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THE CHEMISTRY OF PERFLUOROALKANESULFONYL IODIDES

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SUMMARY

The reaction between silver perfluoroalkanesulfinate(1)(R_F = a, $Cl(CF_2)_6$; b, $Cl(CF_2)_4$) and iodine in dichloromethane at low temperature(e.g. -30°C) resulted in the formation of the corresponding perfluoroalkanesulfonyl iodide(2), which was identified by its ^{19}F NMR spectra. The perfluoroalkanesulfonyl iodide generated in situ reacted with various olefins to form two series of adducts, namely the normal adducts, $R_FSO_2CH_2CHIR$(3) and the adducts resulting from the loss of SO_2, R_FCH_2CHIR(4) in yields ranging from moderate to good. A radical reaction mechanism is proposed and tested by e.s.r. experiments. Perfluoroalkanesulfonyl iodide reacted with acetone and other compounds containing active hydrogen to give iodinated products.

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INTRODUCTION

The chemistry of perfluoroalkanesulfonyl fluoride and chloride have much been studied and reviewed [1-3]. Perfluoroalkanesulfonyl bromide as a class of perfluoroalkanesulfonyl halide has been studied in detail only recently [4]. In order to make a comparative study with these known perfluoroalkanesulfonyl halides, the challenge of preparing the presumably even less stable iodides drew our attention for a long time.

In fact, arenesulfonyl iodides were known before the turn of the century, although alkanesulfonyl iodides were first described only in 1964 [5]. Both of these sulfonyl iodides can be prepared in high yield by the usual method of reducing the sulfonyl chloride to the sulfinate and treating the latter with iodine [5-7]. Alkanesulfonyl iodides have only been obtained as benzene solutions which are quite unstable, and undergo considerable decomposition on standing or when exposed to strong light. Attempts at preparing the trichloromethanesulfonyl iodide or chloromethanesulfonyl iodide met with failure [7]. The explanation is that the equilibrium for the following equation:

$$RSO_2^- + I_3^- \rightleftharpoons RSO_2I + 2I^- \qquad (1)$$

is too unfavourable for the formation of the sulfonyl iodide .

RESULTS AND DISCUSSION

We first followed eq.2, as we found recently that perfluoroalkanesulfinate on treatment with bromine in aqueous solution can be converted to perfluoroalkanesulfonyl bromide in good yield [4],

$$R_FSO_2Na + Br_2 \longrightarrow R_FSO_2Br + NaBr \qquad (2)$$

but it was found that the appropriate sulfinates failed to react with iodine at room temperature in water or aqueous CH_3CN in the presence of KI, whereas reaction took place at 80°C to give R_FI as the sole product.

Later on, we found that the properties of silver perfluoroalkanesulfinate are quite different from that of sodium perfluoroalkanesulfinate, the former is more reactive in the sense that it decomposed spontaneously in the moist air to give perfluorocarboxylic acid on exposure to light [8]. Further studies revealed that silver perfluoroalkanesulfinate reacted readily with iodine in CH_2Cl_2 or CCl_4 at room temperature to give R_FI. If the reaction was carried out in CH_2Cl_2 at -30°C to -40°C and monitored by ^{19}F NMR, it was clearly shown from the ^{19}F NMR spectrum that perfluoroalkanesulfonyl iodide was indeed formed and was stable at this temperature, the characteristic signal δ_{CFCl_3} of $-CF_2SO_2I$ is 105.3ppm, which is similar to that of the sulfonyl bromide, 103.3ppm [4] and chloride, 100.5ppm [9]. None of the characteristic signal for δ $-CF_2I$ was observed. Furthermore, if the reaction mixture was treated with aqueous $Na_2S_2O_4$ at -30°C, the perfluoroalkanesulfonyl iodide was again reduced to the corresponding sulfinate. It seems certain that the following reaction has occurred,

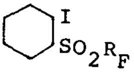
$$\underset{\underline{1}}{R_FSO_2Ag} + I_2 \longrightarrow \underset{\underline{2}}{R_FSO_2I} + AgI \qquad (3)$$

R_F= a, $Cl(CF_2)_6$; b, $Cl(CF_2)_4$

Although the perfluoroalkanesulfonyl iodides were formed in CH_2Cl_2 attempted isolation of them failed. When the solution of perfluoroalkanesulfonyl iodide was warmed up to room temperature, it decomposed slowly to give R_FI and SO_2, this process could be monitored by ^{19}F NMR spectroscopy, the characteristic signal of δ-CF_2I increased steadily, while the signal of δ-CF_2SO_2I decreased. During the decomposition of these sulfonyl iodides in CH_2Cl_2, a free radical intermediate could easily be trapped by t-BuNO to give the stable radical t-Bu(R_F)NO• . The e.s.r. spectrum of the trapped radical is shown in Fig.1 .

Interestingly, the sulfonyl iodides generated in situ reacted with various olefins smoothly at -20°C to form two series of adducts, namely the normal adducts, $R_FSO_2CH_2CHIR$(3) and the adducts resulting from the loss of SO_2 , R_FCH_2CHIR(4) in yields ranging from moderate to good depending on the nature of the olefins and acetylenes used. The results are listed in Table 1 .

TABLE 1

Olefin	Adduct	Yield(%)	
1-Hexene	$CH_3(CH_2)_3CHICH_2SO_2R_F$	3aa	67
		3ab	72
Cyclohexene		3ba	75
$O(CH_2CH=CH_2)_2$	$CH_2=CHCH_2OCH_2CHICH_2SO_2R_F$	3ca	73
$C_6H_5CH=CH_2$	$C_6H_5CHICH_2SO_2R_F$	3da	64
$CH_2=CCl_2$	$CCl_2I-CH_2R_F$	4aa	57
		4ab	52
$CH_2=CHCOOMe$	$R_FCH_2-CHICOOME$	4ba	62
$CH_2=CHCN$	$R_FCH_2-CHICN$	4cb	49
$C_6H_5C\equiv CH$	$C_6H_5CI=CHR_F$	4da	54(E:Z=4:1)
		4db	44(E:Z=4:1)
$HC\equiv CCH_2OH$	$R_FCH=CICH_2OH$	4eb	51(E:Z=2:1)
$CH_2=CHCOCH_3$	$R_FSO_2CH_2CH_2COCH_3$	5aa	75
		5ab	40
$CH_2=CHCHO$	$R_FSO_2CH_2CH_2CHO$	5bb	57

Sulfonyl iodide chemistry is dominated by free radical processes involving easy homolytic cleavage of the sulfur-iodine bond to give the electrophilic $RSO_2\cdot$ radical. For its addition to olefins, the chain mechanism as shown in Scheme I is generally accepted, for example,

$$PhSO_2X \xrightarrow{In} PhSO_2\cdot + X\cdot \qquad (1)$$

$$PhSO_2\cdot + RCH{=}CH_2 \longrightarrow R\dot{C}H{-}CH_2SO_2Ph \qquad (2)$$

$$R\dot{C}H{-}CH_2SO_2Ph + PhSO_2X \longrightarrow RCHX{-}CH_2SO_2Ph + PhSO_2\cdot \qquad (3)$$

Scheme I

Step 1 is the initiating step, steps 2, 3 are the propagating steps, Cristol and Davies reported [10] that there was a marked difference in the rates at which different sulfonyl halides undergo step 1 and steps 2, 3. The benzene sulfonyl iodide addition to norbornadiene followed the above sequences in a violent and exothermic manner, the reaction product being predominantly unsaturated monoadduct in 68% yield, while the benzene sulfonyl chloride combined with norbornadiene very slowly, the reaction product being predominantly saturated rearranged product in 7.3% yield. Apparently, the rate of chain transfer in the reaction of sulfonyl iodides is much faster than that of rearrangement, whereas the reverse is true in the reaction of the corresponding chlorides or bromides.

It is believed that thermal or light induced decomposition and the addition of perfluoroalkanesulfonyl iodides to unsaturated compounds also follows a radical pathway, whilst the strongly electron-withdrawing R_F group causes the perfluoroalkanesulfonyl radical to be more electrophilic than the alkanesulfonyl radical. Consequently, the addition of $R_FSO_2\cdot$ to the electron-rich carbon-carbon double bonds to give the normal 1:1 adduct is more favoured. Although diallyl ether usually forms a cyclic adduct and styrene usually forms polymeric product in a typical free radical addition, the very fast chain transfer step for perfluoroalkane sulfonyl iodides may offer an explanation for the formation of only 1:1 monoadducts without rearrangement or chain propagation. In the addition to acrylonitrile, the sulfonyl iodide is capable of undergoing chain transfer rapidly enough to compete with polymerization.

In the case of the spontaneous addition of perfluoroalkanesulfonyl iodide to alkenes with electron-withdrawing substituents, sulfur dioxide was eliminated and the adduct was <u>4</u>, furthermore, some R_FI was always found to present as a byproduct. These phenomena can be explained through the reduced reactivity of the electrophilic perfluoroalkanesulfonyl radical toward these olefins so as to allow the $R_FSO_2\cdot$ radical to decompose further to give the $R_F\cdot$ radical. In the reaction with methyl acrylate, it was found that perfluoroalkanesulfonyl iodide reacted very slowly, and was very stable in this reaction mixture even at room temperature(20°C).

Interestingly, perfluoroalkane sulfonyl iodides were found to add readily to methyl vinyl ketone or acrolein to give iodine-free adducts(5). These results are different from those mentioned above, and can be explained through the abstraction of hydrogen atoms by the resonance radical intermediate $[RFSO_2CH_2CH{=}C({=}O)X]\cdot$, resulting from the addition of the perfluoroalkane sulfonyl radical to these substrates.

In order to further confirm these possible reaction pathways, scavenging experiments and e.s.r. spectroscopic studies on these reactions were carried out during the decomposition of R_FSO_2I in CH_2Cl_2 solution with raising temperature. To the colourless solution of R_FSO_2I in CH_2Cl_2 at -70°C was added a solution of 1-nitroso-t-butane in F_{113} . A well resolved and intense e.s.r. spectrum of the trapped radical, $R_F(t\text{-}Bu)NO\cdot$ was readily observed at 22°C.(Fig.1, $R_F=Cl(CF_2)_6$, $a_N= 11.76G$; $a_F= 18.88G$; $g= 22.0054$) [2],

$$\begin{tikzcd}
R_FSO_2I \arrow[r] & R_FSO_2\cdot + I\cdot \arrow[d] \\
 & R_F\cdot + SO_2
\end{tikzcd}$$

$$R_F\cdot + t\text{-}BuNO \longrightarrow R_F(t\text{-}Bu)NO\cdot$$

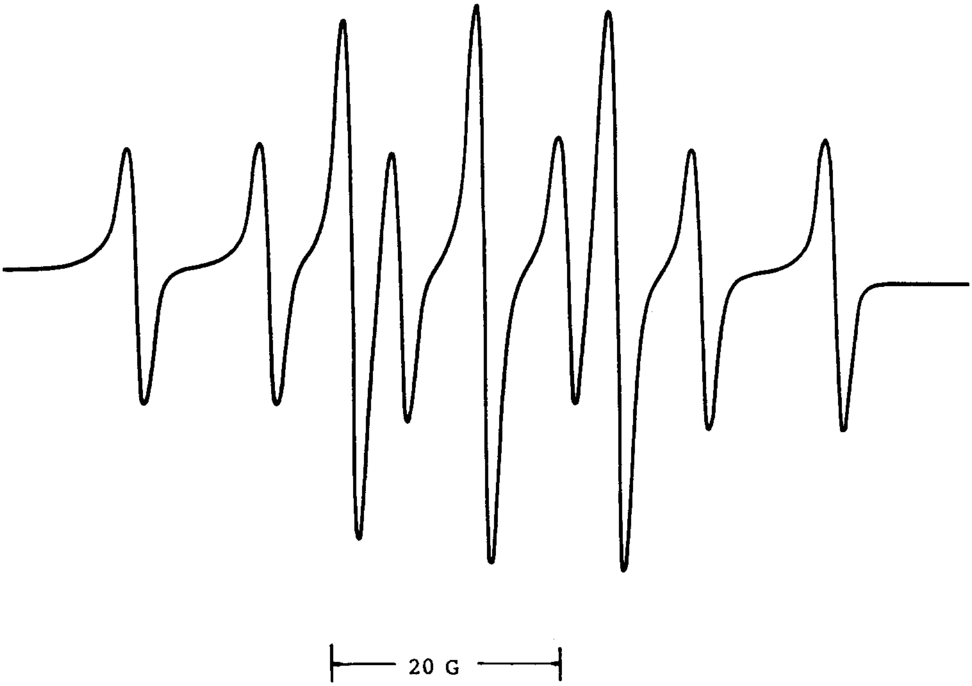


Fig. 1. E.S.R. spectrum of R_F(t-Bu)NO$^\cdot$ at 22°C (R_F=Cl$(CF_2)_6$)

Furthermore, when the solution of nitroso-t-butane in F_{113} was mixed with various unsaturated compounds such as methyl acrylate, acrylonitrile, phenylacetylene, etc. in e.s.r. tubes, no e.s.r. signals were observed. When a solution of R_FSO_2I in CH_2Cl_2 was added again, the same well resolved e.s.r. spectra as in Fig.1 were observed at 22°C. Apparently, the perfluoroalkyl radical is trapped by t-BuNO, before adding to alkenes.

In the reaction of R_FSO_2I with acetone and other substrates containing active methylene groups such as acetoacetic ester, the α-iodo derivatives were obtained in moderate to good yields, accompanied by a little R_FI, resulting from the decomposition of R_FSO_2I. A halophilic attack on iodine in R_FSO_2I seems to have occurred in this reaction, similar to the reactions of R_FSO_2Br [4] and of some alkanesulfonyl iodides [11].

EXPERIMENTAL

The melting points, boiling points are uncorrected , ^{19}F NMR spectra were measured on a Varian EM-360L spectrometer, using CF_3COOH as external standard. In ^{19}F NMR spectra, δ_{CFCl_3} (positive up field) were calculated by $\delta_{CF_3COOH} + 76.8$. ^1H NMR spectra were recorded on a Varian EM-360A using TMS as external standard. IR spectra were measured with a Carl Zeiss 75 IR spectrometer. Mass spectra were recorded on a Finnigan-4021 spectrometer. E.s.r. spectra were recorded with a Varian E-112 EPR spectrometer. The column chromatography was performed by using silica gel HF-254, particle size 10-9μ with a positive nitrogen pressure of 0.5-1 atm.

Preparation of <u>1a</u> : With magnetic stirring, a solution of 42.2g (0.1 mol) $Cl(CF_2)_6SO_2Na$ dissolved in 200 mL H_2O was mixed with a solution of 25.5 g (0.15 mol) $AgNO_3$ dissolved in 200 mL H_2O. the white silver salt(1a) was deposited instantly. The precipitate of $Cl(CF_2)_6SO_2Ag$ was filtered, and washed with distilled water, the product was dried in vacuum to give 48 g <u>1a</u> yield 95%, and kept without exposure to light .

<u>1b</u> was prepared similarly, yield 98% .

General procedure

With magnetic stirring, 2.5 g <u>1a</u>(4.9 mmol) and 0.62 g(7.4 mmol) 1-hexene were mixed in 50 mL CH_2Cl_2, the reaction mixture was cooled with dry ice to -20°C, 1.2 g (4.7 mmol) finely powdered I_2 was added, and allowed to react at this temperature for 0.5h. The reaction mixture was filtered, the precipitate of AgI was discarded, the colourless filtrate was washed to neutral with aqueous $NaHCO_3$ solution and then with water, dried with Na_2SO_4 , after removal of the CH_2Cl_2 and unreacted alkene, the residual crude product was chromatographed on a silica gel column using petroleum ether and acetone (20 : 1) as eluant to give 2 g <u>3aa</u>, yield 67%.

<u>3aa</u>: ^1H NMR: δ 1.0(t, 3H, CH_3), 1.4(m, 4H, CH_2CH_2), 1.8(m, 2H, CH_2), 3.3-4.4(m, 3H); ^{19}F NMR: δ 66.8(t, 2F, $ClCF_2$), 128.3, 129.3(m, 10F, 5×CF_2); IR : 2930, 2900, 2840 (m), 1460 (m), 1200, 1145(vs)cm^{-1}; m/z : 611, 613([M^+]), 483, 485($[M-I]^+$), 211($[M-Cl(CF_2)_6SO_2]^+$).

<u>3ab</u>: ^1H NMR: δ 1.0(t, 3H, CH_3), 1.5(m, 4H, 2×CH_2), 1.9(m, 2H, CH_2), 3.4-4.4(m, 3H); ^{19}F NMR: δ 66.8(t, 2F, $ClCF_2$), 118.3(m, 6F, 3XCF_2);

IR : 2930, 2900, 2850(m), 1430(m), 1200, 1130(vs)cm^{-1}; m/z: 383, 385([M-I]$^+$), 211([M-Cl(CF$_2$)$_4$SO$_2$]$^+$); Anal. $C_{10}H_{12}ClF_8IO_2S$, Calcd. : C, 23.53; H, 2.35; F, 29.80; S, 6.27; Found: C, 23.27; H, 2.38; F, 30.56; S, 6.08.

Preparation of 3ba : With magnetic stirring, 5 g(9.85 mmol) 1a and 1.7 g (20.7 mmol) cyclohexene in 60 mL CH_2Cl_2 were cooled to -20°C, the reaction mixture was treated with 2.5 g (9.85 mmol) finely powdered I_2 and allowed to react for 0.5h. The reaction product was isolated and purified similarly to give 4.5 g 3ba, yield 75%.

3ba: ^{1}H NMR: δ 1.6, 2.2 (m, 8H, 4×CH$_2$), 4.5, 4.1(m, 2H, 2×CH); ^{19}F NMR: δ 67.8(t, 2F, ClCF$_2$), 119.8, 120.4(m, 10F, 5×CF$_2$); IR: 2950, 2860(m), 1450(m), 1215,1150(vs)cm^{-1}; m/z: 483, 481([M-I]$^+$), 209([M-Cl(CF$_2$)$_6$SO$_2$]$^+$); Anal. $C_{12}H_{10}ClF_{12}IO_2S$, Calcd.: C, 23.68; H, 1.66; F, 37.46; S, 5.27; Found: C, 21.87; H, 1.35; F, 33.13; S, 5.29.

3ca : 5.6 g (11 mmol) 1a, 1.6 g (16.5 mmol) allyl ether in 50 mL CH_2Cl_2 was reacted with 2.8 g (11 mmol) finely powdered I_2 at -20°C for 0.5h to give 5 g 3ca, yield 73%. ^{1}H NMR: δ 5.1(m, 1H, CH=C), 4.8(m, 2H, CH$_2$=C), 4.5(m, 1H, CHI), 4.0(m, 4H, CH$_2$OCH$_2$), 3.5 (m, 2H, CH$_2$SO$_2$); ^{19}F NMR: δ 66.8(t, 2F, ClCF$_2$), 118.1, 118.8, 119.1(m, 10F, 5×CF$_2$); IR: 2980, 2950(m), 1650(m), 1450(m), 1220, 1150(vs)cm^{-1}; m/z: 625, 623([M$^+$]); Anal. $C_{12}H_{10}ClF_{12}IO_3S$, Calcd. : C, 23.06; H, 1.60; F, 36.51; S, 5.12; Found: C, 23.15; H, 1.60; F, 35.39; S, 5.26.

3da: 5 g (9.85 mmol) 1a, 2.1 g (20.16 mmol)styrene in 50 mL CH_2Cl_2 was reacted with 2.5 g (9.85 mmol) finely powdered I_2 for 0.5h at -20°C and recrystallized from MeOH to give 4 g 3da, yield 64%. White solid, m.p. 122°C; ^{1}H NMR: δ 7.5(s, 5H, C_6H_5), 4.8, 4.6 (m, 1H, CIH), 4.2, 3.8(m, 2H, CH_2SO_2); ^{19}F NMR:δ 67.8(t, 2F, $ClCF_2$), 107.8(t, 2F, CF_2SO_2), 119.5, 120.5(m, 8F, 4×CF_2); IR: 2970(m), 1492(m), 1361, 1207(s), 1148, 1107, 1080(s)cm^{-1}; Anal. $C_{14}H_8ClF_{12}IO_2S$, Calcd. : C, 26.66; H, 1.28; F, 36.15; S, 5.08; Found: C, 27.25; H, 1.19, F, 36.09; S, 5.12.

4aa: 5.1 g (10 mmol) 1a, 2 g (20.6 mmol) 1,1-dichloro-ethene in 50 mL CH_2Cl_2 at -20°C, was reacted for 0.5h with 2.54 g (10 mmol) finely powdered I_2 to give 3.2 g 4aa, yield 57% , the ^{19}F NMR showed that a little R_FI was formed as byproduct. 4aa: ^{1}H NMR: δ 3.7 (t, 2H, CH_2CF_2, J_{H-F} = 15.6Hz); ^{19}F NMR: δ66.5(t, 2F, $ClCF_2$), 110.8(m, 2F, CH_2CF_2), 118.1, 119.1, 121.3(m, 8F, 4×CF_2); IR: 2980(m), 1210, 1150(vs)cm^{-1}; Anal. $C_8H_2Cl_3F_{12}I$, Calcd. : C, 17.16; H, 0.35; F, 40.7; Found: C, 18.19; H, 0.37; F, 36.88.

4ab: ^{1}H NMR: 4.0(t, 2H, CH_2CF_2, J_{H-F} = 16Hz); ^{19}F NMR: δ66.2 (t, 2F, $ClCF_2$), 110.8(t, 2F, CF_2CH_2), 117.4, 121.1(m, 4F, 2×CF_2);

IR: 2980(m), 1230, 1200(vs)cm^{-1}; Anal. $C_6H_2Cl_3F_8I$, Calcd. : C, 15.69; H, 0.44; F, 33.09; Found: C, 15.32; H, 0.34; F, 32.86.

4ba: 5 g (9.85 mmol) 1a and 2.5 g (29 mmol) methyl acrylate in 50 mL CH_2Cl_2 were cooled to -30°C, the mixture was treated with 2.5 g (9.85 mmol) finely powdered I_2 and allowed to react for 0.5h, then it was warmed up slowly to room temperature. ^{19}F NMR spectrum showed that the generated $Cl(CF_2)_6SO_2I$ was stable in this reaction mixture, the ratio of unreacted perfluoroalkane sulfonyl iodide to the formed adduct was 85 : 15 ($Cl(CF_2)_6SO_2I$, ^{19}F NMR: δ68.1(t, 2F, $ClCF_2$), 105.5(t, 2F, CF_2SO_2I), 119.8, 120.9(m, 8F, 4×CF_2). On treating the reaction mixture with an aqueous saturated solution of $Na_2S_2O_4$, the perfluoroalkanesulfonyl iodide was reduced to the corresponding sulfinate, which was recovered following the literature method [12] . The reaction product was isolated and purified similarly to give 0.5 g 4ba, yield 62% (based on the 15% reacted silver perfluoroalkanesulfinate).

4ba: oily liquid, ^1H NMR: δ4.6(m, 1H, CHI), 3.8(s, 3H, OCH_3), 2.4-3.6(m, 2H, CH_2CF_2); ^{19}F NMR: δ67.0(t, 2F, $ClCF_2$), 113.8 (m, 2F, CF_2CH_2), 119.8, 120.8, 122.8(m, 8F, 4×CF_2); IR: 2959(m), 1746(s), 1440, 1210, 1150(vs)cm^{-1}; Anal. $C_{10}H_6ClF_{12}IO_2$, Calcd. : C, 21.90; H, 1.10; Found: C, 22.44; H, 0.98.

4cb: 4 g (9.8 mmol) 1b, 1 g (19.6 mmol) acrylonitrile in 50 mL CH_2Cl_2 was reacted with 2.5 g (9.85 mmol) finely powdered I_2 at -20°C for 1h to give 2 g 4cb, yield 49%. Oily liquid, ^{1}H NMR: δ 4.9 (m, 1H, CH), 2.7(m, 2H, CH_2CF_2); ^{19}F NMR: δ 67.8(t, 2F, $ClCF_2$), 113.1(m, 2F, CF_2CH_2), 119.8, 122.8(m, 4F, 2×CF_2); IR: 2980(w), 2225(w), 1185, 1130(vs)cm^{-1}; Anal. $C_7H_3ClF_8IN$, Calcd.: C, 20.24; H, 0.73; N, 3.37; Found: C, 20.59; H, 0.46; N, 3.38.

4da: 5 g (9.85 mmol) 1a, 3 g (29.4 mmol) phenylacetylene in 50 mL CH_2Cl_2 was reacted with 2.5 g (9.85 mmol) finely powdered I_2 and allowed to react for 10 min. at -20°C, when the colour of iodine faded, 0.5 g iodine was again added and further reaction at this temperature for 0.5h, gave 3g 4da (E : Z = 4 : 1, based on ^{19}F NMR peak areas), yield 54% and byproduct PhC≡CI 0.5 g, ^{1}H NMR: δ 7.5(s, 5H); m/z: 228([M^+]); 101([M^+-I]).

4da: White solid, m.p. 34-36°C (E, Z mixture), ^{1}H NMR: δ 7.3 (5H, s, C_6H_5), 6.95, 6.70, 6.45(t, 1H, $CHCF_2$, J_{H-F} = 13Hz); ^{19}F NMR: δ E, 67.2(t, 2F, $ClCF_2$), 104.4(m, 2F, CF_2CH), 119.4, 120.4, 121.8(m, 8F, 4×CF_2); δ Z, 67.2(t, 2F, $ClCF_2$), 108.1 (d, 2F, CF_2CH), 119.4, 120.4, 121.8(m, 8F, 4×CF_2); IR: 3075(m), 1643(m), 1594, 1255, 1210, 1145(vs), 1086(s)cm^{-1}; m/z: 564, 566 ([M^+]), 437, 439([M^+-I]); Anal.$C_{14}H_6ClF_{12}I$, Calcd.: C, 29.78; H, 1.07; F, 40.38; Found: C, 29.77; H, 0.80; F, 39.65.

4db (E, Z mixture, E : Z = 4 : 1 based on ^{19}F NMR peak areas.) was prepared and isolated similarly in a yield of 44% and accompanied with some byproduct PhC≡CI 0.3g.

4db: oily liquid(E, Z mixture), ^{1}H NMR: δ 7.3(5H, s, C_6H_5), 6.5 (t, 1H, $CHCF_2$, J_{H-F} = 13Hz); ^{19}F NMR: δ E, 66.5(t, 2F, $ClCF_2$), 103.1(m, 2F, CF_2CH), 117.8, 120.1(m, 4F, 2×CF_2); δ Z, 66.5 (t, 2F, $ClCF_2$), 106.8(d, 2F, CF_2CH), 117.8, 120.1(m, 4F, 2×CF_2); IR: 3070(m), 1640(m), 1230, 1210, 1145(vs)cm^{-1}; m/z: 465, 467([M^+]), 337, 339([M^+-I]); Anal. $C_{12}H_6ClF_8I$, Calcd. : C, 31.03; H, 1.30; F, 32.72; Found: C, 31.07; H, 1.21; F, 31.81.

4eb: 4 g (9.8 mmol) 1b, 1.1 g (19.6 mmol) propynol in 50 mL CH_2Cl_2 was reacted with 2.5 g (9.8 mmol) finely powdered I_2 at -20^{o}C to give 2.1 g 4eb (E, Z mixture, E : Z = 2 : 1 based on the ^{19}F NMR peak areas), yield 51% and 0.9 g $Cl(CF_2)_4SO_2CH{=}ClCH_2OH$, yield 19%.

4eb: White solid (E, Z mixture), m.p. 35°C, ^{1}H NMR: δ 6.6(t, 1H, $CF_2CH{=}$, J_{H-F} = 10Hz), 4.2(m, 2H, CH_2O), 2.3(m, 1H, OH); ^{19}F NMR: δ E, 67.5(t, 2F, $ClCF_2$), 104.8(m, 2F, CF_2CH), 119.1, 121.8 (m, 4F, 2×CF_2); δ Z, 67.5(t, 2F, $ClCF_2$), 107.8(m, 2F, CF_2CH), 119.1, 121.8(m, 4F, 2×CF_2); IR: 3350(s), 3050, 2900(m), 1630(m), 1190(vs), 1130(vs)cm^{-1}; HMS: $C_7H_4ClF_8IO$, 419, 417([M^+]), 400, 398([M^+-F]), 292, 290([M^+-I]).
$Cl(CF_2)_4SO_2CH{=}ClCH_2OH$, ^{1}H NMR: δ 7.0(s, 1H, $SO_2CH{=}$), 4.2 (s, 2H, CH_2O), 2.3(w, 1H, OH); ^{19}F NMR: 67.5(t, 2F, $ClCF_2$),

104.5(t, 2F, CF_2SO_2), 119.1, 121.8(m, 4F, 2×CF_2); m/z: 482, 484([M^+]), 418([M^+-SO_2]).

<u>5aa</u>: 5 g (9.85 mmol) <u>1a</u>, 1.4 g (19.97mol) methyl vinylketone in 50mL CH_2Cl_2 was reacted with 2.5 g (9.85 mmol) finely powdered I_2 at -20°C for 0.5h and the crude product purified by recrystallization from petroleum ether to give 3.5 g <u>5aa</u>, yield 75%. White solid, m.p. 66-68°C, ^1H NMR: δ2.3(s, 3H, CH_3), 3.4 (t, 2H, CH_2SO_2), 3.0(t, 2H, CH_2CO); ^{19}F NMR: δ68.1(t, 2F, $ClCF_2$), 112.6(s, 2F, CF_2SO_2), 119.8, 120.8(m, 8F, 4×CF_2); IR: 3000, 2950(m), 1722(s), 1417(m), 1358, 1284, 1211(vs), 1083, 1039(s)cm^{-1}; Anal. $C_{10}H_7ClF_{12}O_3S$, Calcd.: C, 25.52; H, 1.50; Found: C, 25.44; H, 1.40.

<u>5ab</u>: White solid, m.p. 72-74°C, ^1H NMR: δ2.3(s, 3H, CH_3), 3.6(t, 2H, CH_2SO_2), 3.1(t, 2H, CH_2CO); ^{19}F NMR: δ66.8(t, 2F, $ClCF_2$), 111.5(s, 2F, CF_2SO_2), 118.1(m, 4F, 2×CF_2); IR: 3000, 2950(m), 1720(s), 1420(m), 1200(vs), 1130(s)cm^{-1}; m/z: 337, 339 ([M^+-MeCO]); Anal. $C_8H_7ClF_8O_3S$, Calcd.: C, 25.92; H, 1.90; Cl, 9.56; F, 41.00; Found: C, 25.91; H, 1.89; Cl, 9.44; F, 40.10.

<u>5bb</u>: 4 g (9.8 mmol) <u>1b</u>, 1.1 g (19.6 mmol) acrolein in 50 mL CH_2Cl_2 was reacted with 2.5 g (9.8 mmol) finely powdered I_2 at -20°C for 0.5h and the crude product purified by recrystallization from CCl_4 to give 2 g <u>5bb</u>, yield 57%. White solid, m.p. 68°C, ^1H NMR: δ

9.9(t, 1H, CHO), 3.5(t, 2H, CH_2SO_2), 3.2(m, 2H, CH_2CHO); ^{19}F NMR: δ 67.8(t, 2F, $ClCF_2$), 112.8(t, 2F, CF_2SO_2), 119.5(m, 4F, 2×CF_2); IR: 2900, 2800(m), 1720(s), 1350(s), 1190(vs), 1130(s)cm^{-1}; m/z: 357, 359([M^++1]); Anal. $C_7H_5ClF_8O_3S$, Calcd.: C, 23.57; H, 1.41; S, 8.99; Found: C, 23.39; H, 1.32; S, 9.70.

E.S.R. study of perfluoroalkanesulfonyl iodide (2a) under a nitrogen atmosphere in the presence of 1-nitroso-t-butane in F_{113}: the colourless solution of R_FSO_2I in CH_2Cl_2 was prepared by reacting silver perfluoroalkanesulfinate(1a) with iodine at -30°C; after the intense purple colour of iodine had rapidly faded, the supernatant solution was separated and cooled to -70°C, (^{19}F NMR: δ 68.1(t, 2F, $ClCF_2$), 105.3(t, 2F, CF_2SO_2I), 119.8, 120.8(m, 8F, 4×CF_2), this solution was syringed into an e.s.r. tube, which contained a solution of 1-nitroso-t-butane in F_{113}, and mixed as quickly as possible by shaking the sample tube at room temperature(22°C). The e.s.r. spectrum was monitored at appropriate time intervals. A well resolved and intense e.s.r. spectrum of the trapped radical intermediate was recorded as shown in Figure 1 [2] at 22°C.

No e.s.r. signals were observed, when the solution of nitroso-t-butane in F_{113} was mixed with various unsaturated compounds, methyl acrylate, acrylonitrile, phenylacetylene, etc. in e.s.r. tubes. After a solution of R_FSO_2I in CH_2Cl_2 was added, the same well resolved e.s.r. spectra as Fig.1 were observed at 22°C.

The iodination of acetone: With magnetic stirring, 4 g (9.8 mmol) 1b and 10 mL acetone in 30 mL CH_2Cl_2 were cooled to 0°C, the mixture was treated with 2.5 g (9.8 mmol) finely powdered I_2 and allowed to react for 0.5h. ^{19}F NMR showed that the perfluoroalkanesulfinic acid($Cl(CF_2)_4SO_2H$) was formed almost quantitatively accompanied with only a little $Cl(CF_2)_4I$ as by-product. The reaction mixture was filtered, the precipitate of AgI was discarded. The colourless filtrate was chromatographed on a silica gel column using petroleum ether as eluant to give the solution of iodoacetone in petroleum ether, which was distilled to give 1.4 g iodo-acetone, yield 78%, b.p. 50°C/11mmHg. ^1H NMR:δ2.4(s, 3H, CH_3), 3.7(s, 2H, CH_2I).

5 g (9.85 mmol) 1a, 1.5 g (11.5 mmol) $CH_3COCH_2CO_2Et$ in 50 mL CH_2Cl_2 reacted with 2.5 g (9.85 mmol) finely powdered I_2 at 0°C for 0.5h the crude product was purified similarly to give 2 g $CH_3COCHICO_2Et$, yield 79%. ^1H NMR: δ4.7(s, 1H, CHI), 3.9(q, 2H, OCH_2), 2.2(s, 3H, CH_3), 1.1(t, 3H, CH_3).

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