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SYNTHESES AND PROPERTIES OF (PERFLUOROALKYL)PHENYLIODONIUM TRIFLATES (FITS REAGENTS) AND THEIR ANALOGUES

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SUMMARY

A variety of (per- and polyfluoroalkyl)phenyl- and p-fluorophenyliodonium triflates 3 were synthesized in good yields by the oxidation of the corresponding iodofluoroalkanes with trifluoroperacetic acid followed by the treatment with benzene or fluorobenzene and triflic acid. It was also shown that elemental fluorine was used as a substitute for the peracid. The use of fluorosulfonic, sulfuric, and methanesulfonic acids instead of triflic acid afforded the fluoroalkylaryliodonium fluorosulfonates 5, sulfates 6, and methanesulfonate 7, respectively. Similarly perfluoroalkylene-α,ω-bisaryliodonium triflates 10 were synthesized from α,ω-diiodoperfluoroalkanes. On the other hand, the treatment of (perfluoroalkyl)-p-tolyliodonium chlorides with silver sulfonates gave the iodonium benzenesulfonate 13, methanesulfonate 12, and triflate 14, and bisiodonium sulfate 15. Thermolysis of (perfluorooctyl)phenyliodonium triflate at about 150°C afforded perfluorooctyl triflate, iodobenzene, and (perfluorooctyl)iodobenzene in 73, 63, and 25% yields, respectively.

INTRODUCTION

Among the organic derivatives of trivalent iodine there have been many investigations on the syntheses, properties, and reactivities of diaryliodonium salts, but aliphatic-aromatic

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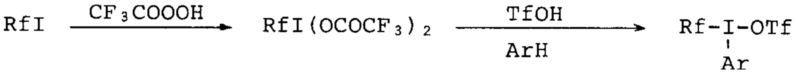
iodonium salts have scarcely been synthesized [1-3]. Yagupol'skii reported on the synthesis or reactivity of the fluoroanalogues, (perfluoroalkyl)aryliodonium halides [4,5], trifluoroacetates [4], or tetrafluoroborates [6] where the electronegative perfluoroalkyl groups bond directly to the trivalent iodine atoms. In order to develop reactive electrophilic perfluoroalkylating agents, it is of great significance to synthesize (perfluoroalkyl)aryliodonium triflates, because the iodine atom bears the strongest leaving group, OTf. We have already reported that (perfluoroalkyl)phenyliodonium triflates (FITS reagents) are highly reactive electrophilic perfluoroalkylating [7-13,15] or novel oxy-perfluoroalkylating [14,15] agents. This paper describes the syntheses and properties of variety of fluoroalkylaryliodonium triflates and their analogues [16,17].

RESULTS AND DISCUSSION

(Perfluoro- and ω-H- or ω-bromoperfluoroalkyl)aryliodonium triflates 3

The triflates 3 were synthesized from fluoroalkyliodides 1 according Eq. 1. Yagupol'skii *et al.* reported that iodoper-



$$\mathrm{RfI} \xrightarrow{\mathrm{CF_3COOOH}} \mathrm{RfI(OCOCF_3)_2} \xrightarrow[\mathrm{ArH}\;\; 0^\circ\mathrm{C} \rightarrow \mathrm{R.t.}]{\mathrm{TfOH}} \underset{\mathrm{Ar}}{\mathrm{Rf{-}I{-}OTf}} \qquad (1)$$

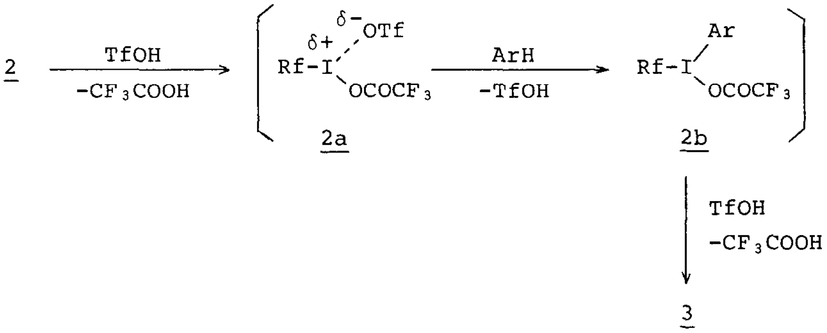
1 (Rf=fluoroalkyl)

2

3a (Ar=Ph)

3b (Ar=p-F-Ph)

fluoroalkanes were oxidized to bis(trifluoroacetoxy)iodo compounds 2 (Rf=perfluoroalkyl) by trifluoroperacetic acid [4]. Since the reaction of 2 with a nonactivated aromatic compound, benzene, was very slow [4], we examined whether a superacid catalyzes the reaction or not. As the result, we found that 2 smoothly reacted with benzene in the presence of an equivalent amount of triflic acid in 1,1,2-trichlorotrifluoroethane or trifluoroacetic acid at 0°C to room temperature to give the triflates 3 in good yields. The reaction was not catalyzed by a small amount of triflic acid. An equimolar amount of the acid to 2 was needed for the smooth completion of the reaction. It indicates that trifluoroacetoxy group of 2 is easily replaced with OTf group and reverse substitution does not occur. The formation of 3 can be best explained by the following mechanism; (1) displacement of a trifluoroacetoxy group of 2 with a TfO group, (2) easy electrophilic reaction between activated intermediate 2a and benzene, (3) the formation of 3 by displacement of another trifluoroacetoxy group with triflic acid liberated (Scheme 1).



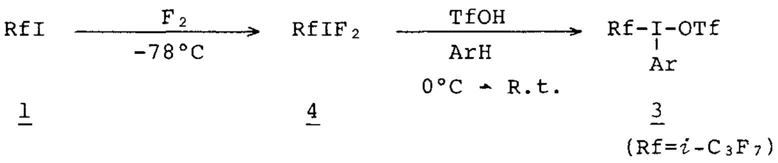
Scheme 1

Similarly, fluorobenzene reacted with 2 and triflic acid to afford the p-fluorophenyliodonium triflates only. Other isomers could not be detected. Benzotrifluoride no longer reacted with 2 in the presence of triflic acid.

A variety of aryliodonium triflates having perfluoroalkyl and ω-H- or ω-bromoperfluoroalkyl groups of carbon number two to ten were synthesized by this method (Table 1).

1,1,2-Trichlorotrifluoroethane was better as the reaction solvent than trifluoroacetic acid, since clean crystals of the triflates were obtained. In particular, the trichlorotrifluoroethane must be used for the synthesis of 3(Rf=i-C_3F_7) because the triflates could not be isolated when trifluoroacetic acid was used as the solvent.

It was reported that iodoperfluoroalkanes were oxidized to difluoroiodoperfluoroalkanes by elemental fluorine at low temperature[18,19]. 3 ($Rf=\mathit{i}\text{-}C_3F_7$) were also synthesized by the oxidation of 2-iodoheptafluoropropane with elemental fluorine followed by the treatment with benzene or fluorobenzene and triflic acid. The reaction mechanism would be similar to Scheme 1. But this method is not convenient because of the



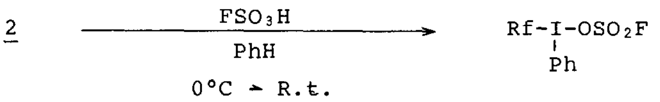
$$\underset{\underline{1}}{\mathrm{RfI}} \xrightarrow[-78^\circ\mathrm{C}]{F_2} \underset{\underline{4}}{\mathrm{RfIF_2}} \xrightarrow[\substack{\mathrm{ArH}\\ 0^\circ\mathrm{C}\,\rightarrow\,\mathrm{R.t.}}]{\mathrm{TfOH}} \underset{\substack{\underline{3}\\ (\mathrm{Rf}=\mathit{i}\text{-}\mathrm{C_3F_7})}}{\underset{\mathrm{Ar}}{\mathrm{Rf{-}I{-}OTf}}} \qquad (2)$$

difficulty in handling of elemental fluorine. Neither the method using elemental fluorine nor that using trifluoroperacetic acid as an oxidizer gave trifluoromethylaryliodonium triflates.

The triflates 3 thus synthesized are nonhygroscopic white crystals and the stability is relatively high. They can be recrystallized from hot chloroform, acetonitrile, or ethyl acetate. The stability increases with an increase of carbon number of the perfluoroalkyl groups. 3 with long fluoroalkyl groups, for example, 3a ($Rf=\mathit{n}\text{-}C_8F_{17}$), are sufficiently stable at room temperature. 3 with short fluoroalkyl groups must be placed in a refrigerator for storage. 3, particularly, with the short fluoroalkyl groups are soluble in usual organic solvents such as methylene chloride, chloroform, acetonitrile, ether, THF, ethyl acetate, methanol, acetone, and so on. The solubility of 3 with the long alkyl groups decreases in some degree. 3 decomposed gradually in acetone and soon in ether or THF at room temperature. The relative high solubility to non-polar solvents would suggest that the bond between the iodine and the acid group is more covalent than the corresponding bond in diaryliodonium salts.

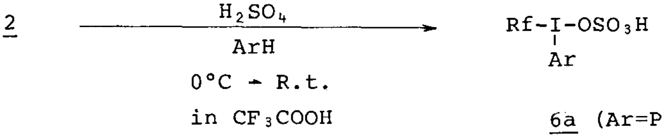
(Perfluoro- or ω-H-perfluoroalkyl)aryliodonium fluorosulfonates, 5, sulfates 6, and methanesulfonate 7

Similarly, other strong acids such as fluorosulfonic acid and sulfuric acid smoothly produced the corresponding iodonium salts 5 and 6 in good yields as shown in Eq. 3 and 4. 5 [Rf= n-C_8F_{17} and $H(CF_2)_{10}$] were easily isolated by filtration since the precipitates appeared during the reaction. But 5 were moisture-sensitive and easily hydrolyzed to sulfates 6 during recrystallization. So the complete assignment was done as sulfates 6. The reaction with a weak sulfonic acid, methanesulfonic acid, was very slow and the yield of 7 was low (Eq. 5). 6 and 7 are stable crystals and can be recrystallized from organic solvents.



$$\underline{2}\ \xrightarrow[\substack{\text{PhH}\\ 0^\circ\text{C} \to \text{R.t.}\\ \text{in } CCl_2FCF_2Cl}]{FSO_3H}\ \underset{\text{Ph}}{\underset{|}{\text{Rf-I-}OSO_2F}} \qquad (3)$$

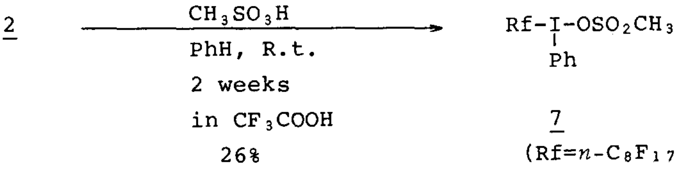
5



$$\underline{2}\ \xrightarrow[\substack{\text{ArH}\\ 0^\circ\text{C} \to \text{R.t.}\\ \text{in } CF_3COOH}]{H_2SO_4}\ \underset{\text{Ar}}{\underset{|}{\text{Rf-I-}OSO_3H}} \qquad (4)$$

6a (Ar=Ph)
6b (Ar=p-F-Ph)

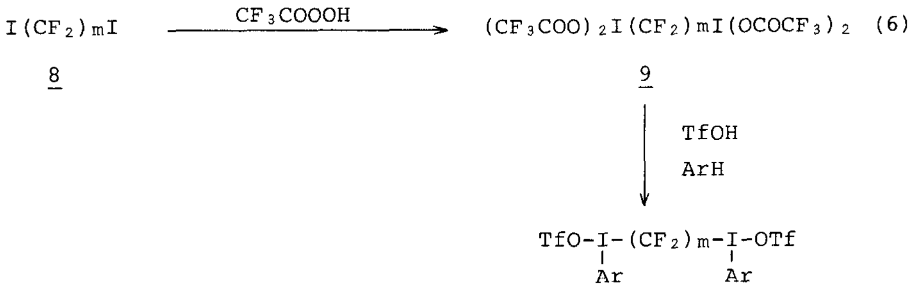
(Rf=fluoroalkyl)



$$\underline{2}\ \xrightarrow[\substack{\text{PhH, R.t.}\\ \text{2 weeks}\\ \text{in } CF_3COOH\\ 26\%}]{CH_3SO_3H}\ \underset{\text{Ph}}{\underset{|}{\text{Rf-I-}OSO_2CH_3}} \qquad (5)$$

7
(Rf=n-C_8F_{17})

Perfluoroalkylene-α,ω-bisaryliodonium triflates 10



$$\mathrm{I(CF_2)_mI} \xrightarrow{\mathrm{CF_3COOOH}} \mathrm{(CF_3COO)_2I(CF_2)_mI(OCOCF_3)_2} \quad (6)$$

8 → 9

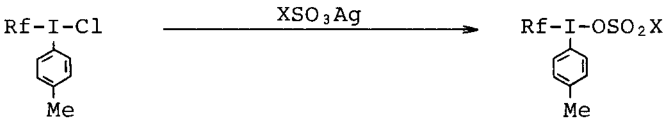
$$\mathbf{9} \xrightarrow{\mathrm{TfOH,\ ArH}} \mathrm{TfO{-}\underset{Ar}{I}{-}(CF_2)_m{-}\underset{Ar}{I}{-}OTf}$$

10a (Ar=Ph)
10b (Ar=p-F-Ph)

Triflates 10 were synthesized according to Eq. 6. Trifluoroacetates 9 (m=3 and 8) were prepared almost quantitatively by oxidizing 8 with trifluoroperacetic acid. 9 were treated with 2 equimolar amount of triflic acid and 2.4 equimolar amount of benzene in 1,1,2-trichlorotrifluoroethane at 0°C to room temperature for 1 d and then at room temperature for 2 d to give 10 in good yields. The reaction with fluorobenzene proceeded well in trifluoroacetic acid. We synthesized bistriflates having perfluoroalkylene chains of three or eight carbons by this method, but we failed to synthesize bistriflates with a chain of two carbons (10, m=2). Recently Yagupol'skii *et al*. reported that 9 (m=2) reacted with benzene in trifluoroacetic acid for 7 d at 25°C to give the corresponding bisiodonium trifluoroacetate [20].

(Perfluoroalkyl)-p-tolyliodonium methane- and benzenesulfonates 12, 13, triflate 14, and bis[(perfluoroalkyl)-p-tolyliodonium] sulfate 15

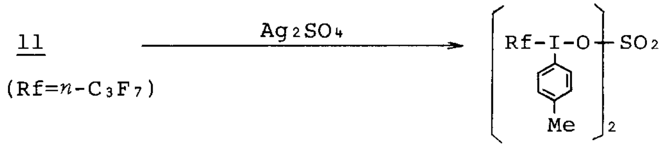
Salts 12-15 were synthesized by the reaction of the iodonium chloride 11 with silver methanesulfonate, benzenesulfonate, trifluoromethanesulfonate, and sulfate, respectively. 11 was pre-



11 (Rf=n-C_3F_7)

12 (X=CH_3)
13 (X=Ph)
14 (X=CF_3)

(7)



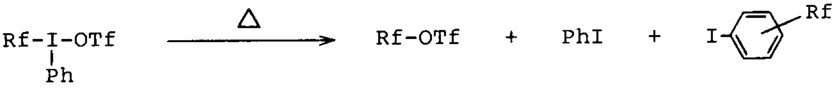
15

(8)

pared according to Yagupol'skii's procedure [4]. 12, 13, and 15 are stable crystals at room temperature. However, the crystals of 14 decomposed almost after a day at room temperature. In this way, the very strong leaving group lowers the stability of the tolyliodonium salts. It is interesting to note that the corresponding phenyliodonium triflates 3a are considerably stable at room temperature. The stability is related to the nature of aromatic rings. Electron-releasing substituents in the ring decrease the stability, while electron-withdrawing ones increase the stability. Thus the p-fluorophenyliodonium salts have relatively high stability.

Thermolysis of (perfluoroalkyl)phenyliodonium triflates 3a

(Perfluorooctyl)phenyliodonium triflate was heated for 30 min at 145-151°C under vacuum with a trap cooled in a dry ice-



(9)

3a (Rf=n-C_8F_{17})

16 (73%)

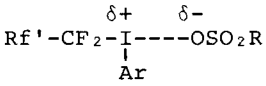
(63%)

17 (25%)

acetone bath to yield perfluorooctyl triflate 16, iodobenzene, and (perfluorooctyl)iodobenzene 17 in 73, 63, and 25% yields, respectively. Products resulting from the bond fission between phenyl and iodine atom were not detected. 17 was a mixture of 8:10:1 of three isomers from gas chromatography, though the structures were not assigned. These results show that the bond fission between Rf and iodine atom occurs favorably.

^{19}F NMR spectra of the iodonium triflates and their analogues

^{19}F NMR spectra of a series of (perfluoroalkyl)aryliodonium sulfonates showed an interesting behavior of the chemical shifts of difluoromethylene groups bonding to the iodine atoms. The corresponding signals of triflate 3a ($Rf=n\text{-}C_8F_{17}$), sulfate 6a ($Rf=n\text{-}C_8F_{17}$), methanesulfonate 7, and chloride 11($Rf=n\text{-}C_8F_{17}$)* appear in the order of 3a (67.8 ppm), 6a (73.7), 7 (78.4), and 11 (85.5). It is in good agreement with the order the leaving ability of the groups($TfO > OSO_3H > OSO_2CH_3 > Cl$). The down-field shift of the difluoromethylene in the order would be due to the degree of the positive polarization of the iodine atom as shown in the following figure. The iodonium triflates



$$Rf'\text{-}CF_2\text{-}\underset{\displaystyle Ar}{\overset{\delta+}{I}}\text{----}\overset{\delta-}{OSO_2R}$$

have the highest polarization by the strongest leaving ability of OTf and thus the triflates are expected to be highly reactive to nucleophiles.

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*Heptadecafluorooctyl-p-tolyliodonium chloride was prepared according to Yagupol'skii's procedure [4,5], crude yield 81%, Yield after recrystallization from hot CH_3CN was 24% because of decomposition of the significant amount of the chloride, mp 143-4°C, ^{19}F NMR (ppm, $CDCl_3$, int. $CFCl_3$); 80.3(3F, t, J=10 Hz, CF_3), 85.5(2F, m, CF_2I), 114.8(2F, m, CF_2), 120.5(8F, m, $5xCF_2$), 124.9(2F, m, CF_2), ^1H NMR (δ, $CDCl_3$); 2.45(3H, s, CH_3), 7.35(2H, d, J=9 Hz, ArH), 8.02 (2H, d, J=9 Hz, ArH).

EXPERIMENTAL

Melting points were uncorrected. ^1H NMR spectra were determined with a Varian HA-100 NMR spectrometer or a Varian EM 390 NMR spectrometer. ^{19}F NMR spectra were determined with a Varian XL-100A NMR spectrometer or a Hitachi R-20B NMR spectrometer. Perfluoroalkyl and ω-bromotetrafluoroethyl iodides were commercial materials. ω-H-perfluoroalkyl iodides and α,ω-diiodoperfluoroalkanes were prepared by the methods described in the literature [21, 22]. Highly pure benzene (for spectroscopy, Merck) was better to obtain very white crystals of FITS reagents and their analogues.

Preparation of 3, 5, 6, 7, and 10

Typical procedure; 60% Hydrogen peroxide (9.65 ml, H_2O_2 0.211 mol, H_2O 0.266 mol) was added dropwise into a mixture of 105 ml (0.745 mol) of trifluoroacetic anhydride and 1 ml of trifluoroacetic acid with stirring on an ice bath. After that, 100 g (0.183 mol) of 1 (Rf=*n*-C_8F_{17}) was added into the solution. The reaction mixture was gradually warmed to room temperature for a period of 24 h with stirring. Then the solvent was completely evaporated up at room temperature by using a vacuum pump and 133.5 g (94.4%) of 2 (Rf=*n*-C_8F_{17}) was obtained as white crystals, which were used for the next reaction without further purification. Triflic acid (15.2 ml, 0.172 mol) was dropwise added into a mixture of 133.2 g (0.172 mol) of 2 (Rf=*n*-C_8F_{17}) and 450 ml of 1,1,2-trichlorotrifluoroethane with stirring at 0°C. After that, 18.4 ml (0.207 mol) of benzene was added dropwise into the mixture at 0°C. The reaction mixture was gradually warmed to room temperature overnight and stirred at room temperature for an additional day. (The whole reaction time was about 20 h for a small scale experiment) The reaction mixture became homogeneous. Then the solvent and trifluoroacetic acid liberated were completely evaporated up by using an aspirator and then a vacuum pump. After 100 ml of acetonitrile was added into the residue (crystals), the mixture was allowed to stand overnight. Filtration gave 103.4 g (78%) of 3a (Rf=*n*-C_8F_{17}) as white crystals. The filtrate was completely evaporated up similarly. Then an adequate amount of acetonitrile was added into it and the mixture was cooled on an ice bath for 2 h. The filtration gave 9.5 g (7%) of the crystals. Further repeated procedure of the crystallization gave 0.97 g (0.7%) of 3a. Total yield was 86%. The crystals were recrystallized from hot acetonitrile for further purification.

A solvent for crystallization or recrystallization for each iodonium salt is shown in Table 1. Fluorosulfonates 7 appeared as crystals during the reaction in 1,1,2-trichlorotrifluoroethane. The oxidation of 1 and 8 was almost quantitative except for 2-iodoheptafluoropropane of which oxidation yield was 58%. In general, 2 are stable crystals except for 2(Rf=i-C_3F_7) which is unstable crystals in air and thus must be treated under argon or nitrogen atmosphere for the next reaction. The reaction conditions for 7 and 10 were shown in Discussion and Results.

Preparation of 3 (Rf=i-C_3F_7) by using elemental fluorine

Typical procedure; Fluorine (20% in nitrogen, 2.5 l, F_2 22 mmol) was introduced into a solution of 2.96 g (10 mmol) of 2-iodoheptafluoropropane in 30 ml of trichlorofluoromethane for a period of about 10 min with vigorous stirring at -78°C. After that, the reaction mixture was stirred for 1 h and warmed to room temperature. After evaporation of the solvent under reduced pressure, 25 ml of 1,1,2-trichlorotrifluoroethane was added into the flask. Fluorobenzene (0.94 ml, 10 mmol) and then 0.90 ml(10 mmol) of triflic acid were added dropwise into the solution with stirring under argon atmosphere at 0°C. The reaction mixture was then stirred for 2 d and warmed to room temperature. The resulting precipitates were collected by filtration and extracted with acetonitrile. The acetonitrile solution was evaporated up and the resulting yellow crystals were recrystallized from chloroform to give 1.74 g (32%) of 3b(Rf=i-C_3F_7) as white crystals.

Preparation of 12, 13, and 14

Typical procedure; A solution of 0.5 g (1.18 mmol) of 11 (Rf=n-C_3F_7) in 8 ml of acetonitrile was dropwise added into a solution of 0.24 g (1.18 mmol) of silver methanesulfonate in 7 ml of acetonitrile with stirring under argon atmosphere at 0°C. After the reaction mixture was stirred for an additional hour, the resulting precipitates were removed by filtration. The filtrate was evaporated up and the resulting solid was recrystallized from methylene chloride-pentane to give 0.35 g (61%) of 12 as white crystals.

Preparation of 15

A solution of 0.51 g (1.20 mmol) of 11 (Rf=n-C_3F_7) in 9 ml of acetonitrile was dropwise added into a solution of 0.188 g (0.60 mmol) of silver sulfate in 12 ml of acetonitrile with stirring under argon atmosphere at 0°C. After that, the mixture was stirred for 1 h at 0°C and then for 1 d at room temperature. The resulting precipitates were collected by filtration and extracted with methylene chloride. After filtration the methylene chloride solution was evaporated up to give 0.272 g (52%) of 15 as white crystals. Further purification was done by recrystallization from chloroform.

Thermolysis of 3a (Rf=n-C_8F_{17})

In a flask fitted with a trap cooled in a dry ice-acetone bath, 2.00 g (2.59 mmol) of 3a (Rf=n-C_8F_{17}) was placed and heated at 145 to 151°C for 30 min under vacuum (0.2 to 0.12 mmHg). Analysis of the products (1.95 g) left in the trap by GC or ^{19}F NMR showed that 1.88 mmol (73%) of 16 and 1.64 mmol (63%) of iodobenzene were formed. Fractional distillation of the mixture gave 0.408 g (0.66 mmol, 25%) of 17 other than 16 and iodobenzene. Iodobenzene was in agreement with an authentic sample. 16; bp (bath temp.) 98°C/19 mmHg, ^{19}F NMR (ppm, $CDCl_3$, int. $CFCl_3$) 73.5 (3F, t, J=5.6 Hz, CF_3S), 79.1 (2F, m, CF_2O), 81.0 (3F, t, J=8.7 Hz, CF_3), 121.5 (8F, m, 4xCF_2),

TABLE 1

Syntheses and properties of (perfluoroalkyl)aryliodonium triflates and their analogues

Iodonium Salt	Yield (%)	Mp[a] (°C)	^{1}H-NMR		^{19}F-NMR[c]		Found (Calcd)	
			Solv.[b)]	δ (J; Hz)	Solv.[b)]	ppm (J; Hz)	C(%)	H(%)
3a Rf:								
n-$C_{10}F_{21}$	73[d]	162-6 [$CHCl_3$]	A	7.53-8.06(3H,m) 8.26(2H,d,J=8)	A	67.44(2F,t,J=10,CF_2I) 78.18(3F,s,CF_3S), 80.27 (3F,t,J=10,CF_3), 112.8-125.3(16F,m,8xCF_2)	23.49 (23.41)	0.59 (0.58)
n-C_8F_{17}	85[d] 86[e]	149-151 (Dec) [$CHCl_3$ or CH_3CN]	A	7.53-8.00(3H,m) 8.26(2H,d,J=8)	A	67.82(2F,t,J=12,CF_2I) 78.07(3F,s,CF_3S), 80.25 (3F,t,J=10,CF_3), 112.8 (2F,m,CF_2), 120.7(6F,m, 3xCF_2), 121.7(2F,m,CF_2) 125.3(2F,m,CF_2)	23.28 (23.33)	0.59 (0.65)
n-C_7F_{15}	75[d]	148-150 (Dec) [$CHCl_3$]	B	7.68-8.15(3H,m) 8.66(2H,dd,J=8,2)	B	71.41(2F,t,J=12,CF_2I) 78.07(3F,s,CF_3S), 80.59 (3F,t,J=10,CF_3), 113.3 (2F,m,CF_2), 121.0(4F,m, 2xCF_2),122.1(2F,m,CF_2) 125.6(2F,m,CF_2)	23.26 (23.29)	0.61 (0.70)
n-C_6F_{13}	82[d]	120-3 (Dec) [$CHCl_3$ or CH_3CN]	C	7.50-7.97(3H,m) 8.26(2H,dd,J=8,2)	C	70.35(2F,m,CF_2I), 79.00 (3F,s,CF_3S), 81.28(3F, t,J=10,CF_3), 114.2(2F, m,CF_2), 121.7(2F,m,CF_2) 123.0(2F,m,CF_2), 126.5 (2F,m,CF_2)	23.13 (23.23)	0.73 (0.75)
n-C_4F_9	77[e]	125-7 [$CHCl_3$]	A	7.64-8.08(3H,m) 8.34(2H,d,J=8)	A	68.63(2F,t,J=10,CF_2I) 78.02(3F,s,CF_3S), 80.27 (3F,t,J=10,CF_3), 113.9 (2F,m,CF_2),124.7(2F,m,CF_2)	22.96 (23.09)	0.89 (0.88)

3a Rf:								
n-C_3F_7	75[d]	124.5-127 (Dec) [$CHCl_3$]	C	7.42-7.85(3H,m) 8.12(2H,d,J=8)	C	70.65(2F,bs,CF_2I), 79.00 (3F,s,CF_3S),79.70(3F,t, J=8,CF_3), 118.5(2F,s,CF_2)	22.93 (23.01)	0.93 (0.97)
i-C_3F_7	32[e] 29[f]	125 (Dec) [AcOEt or $CHCl_3$]	A	7.59-7.99(3H,m) 8.25(2H,d,J=8)	A	71.05(6F,d,J=12,2xCF_3) 78.22(3F,s,CF_3S), 149.3 (1F,heptet,J=12,CF)	22.87 (23.01)	0.99 (0.97)
C_2F_5	67[d]	116-120 (Dec) [$CHCl_3$]	C	7.54-7.94(3H,m) 8.16(2H,d,J=8)	C	76.03(2F,q,J=4,CF_2) 78.93(3F,s,CF_3S), 80.94 (3F,t,J=4,CF_3)	22.62 (22.90)	1.07 (1.07)
$H(CF_2)_{10}$	69[e]	142.5-143 [$CHCl_3$]	B	6.65(1H,tt,J= 50.6,4.8,CF_2H) 7.34-7.81(3H,m) 8.36(2H,d,J=8.8)	B	70.43(2F,m,CF_2I), 77.03 (3F,s,CF_3S),111.5(2F,m, CF_2CF_2I), 116.3-122.6 (12F,m,6xCF_2), 127.1(2F, m,CF_2CF_2H), 136.7(2F,d, J=50.6, CF_2H)	23.88 (23.91)	0.69 (0.71)
$Br(CF_2)_2$	66[e]	119.5-123.5 [$CHCl_3$]	C	7.49-7.83(3H,m) 8.10(2H,d,J=8)	C	61.19(2F,t,J=9,CF_2) 67.93(2F,t,J=9,CF_2) 78.97(3F,s,CF_3)	20.24 (20.28)	0.97 (0.95)
3b Rf:								
n-$C_{10}F_{21}$	91[e]	165-8 [$CHCl_3$]	A	7.48(2H,dd,J=9, 8), 8.35(2H,dd, J=9,5)	A	66.90(2F,m,CF_2I), 78.06 (3F,s,CF_3S), 80.25(3F,t, J=9.5,CF_3), 100.3(1F,m, ArF), 112.7(2F,m,CF_2) 119.8-120.7(10F,m,5xCF_2) 121.7(2F,m,CF_2), 125.2 (2F,m,CF_2)	22.52 (22.92)	0.37 (0.45)

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TABLE 1 (cont.)

Iodonium salt	Yield	Mp		^{1}H-NMR		^{19}F-NMR	Found (Calcd)	
3b Rf:								
n-C_8F_{17}	86^e	145-7 [$CHCl_3$]	A	7.48(2H,dd,J=9, 8), 8.37(2H,dd, J=9,5)	A	67.65(2F,t,J=12,CF_2I) 78.01(3F,s,CF_3S), 80.18 (3F,t,J=10,CF_3), 100.7 (1F,m,ArF), 112.9(2F,m, CF_2), 120.6-121.8(10F, m,5xCF_2), 125.3(2F,m,CF_2)	22.68 (22.78)	0.58 (0.51)
n-C_6F_{13}	62^e	139-142 [$CHCl_3$]	A	7.40(2H,dd,J=9, 8), 8.30(2H,dd, J=9,5)	A	68.04(2F,t,J=13,CF_2I) 78.02(3F,s,CF_3S), 80.25 (3F,t,J=10,CF_3), 100.8 (1F,m,ArF), 113.0(2F,m, CF_2), 120.5(2F,m,CF_2) 121.8(2F,m,CF_2), 125.3 (2F,m,CF_2)	22.39 (22.61)	0.70 (0.58)
n-C_3F_7	82^e	150-1 (Dec) [$CHCl_3$]	A	7.45(2H,dd,J=9, 9), 8.38(2H,dd, J=9,5)	A	69.91(2F,q,J=10,CF_2I) 78.01(3F,s,CF_3S), 78.77 (3F,t,J=10,CF_3), 100.9 (1F,m,ArF), 117.6(2F, bs, CF_2)	22.33 (22.24)	0.93 (0.75)
i-C_3F_7	61^e 32^f	142-5 [$CHCl_3$]	A	7.48(2H,dd,J=9.2, 8.2), 8.36(2H,dd, J=8.2,4.8)	A	70.74(6F,d,J=12,2xCF_3) 78.01(3F,s,CF_3S), 99.87 (1F,m,ArF), 148.7(1F, heptet,J=12,1F)	22.03 (22.24)	0.77 (0.75)
C_2F_5	73^e	130-5 [$CHCl_3$ or CH_3CN]	A	7.40(2H,dd,J=9.0, 8.4), 8.30(2H,dd, J=8.4,4.6)	A	74.82(2F,m,CF_2I), 77.97 (3F,s,CF_3S), 80.10(3F, m, CF_3), 101.0(1F,m, ArF)	21.96 (22.06)	0.79 (0.82)

3b Rf:								
$H(CF_2)_{10}$	74^d	107.2-109.8 [$CHCl_3$]	B	6.79(1H,tt,J=49.6, 5.4,CF_2H), 7.60 (2H,dd,J=9.0,9.0) 8.66(2H,dd,J=9.0, 5.0)	B	70.65(2F,m,CF_2I), 77.55 (3F,s,CF_3),100.4(m,ArF) 111.8(2F,m,CF_2),118.4-122.6 (12F,m,6CF_2),127.4(2F,m,CF_2) 137.0(2F,d,J=49.6,CF_2H)	—	—
$Br(CF_2)_2$	65^e	114-6 [$CHCl_3$]	A	7.23-7.52(2H,m) 8.15-8.39(2H,m)	C	61.02(2F,t,J=9,CF_2) 67.29(2F,t,J=9,CF_2) 78.88(3F,s,CF_3), 100.4 (1F,m,ArF)	19.83 (19.62)	0.81 (0.73)
5 Rf:								
n-C_8F_{17}	70^e	113-6 (Dec)		—	B	-39.38(1F,s,FSO_2) 72.68(2F,m,CF_2I), 80.03 (3F,t,J=10,CF_3), 112.6 (2F,m,CF_2), 120.0(8F, m,4xCF_2), 124.7(2F,m,CF_2)	—	—
$H(CF_2)_{10}$	90^e	124.3-125.2	D	7.10(1H,tt,J=50.1, 5.6, CF_2H), 7.24-8.13(3H,m), 8.49 (2H,d,J=7.5)	D	-40.73(1F,s,FSO_2) 77.93(2F,m,CF_2I), 113.1 (2F,m,CF_2CF_2I), 119.0-123.2(12F,m,6xCF_2) 127.6(2F,m,CF_2CF_2H) 137.6(2F,d,J=50.1, CF_2H)	—	—
6a Rf:								
n-$C_{10}F_{21}{}^g$	81^d	129-132 [CH_3CN]	A	7.50-7.96(3H,m) 8.25(2H,d,J=8)	A	73.27(2F,m,CF_2I), 80.15 (3F,t,J=10,CF_3), 113.2 (2F,m,CF_2), 120.6(10F, m,5xCF_2), 121.6(2F,m,CF_2) 125.1(2F,m,CF_2)	23.00 (22.93)	0.92 (0.96)

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TABLE 1 (cont.)

Iodonium salt	Yield	Mp	^{1}H-NMR		^{19}F-NMR		Found (Cald)	
6a Rf:								
n-C_8F_{17}^{g}	95^d	114-8 [CH_3CN]	A	7.50-8.00(3H,m) 8.30(2H,d,J=9)	A	73.67(2F,m,CF_2I), 80.27 (3F,t,J=9,CF_3), 113.4 (2F,m,CF_2), 120.7(6F,m, 3xCF_2), 121.7(2F,m,CF_2) 125.2(2F,m,CF_2)	22.81 (22.78)	0.96 (1.09)
n-C_7F_{15}^{g}	68^d	116-8 [CH_3CN]	A	7.50-7.97(3H,m) 8.25(2H,d,J=8)	A	74.28(2F,t,J=13,CF_2I) 80.25(3F,t,J=10,CF_3) 113.4(2F,m,CF_2), 120.6 (4F,m,2xCF_2), 121.7(2F, m,CF_2), 125.2(2F,m,CF_2)	22.96 (22.69)	0.95 (1.17)
n-C_6F_{13}	66^d	107-8 [AcOEt]	C	7.52-7.98(3H,m) 8.27(2H,d,J=8)	A	74.23(2F,t,J=14,CF_2I) 80.28(3F,tt,J=10,3,CF_3) 113.4(2F,m,CF_2), 120.6 (2F,m,CF_2), 121.7(2F,m, CF_2), 125.2(2F,m,CF_2)	23.20 (23.24)	1.06 (0.98)
n-C_3F_7	76^d	109-111 [AcOEt]	C	7.40-7.90(3H,m) 8.20(2H,d,J=9)	A	75.65(2F,q,J=10,CF_2I) 78.94(3F,t,J=10,CF_3) 118.1(2F,s,CF_2)	23.04 (23.00)	1.34 (1.29)
C_2F_5	90^d	107-8 [CH_3CN or AcOEt]	E	7.58-8.03(3H,m) 8.37(2H,d,J=7.5)	E	79.81(2F,q,J=4,CF_2) 80.87(3F,t,J=4,CF_3)	22.92 (22.87)	1.41 (1.44)
$H(CF_2)_{10}$	69^d	135.6-136 [CH_3CN]	D	7.11(1H,tt,J= 49.5,5.3,CF_2H) 7.20-8.20(3H, m), 8.50(2H,d, J=7.5)	D	77.93(2F,m,CF_2I), 113.0 (2F,m,CF_2CF_2I), 118.4-122.5(12F,m,6xCF_2) 127.1(2F,m,CF_2CF_2H) 137.0(2F,d,J=49.5,CF_2H)	23.42 (23.96)	0.88 (0.88)

6b Rf: n-C_8F_{17}	58[d]	120-1 [CH_3CN]	A	7.38(2H,dd,J=9,9) 8.34(2H,dd,J=9,6)	A	73.78(2F,t,J=12.9,CF_2I) 80.28(3F,t,J=9.4,CF_3) 102.0(1F,m,ArF), 113.4 (2F,m,CF_2), 120.6(6F,m, 3xCF_2),121.7(2F,m,CF_2) 125.2(2F,m,CF_2)	22.53 (22.78)	0.83 (0.68)
7	26[d]	140-1 [CH_3CN]	C	2.50(3H,s,CH_3) 7.50-7.90(3H,m) 8.24(2H,d,J=8)	A	78.36(2F,t,J=10,CF_2I) 80.27(3F,t,J=10,CF_3) 113.9(2F,m,CF_2), 120.8 (6F,m,3xCF_2), 121.9(2F, m,CF_2), 125.2(2F,m,CF_2)	25.09 (25.09)	1.04 (1.12)
10a m=8	62[e]	138.9-139.1 (Dec) [AcOEt]	A	7.62-8.07(6H,m) 8.35(4H,d,J=8)	A	68.10(4F,m,2xCF_2I) 77.78(6F,s,2xCF_3) 111.6(4F,m,CF_2CF_2I) 119.1(8F,m,4xCF_2)	23.77 (23.89)	0.84 (0.91)
10a m=3	49[e]	163.5-163.8 (Dec) [AcOEt]	B	7.68-8.14(6H,m) 8.58(4H,d,J=7)	B	70.73(4F,m,2xCF_2) 77.48(6F,s,2xCF_3) 105.5(2F,m,CF_2)	23.68 (23.85)	1.12 (1.18)
10b m=8	55[d]	193.5-193.7 (Dec) [$CHCl_3$]	B	7.56(4H,dd,J=9,9) 8.67(4H,dd,J=9,5)	B	70.80(4F,m,2xCF_2I) 77.63(6F,s,2xCF_3) 100.8(2F,m,2xArF) 112.0(4F,m,2xCF_2CF_2I) 119.3(8F,m,4xCF_2)	22.82 (23.13)	0.64 (0.71)

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TABLE 1 (cont.)

Iodonium salt	Yield	Mp	^{1}H-NMR		^{19}F-NMR		Found (Calcd)	
12	61	117.5-119 [CH_2Cl_2-Pentane]	C	2.55(3H,s,CH_3) 2.68(3H,s,CH_3) 7.52(2H,d,J=9) 8.22(2H,d,J=9)	C	78.05(2F,q,J=8,CF_2I) 79.74(3F,t,J=8,CF_3) 119.3(2F,bs,CF_2)	27.41 (27.40)	2.15 (2.09)
13	66	128-130 [CH_2Cl_2-Pentane]	C	2.40(3H,s,CH_3) 7.24(5H,m,Ph) 7.54(2H,bd,J=8) 7.94(2H,d,J=8)	C	78.38(2F,q,J=8,CF_2I) 79.79(3F,t,J=8,CF_3) 119.3(2F,bs,CF_2)	35.21 (35.31)	2.17 (2.22)
14	88	91-5 [CH_2Cl_2-Hexane]	C	2.45(3H,s,CH_3) 7.31(2H,d,J=8.5) 7.95(2H,d,J=8.5)	C	71.76(2F,m,CF_2I) 78.92(3F,s,CF_3S) 79.74(3F,t,J=8,CF_3) 118.7(2F,m,CF_2)	—	—
15[g]	52	107-9 [$CHCl_3$]	C	2.42(3H,s,CH_3) 7.27(2H,d,J=8) 7.97(2H,d,J=8)	C	80.03(3F,t,J=10,CF_3) 83.45(2F,q,J=10,CF_2I) 120.1(2F,bs,CF_2)	27.08 (27.05)	1.77 (1.82)

[a] Solvents for crystallization or recrystallization are shown in parentheses.

[b] A=acetonitrile-d_3, B=acetone-d_6, C=chloroform-d, D=dimethylsulfoxide-d_6, E=methanol-d_4.

[c] ^{19}F-Chemical shifts are given upfield from internal trichlorofluoromethane.

[d][e] Trifluoroacetic acid in (d) and 1,1,2-trichlorotrifluoroethane in (e) were used as a solvent for the reaction of 2 or 9 with benzene or fluorobenzene and triflic acid. Yields from 2 or 9 are given.

[f] Elemental fluorine was used as an oxidizer. The figures are overall yields from 2-iodoheptafluoropropane.

[g] Monohydrate.

124.2 (2F, m, CF_2), 125.9 (2F, m, CF_2), IR (cm^{-1}, neat) 1475 (SO_2), 1240-1140 (CF), MS (m/e) 419 (M^+-OTf). Found: C, 19.12 %. Calcd for $C_9F_{20}O_3S$: C, 19.03%. 17; bp (bath temp.) 166-9° C/0.5 mmHg, ^1H NMR (δ, $CDCl_3$) 7.1-8.0 (m), ^{19}F NMR (ppm, $CDCl_3$, int. $CFCl_3$) 81.0 (3F, t, J=10 Hz, CF_3), 111.0 (2F, m, $ArCF_2$), 121.5 (8F, m, $5xCF_2$), 126.0 (2F, m, CF_2), IR (cm^{-1}, neat) 1598 (Ar), 1495 (Ar), 1240-1150 (CF), MS (m/e) 622 (M^+). Found: C, 27.05%; H, 0.64%. Calcd for $C_{14}H_4F_{17}I$: C, 27.03%; H, 0.65%.

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