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PRELIMINARY NOTE

SYNTHESIS OF (PERFLUOROALKYL)ARYLIODONIUM SULFONATES [1]

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SUMMARY

(Perfluoroalkyl)aryliodonium halides [2] and -tetrafluoroborates [3] were previously synthesized. We now wish to report the synthesis of several kinds of (perfluoroalkyl)aryliodonium sulfonates which are important as electrophilic perfluoroalkylating agents [4].

It was known that bis(trifluoroacetoxy)iodoperfluoroalkanes did not react with an inactive aromatic compound such as benzene at a reasonable reaction rate [2]. We found that, when bis(trifluoroacetoxy)iodoperfluoroalkanes were treated with benzene or fluorobenzene in 1,1,2-trichlorotrifluoroethane or trifluoroacetic acid at 0°C to room temperature in the presence of an equivalent amount of some sulfonic acids, the reaction took place smoothly to afford (perfluoroalkyl)-phenyl- or p-fluorophenylidonium sulfonates (1)-(5) in good yields (Scheme 1).

Scheme 1.

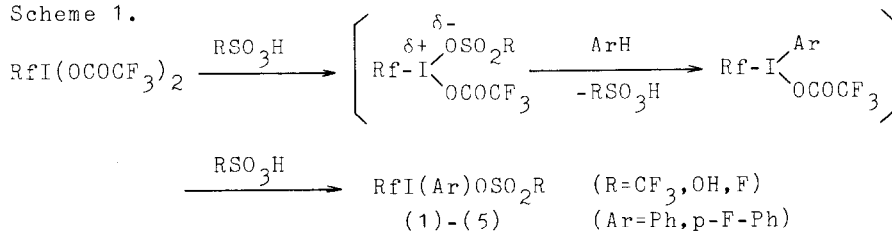


TABLE 1

Preparation of bis(trifluoroacetoxy)iodoperfluoroalkanes

$$\text{RfI} \xrightarrow{30\% \text{H}_2\text{O}_2 - (\text{CF}_3\text{CO})_2\text{O}} \text{RfI}(\text{OCOCF}_3)_2$$

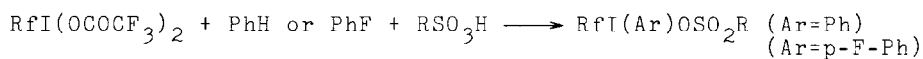
RfI(OCOCF ₃) ₂	Temp.(°C)	Time(h)	Yield(%)	Mp(°C)
Rf=n-C ₁₀ F ₂₁	0	24	86	83-88
n-C ₈ F ₁₇	0 → rt	1 → 20	98	70-74
n-C ₇ F ₁₅	0 → rt	1 → 15	98	68-70
n-C ₆ F ₁₃	0 → rt	2 → 15	97	60-62
n-C ₃ F ₇	0 → rt	1 → 17	98	57-61 (dec)
C ₂ F ₅	0	20	84	27-28 (dec)

It was reported that bis(trifluoroacetoxy)iodoperfluoroalkanes, the starting materials of the present reaction, were prepared from iodoperfluoroalkanes by using 75-85% hydrogen peroxide and trifluoroacetic anhydride [2]. However we found that they could be safely prepared in high yields by using commercial 30% hydrogen peroxide and an excess of trifluoroacetic anhydride in trifluoroacetic acid. Thus, the treatment of iodoperfluoroalkanes (36.6 mmol) with the solution prepared from 30% hydrogen peroxide (4.5 ml, H₂O₂ 44 mmol, H₂O 194 mmol) and trifluoroacetic anhydride (40.2 ml, 286 mmol) in trifluoroacetic acid (30 ml) at 0°C gave bis(trifluoroacetoxy)iodoperfluoroalkanes in high yields. The results and reaction conditions are shown in Table 1.

The typical experimental procedure for the synthesis of the (perfluoroalkyl)aryliodonium sulfonates is as follows: Trifluoromethanesulfonic acid (2.29 ml, 26 mmol) was added dropwise into a mixture of bis(trifluoroacetoxy)iodoheptadecafluoro-n-octane (20 g, 26 mmol) and benzene (2.77 ml, 31 mmol) in trifluoroacetic acid (50 ml) or 1,1,2-trichlorotrifluoroethane (50 ml) on an ice bath with stirring. The solution was stirred for 3 h at 0°C, gradually warmed to room temperature, and furthermore stirred for 12 h at room temperature. After the solvent was evaporated up, the residue was crystallized from acetonitrile or chloroform, or the mixture of them to give

TABLE 2

Synthesis of (perfluoroalkyl)phenyl- and p-fluoro-phenyliodonium sulfonates

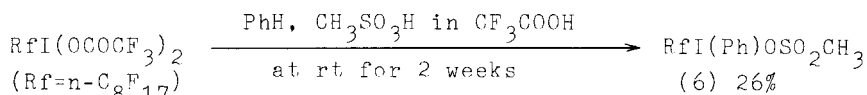


Product	Yield(%)	Mp(°C)	$^{19}\text{F-NMR}(\text{I-CF}_2)^{\text{a}}$
$\text{RfI}(\text{Ph})\text{OSO}_2\text{CF}_3$			
(1a) Rf=n-C ₁₀ F ₂₁	73 ^d	162-166	67.44(t,13) ^f
(1b) n-C ₈ F ₁₇	85 ^d , 77 ^e	149-151(dec)	67.79(t,12) ^f
(1c) n-C ₇ F ₁₅	75 ^d	148-150(dec)	67.78(t,13) ^f
(1d) n-C ₆ F ₁₃	82 ^d	120-123(dec)	68.12(t,12) ^f
(1e) n-C ₃ F ₇	75 ^d	124.5-127(dec)	70.65(m) ^g
(1f) C ₂ F ₅	67 ^d	116-120(dec)	76.03(q,4) ^g
$\text{RfI}(\text{Ph})\text{OSO}_3\text{H}$			
(2a) Rf=n-C ₁₀ F ₂₁ ^b	81 ^d	129-132	73.23(t,12) ^f
(2b) n-C ₈ F ₁₇ ^b	95 ^d	114-118	72.69(m) ^f
(2c) n-C ₇ F ₁₅ ^b	68 ^d	116-118	74.25(t,13) ^f
(2d) n-C ₆ F ₁₃	66 ^d	107-108	74.23(t,14) ^f
(2e) n-C ₃ F ₇	76 ^d	109-111	75.65(q,10) ^f
(2f) C ₂ F ₅	90 ^d	107-108	79.81(q,4) ^h
$\text{RfI}(\text{p-F-Ph})\text{OSO}_2\text{CF}_3$			
(3a) Rf=n-C ₁₀ F ₂₁	91 ^e	165-168	66.90(m) ^f
(3b) n-C ₈ F ₁₇	86 ^e	145-147	67.65(t,14) ^f
(3c) n-C ₆ F ₁₃	62 ^e	139-142	68.04(t,15) ^f
(3d) n-C ₃ F ₇	82 ^e	150-151(dec)	69.91(q,10) ^f
(4) n-C ₈ F ₁₇ I(p-F-Ph)OSO ₃ H	58 ^d	120-121	73.78(t,13) ^f
(5) n-C ₈ F ₁₇ I(Ph)OSO ₂ F ^c	70 ^e	113-116(dec)	72.8(m) ⁱ

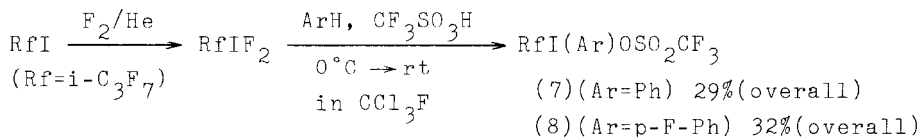
a) Chemical shifts are given in δ ppm upfield from internal CCl₃F. Values in parentheses are coupling constants (Hz).
 b) Monohydrate. c) The compound was hydrolyzed by moisture to give (2b) when recrystallized from acetonitrile. d) Trichlorotrifluoroethane was used as a reaction solvent. e) 1,1,2=Trichlorotrifluoroethane was used as a reaction solvent. f) In acetonitrile-d₃. g) In chloroform-d₁. h) In methanol-d₄. i) In acetone-d₆.

heptadecafluoro-n-octylphenyliodonium trifluoromethanesulfonate in a 85% yield. When 1,1,2-trichlorotrifluoroethane was used as a reaction solvent, clean crystals of the product could be obtained. Table 2 summarizes the results and some physical properties of the iodonium sulfonates (1)-(5).

The reaction of bis(trifluoroacetoxy)iodoperfluoroalkanes with benzene or fluorobenzene in the presence of strong sulfonic acids such as trifluoromethanesulfonic acid, fluorosulfonic acid, and sulfuric acid proceeded smoothly, while that with a weak acid such as methanesulfonic acid was slow and the yield of the product (6) was low.



On the other hand, heptafluoroisopropylaryliodonium sulfonates (7) and (8) could be isolated by direct fluorination [3 and 5] of heptafluoroisopropyl iodide in trichlorofluoromethane at -78°C followed by the treatment with benzene or fluorobenzene, and trifluoromethanesulfonic acid.



- 1 Presented in part at the 7th Symposium on Fluorine Chemistry of Japan, Okayama, Oct., 1981.
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