation is small (eg  $M=K^+$ ).

Their decomposition by  $\alpha$ -fluorine elimination with respect to the oxygen, causes a return to the initial carbonyl compound and MF. The lesser stability of  $R'_fCF_2-OM$  as compared with  $CF_3-OM$  could be attributed to the diminished delocalisation ability of the negative charge on the vicinal fluorine atoms and to the size of anion and cation which are more similar in  $CF_3-OM$  than in  $R'_fCF_2-OM$ .

In our case both cation size and the presence of only two vicinal fluorine atoms would suggest only a low stability of the alkoxide (III). However it appeared stable when isolated and could be kept in a moisture free environment: it can be presumed that the fluorosulfonyl group plays an important role in the anion stabilisation by increasing the delocalisation of the negative charge.

Compound (III) was obtained according to a general method by combining (II) and KF in aprotic solvents. After evaporating the solvent we isolated a yellow powder, whose elemental analysis corresponded to the predicted formula  $C_2F_5O_3KS$ .

The examination of the IR spectra in THF solution and in KBr showed a strong absorption band at around  $1500\text{ cm}^{-1}$ , attributable to C-O stretching frequency as reported for analogous compounds [2b, 3], while the peak attributed to the S-O stretching frequency was at  $1435\text{ cm}^{-1}$  instead of the predicted range  $1470\text{ cm}^{-1}$  for the fluorosulfonyl group.

The  $^{19}F$  NMR spectrum of (III) (recorded on a Varian EM 360 L spectrometer operating at 56,4 MHz) has the following data (relative to internal  $CFCl_3$ )  $\delta$ : + 40.5 ppm ( $-SO_2F$ , t.); -28 ppm ( $-CF_2O-$ , broad); -104.5 ppm ( $-CF_2-$ , d.);  $^3J = 7\text{ Hz}$ . The characteristic signal at -28 ppm which, at room temperature, is broad and without fine structure and also other broad signals, could be explained by the rapid exchange between (II) and (III). Further support of the above assertion, is found in the fine structure of the signal of  $FSO_2-$  which is only a triplet and that of  $FSO_2\overline{CF}_2$  - which is only a doublet.

The presence of moisture can promote the decomposition of compound (III) giving  $\text{CO}_2$  and  $\text{FSO}_2\text{CF}_2\text{H}$  (the  $^{19}\text{F}$  NMR spectrum of  $\text{FSO}_2\text{CF}_2\text{H}$  showed signals at  $-120.5$  ppm ( $-\text{CF}_2\text{H}$ , d.d.) and  $+38$  ppm ( $-\text{SO}_2\text{F}$ , d.t.); the proton NMR spectrum, contained a signal at  $6.7$  ppm (d.t.); the coupling constants are  $^3\text{J}(\text{HF})=7$  Hz and  $^2\text{J}(\text{HF}) = 52$  Hz).

The DTA showed an endothermic transition at  $62^\circ\text{C}$  followed by an exothermic one at  $87^\circ\text{C}$ . The thermal decomposition gave partial loss of  $\text{FSO}_2\text{CF}_2\text{COF}$  (II), the residue at  $125^\circ\text{C}$  was 50% and contained KF.

#### Octafluoro-5-iodo-3-oxapentanesulfonyl fluoride (IV)

The reactivity of the ionic compound (III) appeared to be of the same type as that of the analogous alkoxides  $\text{R}_f\text{-OM}$  [2d]; for example the iododerivative (IV) was obtained:



The reaction was carried out both at atmospheric and at high pressure, in an anhydrous aprotic solvent, in Hastelloy or glass reactors. According to a representative procedure, 750 ml of dry solvent containing 178 g (0.75 mol) of (III) were introduced in a 2l autoclave into which 254 g (2g atoms) of dry iodine were placed.  $\text{C}_2\text{F}_4$  was introduced at 20 bar whilst being stirred; after additional stirring for 4 hours, the residual gases were eliminated and compound (IV) was isolated by pouring the reaction mixture over ice and reducing the iodine with sodium bisulfite, followed by distillation.

During these operations the unconverted compound (III) was transformed into difluoromethanesulfonyl fluoride. A secondary product obtained was  $\text{C}_2\text{F}_4\text{I}_2$ . The conversion of (III) could be improved by an appropriate choice of solvents: 50% or higher conversion was obtained with solvents which could have behaved as hosts for the cation [4]. The partial conversion of (III) was attributed to iodine removal by KI to give polyiodides [2d], as confirmed by addition of  $\text{Br}_2$ , before completion of the reaction, which increased the yield (Table 2).

TABLE 2

Yield of  $\text{FSO}_2\text{-C}_2\text{F}_4\text{-O-C}_2\text{F}_4\text{-I}$  in different solvents.

Solvent	$\delta$ (a) ( $\text{Cal/cm}^3$ ) <sup>1/2</sup>	$\frac{\text{FSO}_2\text{-C}_2\text{F}_4\text{-O-C}_2\text{F}_4\text{-I}}{[\text{FSO}_2\text{-C}_2\text{F}_4\text{-O}]} \text{ K}$ %
DMF	12.1	< 5
$\text{CH}_3\text{CN}$	11.9	20
THF	9.1	25
dimethoxyethane	8.6	41
diglyme	8.3	50
diglyme	8.3	70 <sup>(b)</sup>

a) Solubility parameter

b) After addition of 1/4 mole of  $\text{Br}_2$  to the previous test.

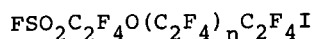
The octafluoro-5-iodo-3-oxapentanesulfonyl fluoride (IV) formed was a colourless liquid boiling at  $127^\circ\text{C}$  and solidifying at  $-142^\circ\text{C}$ .

The  $^{19}\text{F}$  NMR spectrum showed signals at  $+46.5$  ppm ( $-\text{SO}_2\text{F}$ );  $-65.5$  ppm ( $-\text{CF}_2\text{I}$ );  $-83.5$  ppm ( $-\text{S-CF}_2\text{-CF}_2\text{-O-}$ );  $-86.5$  ppm ( $-\text{O-CF}_2\text{-CF}_2\text{I}$ );  $-114$  ppm ( $-\text{S-CF}_2\text{-}$ ).

Mass spectral analysis showed the molecular ion peak at 426 and the fragmentation was consistent with the structure.

#### Perfluoro- $\omega$ -iodo-3-oxaalkanesulfonyl fluoride (V)

Octafluoro-5-iodo-3-oxapentansulfonyl fluoride behaved as a typical perfluoroiodoalkane and reacted with  $\text{C}_2\text{F}_4$  and  $\text{C}_3\text{F}_6$ , producing the expected adducts. The straight chain derivatives of TFE of formula :



were considered as having greatest interest. The telomer having  $n = 1$  (b.p.  $87^\circ\text{C}/70$  mm) is able to be isolated from the mixture of telomers by distillation.

The  $^{19}\text{F}$  NMR showed signals at  $+46.5$  ppm ( $-\text{SO}_2\text{F}$ );  $-59$  ppm ( $\text{CF}_2\text{I}$ );  $-83.5$  ppm ( $-\text{S-CF}_2\text{-CF}_2\text{-O-}$ );  $-84.5$  ppm [ $-\text{O-CF}_2\text{-CF}_2\text{-(CF}_2\text{)}_n\text{-}$ ];  $-114$  ppm ( $-\text{S-CF}_2\text{-}$ );  $-115$  ppm ( $-\text{CF}_2\text{-CF}_2\text{-I}$ );  $-123$  ppm ( $-\text{CF}_2\text{-}$ )<sub>n</sub>;  $-126$  ppm [ $-\text{O-CF}_2\text{-CF}_2\text{-(CF}_2\text{)}_n\text{-}$ ].

The intensity of the signal at -123 ppm is proportional to the chain length and may be useful in determining the average molecular weight of the telomers (V).

#### Perfluoro-3-oxaalkanepotassium sulfonate (VIa)

It was easy to transform the above mentioned telomers into surfactants (VIa) by substitution of the iodine with fluorine: a mixture fluorine-nitrogen 1:3 (10 l/hr) was bubbled into a solution of 32 g of telomers ( $\overline{MW} = 500$ ) in 700 ml of 1,1,2-trichlorotrifluoroethane containing 60 g of NaF and 60 g of  $MgF_2$  for 3 hours. The insoluble salts were filtered, then the organic layer washed with a 10% aqueous solution of  $Na_2CO_3$ . After distillation of the solvent, the residue was treated for 10 hours with 50 ml of KOH 20%. The compound (VIa) was isolated by neutralizing and extracting it with methanol.

The  $^{19}F$  NMR spectrum performed in  $CF_3COOH$  had the following data (relative to external  $CFCl_3$ )  $\delta$ : -81.5 ppm ( $CF_3^-$ ); -125 ppm ( $CF_3-CF_2^-$ ); -116.5 ppm ( $KO_3S-CF_2^-$ ). Other signals were similar to those already seen in the telomers (V).

The perfluoro 3-oxaalkane sulfonate appeared very stable to heat (up to 260°C in air, according to TGA at a heating rate of 10°C/min) and stable to aggressive chemical agents, like chromic acid (30%  $CrO_3$ ) and mixtures of hydrofluoric acid (38%) with nitric acid (62%). They are active in pickling baths for stainless steel and as antimist agents for chromium plating baths.

#### Perfluoro-3-oxa-( $\omega$ -1)-alkenesulfonyl fluoride (VI b)

Telomers (V) proved to be useful not only for transformation into surface active agents, but also into monomers. Perfluorinated olefins can be obtained from iodoperfluoroalkanes through their organometallic compounds [5]:

- 1) by thermal decomposition of perfluoroalkyl magnesium halides.
- 2) by dehalogenation using metallic couples (eg Zn/Cu).

Normally, these two methods produce a complex mixture of compounds which contain internal as well as vinylic double bonds. We were interested in a method which avoided the formation of a double bond in an internal position, while avoiding

the formation of a significant quantity of by-products, that is, a method giving a polymerization monomer.

It was possible to modify method 1): the thermal decomposition of Grignard compounds obtained by combining telomers (V) with  $C_2H_5MgBr$ . Both the displacement of the double bond and other secondary reactions were avoided by removing olefins during their formation.

Following a typical procedure, 74 ml of a 0.8 M solution of  $C_2H_5MgBr$  in ethyl ether, were dropped into 650 ml of a 0.09 M solution of telomers (V) in THF cooled at  $0^\circ C$  and previously introduced into a 1000 ml round bottomed flask fitted with a distillation column of 20 plates. After stirring for 3 hours at room temperature, the mixture was distilled with a reflux ratio of 20:1. The olefin passed out of the top. The distillation was discontinued when no more olefin was detectable by GLC. The yield was 55%. The  $^{19}F$  NMR characteristics of the olefins are similar to those in the literature [5b].

Copolymerisation experiments were carried out with  $C_2H_2F_2$  [monomer molar ratio :  $C_2H_2F_2/VIb = 20$ ; solvent: water; initiator: ammonium persulfate; surfactant: ammonium perfluorooctanoate; temperature:  $80^\circ C$ ; pressure: from 20 to 10 bar] and with  $C_2F_4$  [monomer molar ratio :  $C_2F_4/VIb = 20$ ; solvent: 1,1,2-trichlorotrifluoroethane; initiator: bis(4-terbutylcyclohexyl) peroxydicarbonate; temperature:  $70^\circ C$ ; pressure: from 11 to 5 bar].

Evidence of copolymerisation was derived from elementary analysis, IR spectra (band at  $1435\text{ cm}^{-1}$ ) and, in the case of vinylidene fluoride, from nuclear magnetic resonance.

Further details on copolymerisation will be discussed in a subsequent paper.

## CONCLUSION

The scope of this study was to illustrate new methods for the synthesis of both perfluoroalkane and perfluoroalkene sulfonates, whose particular properties are chemical and thermal inertness. The surfactants which have an ether bridge in the chain show the same characteristics of high temperature stability in the presence of oxygen and acids which distinguish the products of this class. Following the publication of the pa-

tents of this work [6], other studies in the same area have appeared [7]. By the optimization of each individual step in the reaction, we can hope to achieve an alternative synthesis both to electrochemical fluorination in the production of fluoro-sulfonic surfactants and to the addition of the epoxide  $C_3F_6O$  to compound (I) in the production of fluoroalkenesulfonyl fluorides [8].

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