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SYNTHESIS OF DOUBLE FITS REAGENTS

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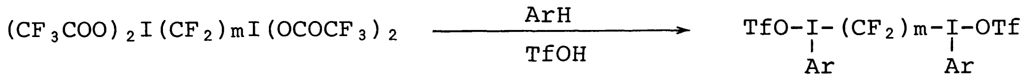
Perfluoroalkylene bisaryliodonium triflates(D-FITS) were synthesized as useful agents for introduction of perfluoroalkylene groups.

We have originated FITS reagents, RfI(Ph)OTf,1) and demonstrated that FITS serve as very useful electrophilic perfluoroalkylating2) or novel oxy-perfluoroalkylating agents3) because of the strongest leaving ability of trifluoromethanesulfonyloxy group. On the other hand, only a few methods have been reported for the preparation of perfluoroalkylene compounds.4) We now wish to describe the synthesis of double FITS, perfluoroalkylene bisaryliodonium triflates (D-FITS), as effective reagents for the introduction of perfluoroalkylene groups. Quite recently, at the end of this work of ours, Yagupol'skii et al. reported the synthesis of perfluoroalkylene bisaryliodonium trifluoroacetates or tetrafluoroborates.5)

α,ω-Bis[di(trifluoroacetoxy)iodo]perfluoroalkanes 1a,b were prepared almost quantitatively by treatment of the corresponding α,ω-diiodoperfluoroalkanes with trifluoroperacetic acid at 0 °C to room temperature for 1 d. 1a reacted with benzene (2.4 molar equiv.) and triflic acid (2 molar equiv.) in 1,1,2-trichlorotrifluoroethane at 0 °C to room temperature for 3 d. After evaporation of the solvent, the residue was crystallized from ethyl acetate to give hexafluoropropane-1,3-bisphenyliodonium triflate 2a6) as white crystals in 49% yield. Similarly,



$$(CF_3COO)_2I(CF_2)_mI(OCOCF_3)_2 \xrightarrow[\text{TfOH}]{\text{ArH}} \text{TfO-}\underset{\text{Ar}}{\text{I}}\text{-}(CF_2)_m\text{-}\underset{\text{Ar}}{\text{I}}\text{-OTf}$$

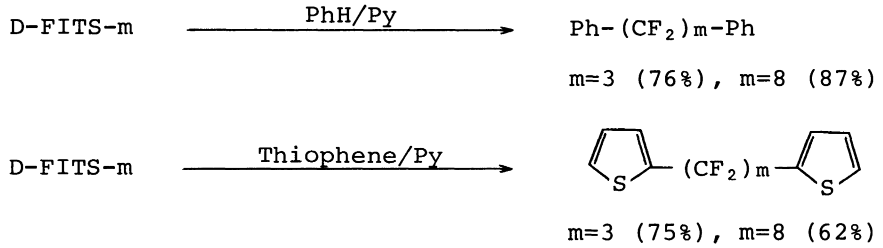
1a (m=3)
1b (m=8)

2a: D-FITS-3 (m=3, Ar=Ph)
2b: D-FITS-8 (m=8, Ar=Ph)
2b': D-FITS(F)-8 (m=8, Ar=p-F-Ph)

1b afforded hexadecafluorooctane-1,8-bisphenyliodonium triflate 2b[6] in 62% yield. On the other hand, 1b was treated with fluorobenzene and triflic acid in trifluoroacetic acid to give hexadecafluorooctane-1,8-bis-*p*-fluorophenyliodonium triflate 2b'[6] as white crystals in 55% yield.

These iodonium triflates are nonhygroscopic crystals which are stable at room temperature. The structures of the triflates were determined from analyses of NMR and IR spectra, and elemental analyses. The ^{19}F NMR spectra showed the characteristic absorption peaks at about 70 ppm upfield from internal $CFCl_3$ peak, which were assigned to difluoromethylene groups bonding to the positively polarized iodine atoms.[6]

Double FITS were expected to be highly reactive reagents for introducing perfluoroalkylene groups. Thus, D-FITS-3 and -8 were heated under reflux in benzene for 2 h in the presence of pyridine (2.2 molar equiv.) to afford α,ω-diphenylperfluoropropane and -perfluorooctane in 76% and 87% isolated yields, respectively. Similarly, D-FITS-3 and -8 reacted with thiophene at room temperature to 60 °C for 2 h to afford α,ω-(2,2'-dithienyl)perfluoropropane and -perfluorooctane in 75% and 62% yields, respectively.



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3) T.Umemoto, Y.Kuriu, and S.Nakayama, Tetrahedron Lett., 23, 4101 (1982).
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6) 2a: Decomp 163.5-163.8 °C, ^{19}F NMR (acetone-d_6, int. $CFCl_3$) 70.73 ppm (bs, CF_2I). 2b: Decomp 138.9-139.1 °C, ^{19}F NMR (acetonitrile-d_3) 68.10 (bs, CF_2I). 2b': Decomp 193.5-193.7 °C, ^{19}F NMR (acetone-d_6) 70.80 (bs, CF_2I). Elemental analyses were consistent with calculated values.

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