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PRELIMINARY NOTE

Syntheses of (1,1-Dihydroperfluoroalkyl)aryliodonium Triflates and Their Analogues

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SUMMARY

(1,1-Dihydroperfluoroalkyl)phenyl- and -p-fluorophenyliodonium triflates 2 and 3 were synthesized by the reaction of 1-bis(trifluoroacetoxy)iodo-1,1-dihydroperfluoroalkanes 1 with triflic acid and benzene or fluorobenzene in 1,1,2-trichlorotrifluoroethane. The use of fluorosulfonic acid and sulfuric acid instead of triflic acid afforded (1,1-dihydroperfluoroalkyl)phenyliodonium fluorosulfonate 4 and sulfate 5, respectively. Similarly, (1,1,ω-trihydroperfluoroalkyl)phenyliodonium triflate 7 and 1,1,5,5-tetrahydroperfluoropentane-1,5-bisphenyliodonium triflate 9 were synthesized.

INTRODUCTION

We have already synthesized a series of (perfluoroalkyl)phenyliodonium triflates [1] and their analogues [1,2] and found that they act as highly reactive electrophilic perfluoroalkylating [1b,3] or novel oxy-perfluoroalkylating agents [4]. In this connection, it is of great interest to study the synthesis and reactivity of (1,1-dihydroperfluoroalkyl)aryliodonium triflates where the trivalent iodine atom is separated from the electronegative perfluoroalkyl group by a methylene unit. The stability of (1,1,ω-trihydroperfluoro-pentyl)- or

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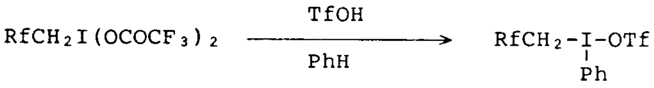
-heptyl)-*p*-tolyliodonium halides and 1,1,6,6-tetrahydroperfluorohexane-1,6-bis-*p*-tolyliodonium halides was shown to be low and only the bromides were isolated in pure form in low yields [5]. We have succeeded in synthesizing (1,1-dihydroperfluoroalkyl)phenyliodonium triflates 2 and their analogues 3, 4, 5, 7, and 9.

RESULTS AND DISCUSSION

1-Bis(trifluoroacetoxy)iodo-1,1-dihydroperfluoroalkanes 1 were prepared quantitatively by treating 1-iodo-1,1-dihydroperfluoroalkanes with trifluoroperacetic acid at 0 °C to room temperature for 1 day, according to Yagupol'skii's procedure [5] Trifluoroperacetic acid could be smoothly prepared *in situ* by adding commercially available 60% hydrogen peroxide to trifluoroacetic anhydride in the presence of a catalytic amount of trifluoroacetic acid at 0 °C. Alkanes 1 were isolated by evaporation of the solvent using a vacuum pump at room temperature, and used without further purification for the next reaction.



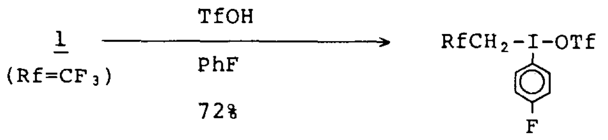
$$\mathrm{RfCH_2I(OCOCF_3)_2} \xrightarrow[\mathrm{PhH}]{\mathrm{TfOH}} \mathrm{RfCH_2\text{-}\underset{\displaystyle Ph}{\underset{|}{I}}\text{-}OTf}$$

1

2a (Rf=CF_3, 88%)
2b (Rf=n-C_3F_7, 70%)
2c (Rf=n-C_7F_{15}, 89%)

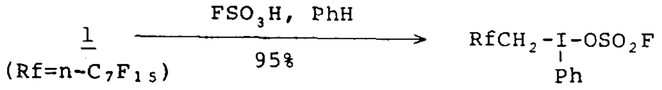
Alkanes 1 were allowed to react with benzene (1.2 molar equiv.) and triflic acid (1 molar equiv.) in 1,1,2-trichlorotrifluoroethane at 0 °C for 1 day. After complete evaporation of the solvent and liberated trifluoroacetic acid using first an aspirator and finally a vacuum pump without heating, the resulting crystals of the triflates 2 were washed with chloroform and collected. A series of (1,1-dihydroperfluoroalkyl)-phenyliodonium triflates 2a, 2b, and 2c were synthesized in good yields.

The use of fluorobenzene instead of benzene gave *p*-fluorophenyliodonium triflate 3 in a good yield.



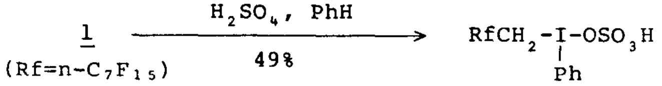
3

Similarly, 1 reacted with benzene and fluorosulfonic acid to give the corresponding iodonium fluorosulfonate 4 in a high yield. The reaction with benzene and sulfuric acid proceeded smoothly using a mixture of 1,1,2-trichlorotrifluoroethane - trifluoroacetic acid (9.6:1) as a solvent to afford the sulfate 5.



$$\underset{(Rf=n\text{-}C_7F_{15})}{\mathbf{1}} \xrightarrow[95\%]{FSO_3H,\ PhH} RfCH_2\text{-}\underset{\underset{Ph}{|}}{I}\text{-}OSO_2F$$

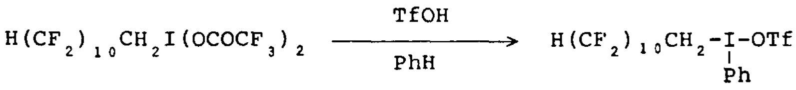
4



$$\underset{(Rf=n\text{-}C_7F_{15})}{\mathbf{1}} \xrightarrow[49\%]{H_2SO_4,\ PhH} RfCH_2\text{-}\underset{\underset{Ph}{|}}{I}\text{-}OSO_3H$$

5

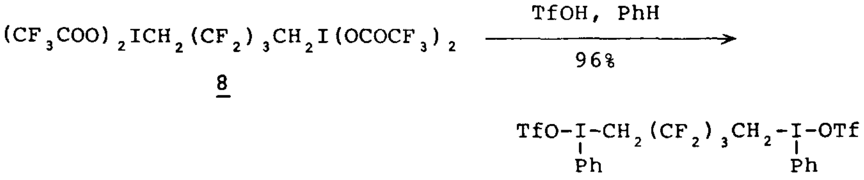
1,1,ω-Trihydroperfluoroalkyl analogue 7 was synthesized by the same method as for 2 except for the use of a mixture of 1,1,2-trichlorotrifluoroethane - trifluoroacetic acid (5:3) as a solvent.



$$H(CF_2)_{10}CH_2I(OCOCF_3)_2 \xrightarrow[PhH]{TfOH} H(CF_2)_{10}CH_2\text{-}\underset{\underset{Ph}{|}}{I}\text{-}OTf$$

6 85% 7

Furthermore, bisiodonium triflate 9 could be synthesized in a high yield by treating diiodide 8 with benzene (2.4 molar equiv.) and triflic acid (2 molar equiv.) in 1,1,2-trichlorotrifluoroethane at 0 °C for 4 days.



$$(CF_3COO)_2ICH_2(CF_2)_3CH_2I(OCOCF_3)_2 \xrightarrow[96\%]{TfOH,\ PhH} TfO\text{-}\underset{\underset{Ph}{|}}{I}\text{-}CH_2(CF_2)_3CH_2\text{-}\underset{\underset{Ph}{|}}{I}\text{-}OTf$$

8

9

TABLE

Some properties of (1,1-dihydroperfluoroalkyl)aryliodonium triflates and their analogues

Compound$^{a)}$	M.p. (°C)	^{1}H-NMR$^{b)}$ (δ, in CD_3CN)	^{19}F-NMR$^{c)d)}$ (in CD_3CN)
2a	88-89^{f} (Decomp)	4.80(q, J=10Hz, 2H) 7.40-7.90(m, 3H) 8.00-8.30(m, 2H)	61.5(t, J=10Hz, 3F) 77.9(s, 3F)
2b	133 (Decomp)	4.80(t, J=18Hz, 2H) 7.60-7.95(m, 3H) 8.10-8.30(m, 2H)	78.1(s, 3F), 80.1(t, J=15 Hz, 3F), 104.4(m, 2F), 125.4(s, 2F)
2c	142-143^{g} (Decomp)	4.83(t, J=18Hz, 2H) 7.40-7.80(m, 3H) 8.05-8.25(m, 2H)	78.0(s, 3F), 80.6(s, 3F), 102.8(m, 2F), 120.8(m, 8F), 124.9 (m, 2F)
3	103-104^{f} (Decomp)	4.77(q, J=10Hz, 2H) 7.33(dd, J=9, 9Hz, 2H), 8.20(dd, J=9, 4.5Hz, 2H)	61.1(t, J=10Hz, 3F) 77.5(s, 3F), 102.8 (bs, 1F)
4	107 (Decomp)	4.83(t, J=18Hz, 2H) 7.40-7.90(m, 3H) 8.10-8.30(m, 2H)	-38.5(s, 1F, SO_2F) 80.3(t, J=10Hz, 3F) 103.2(m, 2F), 120.8 (m, 6F), 122.0(m, 2F) 125.5(m, 2F)
5^{e}	90-91 (Decomp)	5.16(t, J=18Hz, 2H) 7.40-7.80(m, 3H) 8.20-8.40(m, 2H)	80.0(t, J=10Hz, 3F) 120.5(m, 2F), 121,6 (m, 4F), 122.2(m, 2F) 122.8(m, 2F), 125.6 (m, 2F)
7	157-158	4.92(t, J=18Hz, 2H) 6.52(tt, J=51.0, 4.8Hz, 1H), 7.5-8.32(m, 5H)	78.1(s, 3F), 103.1 (bs, 2F), 120.2-123.1 (m, 14F), 128.7(bs, 2F), 137.8(d, J=51.0 Hz, 2F)
9	113-114 (Decomp)	4.80(t, J=18Hz, 4H) 7.40-7.90(m, 6H) 8.00-8.20(m, 4H)	78.0(s, 6F), 102.6 (m, 4F), 120.9(s, 2F)

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[a] The elemental analyses of all the products were in good agreement with the calculated values. [b] Acetone-d_6 was used for 5 as a solvent. [c] Chemical shifts are given in δ ppm upfield from internal $CFCl_3$. [d] Dimethyl sulfoxide-d_6 was used for 5 as a solvent. [e] Monohydrate. [f] Recrystallized from acetonitrile-diethyl ether at room temperature. [g] Recrystallized from hot acetonitrile.

Some properties of (1,1-dihydroperfluoroalkyl)aryliodonium triflates and their analogues are shown in the Table.

Thermolysis of 2c at 140 - 145 °C produced 1,1-dihydroperfluoroalkyl triflate and iodobenzene in high yields.

$$2c \xrightarrow{\Delta} RfCH_2OTf \quad + \quad PhI$$

$$\qquad\qquad 90\% \qquad\qquad 89\%$$

The reactivity of these triflates as highly reactive electrophilic 1,1-dihydroperfluoroalkylating agents will be reported elsewhere.

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