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Synthesis, Properties, and Reactivity of (1*H*,1*H*-Perfluoroalkyl)- and (1*H*-Perfluoro-1-alkenyl)aryliodonium Triflates and Their Analogs

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(1*H*,1*H*-Perfluoroalkyl)phenyl- and -(*p*-fluorophenyl)iodonium triflates, fluorosulfate, sulfate (**3**)—(**7**) were synthesized in good yields by the oxidation of 1-iodo-1*H*,1*H*-perfluoroalkanes ($RfCH_2I$) with trifluoroperacetic acid followed by treatment with triflic acid and benzene or fluorobenzene. (1*H*,1*H*,5*H*,5*H*-Perfluoropentane-1,5-diyl)bisphenylbisiodonium triflate was synthesized similarly. (*trans*-1*H*-Perfluoro-1-alkenyl)phenyliodonium triflates (**11**) were synthesized by dehydrofluorination of **3** with a base in good yields. Thermolysis of **3** produced 1*H*,1*H*-perfluoroalkyl triflate and iodobenzene, while **11** gave (*Z*)-1-iodo-1*H*-perfluoro-1-alkene and phenyl triflate. The thermolysis experiment, including (perfluoroalkyl)phenyliodonium triflate (**17**), demonstrated that the C–I bond strength of the trivalent iodine compounds increased in the order of $RfCH_2$–I, Rf–I<Ph–I<RfCF=CH–I. The ionic mechanism containing $RfCH_2^+$, Ph^+, and Rf^+ for the thermal decomposition of **3**, **11**, and **17**, respectively, was proposed. The reactivities of **3** and **11** to such nucleophiles as phenoxide, alkoxide, and alkanethiolate anions were studied and compared with that of **17**. Remarkable changes in the reactivity were found depending on the nature of the fluoro-alkyl and -alkenyl groups. The reaction of **11** with the oxide anions yielded (2-phenoxy- and -alkoxy-1*H*-perfluoro-1-alkenyl)phenyliodonium triflates.

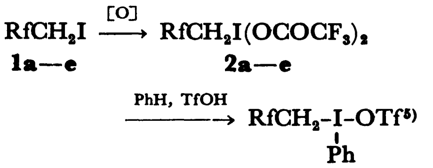
Hypervalent iodine compounds have been of increasing importance from the viewpoint of the consideration of their bonding and structures, or of the organic synthesis as useful reagents or reactive intermediates.[1] Many kinds of hypervalent iodine compounds were synthesized and their properties or reactivities were studied.[1] The hypervalent iodines carrying fluoro-alkyl or -alkenyl groups have been expected to have interesting properties because of the high electronegativity of the fluoro groups.[2]

We have already synthesized a series of (perfluoroalkyl)aryliodonium triflates and their analogs, and have demonstrated that they act as reactive electrophilic perfluoroalkylating agents.[3] In this connection, it is of great interest to study the syntheses and reactivities of (1*H*,1*H*-perfluoroalkyl)- and (polyfluoroalkenyl)-aryliodonium salts where the trivalent iodine atom is separated from the electronegative perfluoroalkyl group by a methylene and a vinyl unit, respectively. It was reported that (1*H*,1*H*,ω*H*-perfluoropentyl or heptyl)-*p*-tolyliodonium halides and (1*H*,1*H*,6*H*,6*H*-perfluorohaxane-1,6-diyl)bis(*p*-tolyl)bisiodonium halides were unstable and only the bromides could be isolated in pure form in low yields.[4] The hypervalent iodines possessing fluorinated alkenyl groups have never been synthesized.

This paper describes the syntheses, properties, and reactivities of a series of (1*H*,1*H*-perfluoroalkyl)- and (1*H*-perfluoro-1-alkenyl)aryliodonium triflates and their analogs.

Results and Discussion

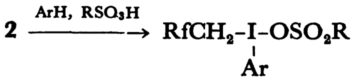
1-[Bis(trifluoroacetoxy)iodo]-1*H*,1*H*-perfluoroalkanes **2** were prepared almost quantitatively by treating 1-iodo-1*H*,1*H*-perfluoroalkanes **1** with trifluoroperacetic acid by the modified Yagupol'skii's procedure.[4] **2a**—**e** were allowed to react with benzene and triflic acid in 1,1,2-trichloro-1,2,2-trifluoroethane at 0 °C for 1 day to give (1*H*,1*H*-perfluoroalkyl)phenyliodonium triflates **3a**—**e** with different carbon numbers of the perfluoroalkyl (Rf) groups in good yields. ^1H NMR spectra of **3** exhibited the characteristic peaks of methylene groups which appeared at δ ca. 4.8 downfield compared to that of **1** (δ ca. 3.7), as triplets or quartets due to coupling with the vicinal fluorine atoms.



$$\underset{\mathbf{1a-e}}{RfCH_2I} \xrightarrow{[O]} \underset{\mathbf{2a-e}}{RfCH_2I(OCOCF_3)_2} \xrightarrow{PhH,\ TfOH} RfCH_2\text{-}\underset{\displaystyle Ph}{I}\text{-}OTf^{5)} \qquad (1)$$

3a ($Rf = CF_3$, 88%)
3b ($Rf = C_2F_5$, 72%)
3c ($Rf = n\text{-}C_3F_7$, 70%)
3d ($Rf = i\text{-}C_3F_7$, 77%)
3e ($Rf = n\text{-}C_7F_{15}$, 89%)

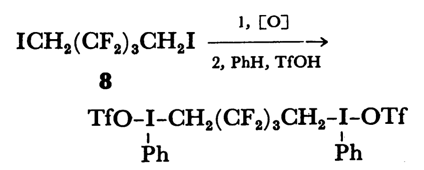
The use of fluorobenzene instead of benzene gave *p*-fluorophenyl isomer **4** exclusively. Fluorosulfuric acid and sulfuric acid, instead of triflic acid, gave fluorosulfate **5** and sulfate **6**, respectively. Similarly, 1-iodo-1*H*,1*H*, ω*H*-perfluorododecane gave **7**.



$$\mathbf{2} \xrightarrow{ArH,\ RSO_3H} RfCH_2\text{-}\underset{\displaystyle Ar}{I}\text{-}OSO_2R \qquad (2)$$

4 ($Ar = p\text{-}FC_6H_4$, $R = CF_3$, $Rf = CF_3$, 72%)
5 ($Ar = Ph$, $R = F$, $Rf = n\text{-}C_7F_{15}$, 95%)
6 ($Ar = Ph$, $R = OH$, $Rf = n\text{-}C_7F_{15}$, 49%)
7 ($Ar = Ph$, $R = CF_3$, $Rf = (CF_2)_{10}H$, 85%)

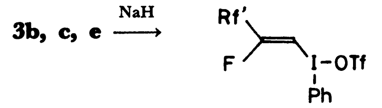
Bis(iodonium) triflate **9** was similarly synthesized from diiodide **8** in high yield.



$$\underset{\mathbf{8}}{ICH_2(CF_2)_3CH_2I} \xrightarrow[2,\ PhH,\ TfOH]{1,\ [O]} TfO\text{-}\underset{Ph}{\underset{|}{I}}\text{-}CH_2(CF_2)_3CH_2\text{-}\underset{Ph}{\underset{|}{I}}\text{-}OTf \quad (3)$$

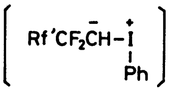
9 96%

We found that triflates **3b**, **3c**, and **3e** underwent easy dehydrofluorination by treatment with sodium hydride in acetonitrile at 0 °C to give (*trans*-1*H*-perfluoro-1-alkenyl)phenyliodonium triflates **11b**, **11c**, and **11e** in good yields. The treatment of **3e** with a weak base, 2,4,6-collidine, at room temperature gave **11e** in a 40% yield. This indicates that the methylene protons of **3** are considerably acidic. **11** were assigned as trans isomers from the coupling constant (33 Hz) between the olefinic proton and the fluorine atom. The NMR resonance (δ ca. 8.2) of the olefinic protons of **11** appeared at a very low magnetic field. The corresponding proton of iodide **15** appeared at δ 6.63. On the other hand, it is interesting that **3a** and **3d** did not afford the expected (2,2-difluorovinyl)- and (2-trifluoromethyl-3,3,3-trifluoro-1-propenyl)-phenyliodonium triflates, **11a** and **11d**, respectively, by the same procedure, but, rather, the decomposition of **3a** and **3d** occurred. We isolated sodium triflate in the latter case. This might be due to the instability or high reactivity of **11a** and **11d** compared to **11b**, **11c**, or **11e**. It is known that the 2,2-difluorovinyl moiety is sensitive to a nucleophilic attack at the C–F carbon site, while the 2,2-bis(trifluormethyl)vinyl moiety is sensitive at the C-1 site.[6)]



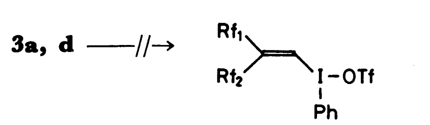
(4)

11b (Rf′ = CF_3, 80%)
11c (Rf′ = C_2F_5, 86%)
11e (Rf′ = n-C_6F_{13}, 87%)



$$\left[Rf'CF_2\overset{-}{C}H\text{-}\underset{Ph}{\underset{|}{\overset{+}{I}}}\right]$$

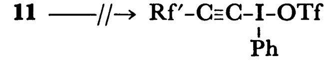
10



(5)

11a ($Rf_1 = Rf_2 = F$)
11d ($Rf_1 = Rf_2 = CF_3$)

We failed in synthesizing the fluoroalkynyl analogs **12** from **11** by the action of sodium hydride in acetonitrile. The decomposition of **11** occurred and sodium triflate was isolated.



$$\mathbf{11} \xrightarrow{NaH} \!\!\!\!\!/\!/\ Rf'\text{-}C{\equiv}C\text{-}\underset{Ph}{\underset{|}{I}}\text{-}OTf \quad (6)$$

12

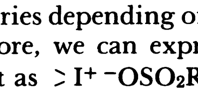
The dehydrofluorination of **3** should occur via interesting halogen ylides **10**. An attempt to react the intermediate **10e** with such an electrophile as benzaldehyde was unsuccessful.

Salts **3** are apparently nonhygroscopic, stable crystals; the stability increases as the chain of a Rf group is lengthened. In general, they are soluble in acetonitrile and almost insoluble in diethyl ether, tetrahydrofuran, or haloalkanes such as dichloromethane. **3e** is satisfactorily stable, but **3a** decomposed very slowly and almost completely in about 3 weeks at room temperature (ca. 25—31 °C). **3a** is stable enough to be handled at room temperature and can be stored for long time in a refrigerator or a freezer. *p*-Fluorophenyl analog **4** is more stable than **3a**, judging from their decomposition points. **4** decomposed completely in 2—3 days in a moist acetonitrile-d_3 solution at room temperature.

Fluoroalkenyl analogs **11** are apparently nonhygroscopic crystals and have a high stability compared to **3**. While **3** decomposed at their melting points, **11** melted without decomposition near the decomposition points of **3**.

Salts **3** appeared to us to be less stable than (perfluoroalkyl)phenyliodonium triflates **17**. This suggests that the stability of the trivalent iodine compounds decreases as the electronegativity of the alkyl groups decreases, and makes it very clear to us that nobody can succeed in the isolation of the hydrocarbon analogs,[1a,7)] alkyl(aryl)iodonium salts, because of the instability arising from the low electronegativity of the hydrocarbon alkyl group.

The I···O bonds of **3**—**7**, **9**, and **11** appear to be highly ionic, but not completely polarized, on the basis of the fact that the ^{19}F NMR analysis of analogous iodine compounds **17** and their derivatives has demonstrated that the I···OSO_2R' bonds are not completely polarized and that the degree of polarization varies depending on the electronegativity of R′.[3a)] Therefore, we can express the bonds as >I–OSO_2R', but not as > I^+ $^-OSO_2R'$.

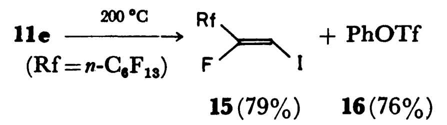


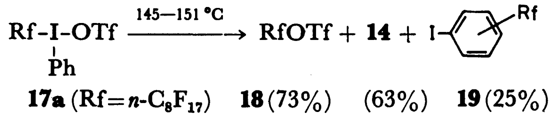
$$R\text{-}\underset{Ph}{\underset{|}{\overset{\delta+}{I}}}\cdots\cdots\overset{\delta-}{O}SO_2R'$$

(R = Rf, $RfCH_2$, RfCF = CH)

The thermolysis of **3** and **11** gave very interesting results: **3e** decomposed at 140—145 °C to produce 1*H*,1*H*-perfluroalkyl triflate **13** and iodobenzene **14** in good yields, while **11e** remained intact at 140 °C and decomposed at 200 °C to give (*Z*)-1-iodo-1*H*-perfluoro-1-alkene **15** and phenyl triflate **16** in good yields. As reported previously, the thermolysis of **17a**

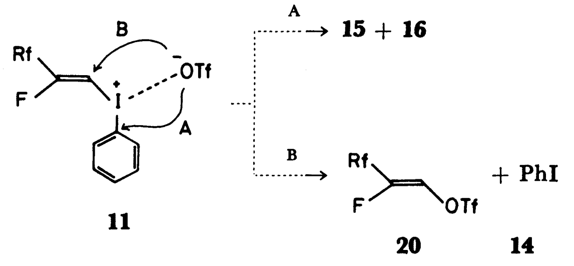
$$\underset{(\mathrm{Rf}=n\text{-}\mathrm{C_7F_{15}})}{\mathbf{3e}} \xrightarrow{140\text{—}145\,^{\circ}\mathrm{C}} \underset{\mathbf{13}(90\%)}{\mathrm{RfCH_2OTf}} + \underset{\mathbf{14}(89\%)}{\mathrm{PhI}} \quad (7)$$


11e (Rf=n-C_6F_{13}) 200 °C **15**(79%) + PhOTf **16**(76%) (8)


17a (Rf=n-C_8F_{17}) 145—151 °C RfOTf **18**(73%) + **14** (63%) + **19**(25%) (9)

at 145—151 °C produced perfluorooctyl triflate **18**, **14**, and (perfluorooctyl)iodobenzene **19**.[3a] It is worth noting that the cleavage of CH_2-I and Rf-I bonds occurred in **3** and **17**, while the Ph-I bond was broken in **11**. **11** and **3** or **17** differ much from each other regarding the fission pattern. The above results clearly demonstrate that the C-I bond strength increases in the order of $RfCH_2$-I, Rf-I<Ph-I<RfCF=CH-I. It is noticeable that the C-I bond of RCF=CH-I is much stronger than that of Ph-I. Furthermore, the thermolysis of **11** is in sharp contrast to that of a hydrocarbon analog, vinyl(phenyl)iodonium bromide, which revealed that the bond fission between the vinyl carbon and the iodine atom occurred exclusively.[1b,8] The vinyl(phenyl)iodonium salts have been shown to be useful vinylating agents.[1b,9] They are based on a weak bonding between the vinyl carbon and the iodine atom compared to the Ph-I bond. The strong bonding between the fluorinated vinyl carbon and the iodine atom of **11** would be due to the high electronegativity of a Rf group and a fluorine atom binding to the vinyl moiety.

The cleavage of the bond between the sp^3 carbon and the iodine of **3** probably proceeds by an ionic mechanism, which is in agreement with the fact that **3** acts as a very useful source of a $RfCH_2$ cation.[10] **15** and **16** should also be formed from **11e** by the ionic mechanism, since the free-radical mechanism containing the homolytic cleavage of the C-I bond should require the improbable formation of the extremely high-energy trifluoromethanesulfonyloxyl radical for the production of **16**. The following two routes for **15** and **16** can be thought as the possible ionic mechanism: (1) The addition of TfO^- to a phenyl nucleus followed by the elimination of the positive iodine atom, and (2) the combination of a phenyl cation generated and TfO^-. Since TfO^- is one of the strongest leaving groups, the nucleophilicity is extremely low.[11] Furthermore, if the mechanism of (1) is real, why doesn't process B that gives **20** and **14** occur rather than A which gives **15** and **16**? The reason is because a Rf group has a strong stabilizing effect on the intermediate anion at the α-position. Neither **20** nor **14** was produced. Accordingly, we


11 A → **15** + **16** B → **20** + PhI **14** (10)

$$\mathbf{11} \longrightarrow \underset{\mathbf{15}}{\mathrm{RfCF{=}CHI}} + \underset{\displaystyle\downarrow \atop \mathrm{PhOTf}\ \ \mathbf{16}}{\underbrace{[\mathrm{Ph^+}] + {}^{-}\mathrm{OTf}}} \quad (11)$$

propose the phenyl cation mechanism (2) (Eq. 11). The relatively easy formation of a phenyl cation compared to the fluorinated vinyl cation is surprising in view of the fact that a phenyl cation is much less stable than a nonfluorinated vinyl cation.[12] It would reflect the strong electronegative effect of a Rf group and a fluorine atom bonding to the vinyl moiety.

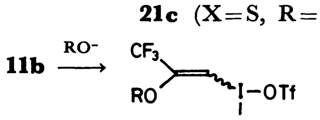
18 and **14** would also be formed from **17** by an ionic mechanism containing a Rf cation. However, it is unclear by which mechanism **19** was formed, ionic or free radical. Since such a compound as **19** was not produced in the case of **3**, the formation of **19** from **17** appears to be closely related to the difference in the electronegativity between Rf and $RfCH_2$ or in the easiness in the formation between their cations, Rf^+ and $RfCH_2^+$. Rf is more electronegative than $RfCH_2$[2] and, thus, Rf^+ is more difficult to generate than $RfCH_2^+$.

The mass spectra of **3** and **11** well reflected the strength of the bonds around the trivalent iodine atoms. All of **3** showed neither peaks corresponding to $[RfCH_2(Ph)I]^+$ nor ones corresponding to $[RfCH_2I]^+$, but base peaks or strong peaks of $[PhI]^+$. The peaks of $[RfCH_2OTf]^+$ were not observed in **3** and **7**. **5** and **6** showed small peaks of $[RfCH_2I]^+$ in addition to the base peak of $[PhI]^+$. On the other hand, all of **11** showed the strong peaks of $[RfCF{=}CHI]^+$ and $[PhOTf]^+$, and **11c** and **11e** exhibited the small peaks of $[RfCF{=}CHI(Ph)]^+$. The mass spectrum of **17** (Rf=n-C_3F_7) showed a strong peak of $[PhI]^+$ and a small peak of $[RfI(Ph)]^+$, but no peak of $[RfI]^+$. In this way, the fission pattern of the iodonium salts in the mass spectra is closely related to the bond strength order mentioned before. Since the mass spectra were measured at 100 °C, the spectrum of **3a** with a decomposition point of less than 100 °C may almost or partly consist of the decomposition products.

As expected from the thermolysis experiment, **3**, **11**, and **17** are very different from each other regarding reactivity. As reported, **3** reacted with phenoxide, alkoxide, and alkanethiolate anions to give 1*H*,1*H*-perfluoroalkyl phenyl ether **21a**, alkyl ether **21b**, and alkyl sulfide **21c** in good yields, respectively,[10] indicating an easy heterolytic fission of the C–I bonds of **3**. However, the treatment of **11b** with phenoxide and 2-phenylethoxide anions gave [[2-phenoxy- and 2-phenylethoxy-2-trifluoromethyl]vinyl]phenyliodonium triflates, **22** and **23**, in 42 and 32% yields, respectively. This should be due to a strong C–I bonding around the iodine atom of **11**. **22** was one isomer and **23** was a 12:88 mixture of two isomers. The structures could not be determined. On the other hand, it is interesting that **11b** reacted with an arenethiolate anion to afford monosulfide **24** and disulfide **25** in 16 and 32% yields, respectively, as a mixture of each two structural isomers. Although the detailed reaction mechanism is unclear, the difference between the oxide and the thiolate anions may be attributed to the high nucleophilicity of the thiolate anion since **11** has a double bond activated with two leaving groups, a fluorine atom and the polarized iodine atom.

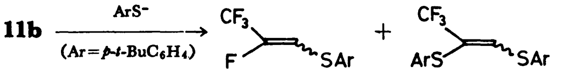
$$\mathbf{3} \xrightarrow{RX^-} RXCH_2Rf \qquad (12)$$

21a (X=O, R=Ph)
21b (X=O, R=CH_2CH_2Ph)
21c (X=S, R=n-$C_{12}H_{25}$)



(13)

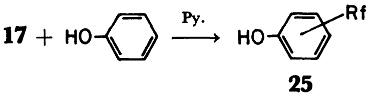
22 (42%, R=Ph)
23 (32%, R=CH_2CH_2Ph)



(14)

24 (16%, E/Z=1/4) **25** (32%, E/Z or Z/E=1/6)

3 are quite different from **17** in their reactivities. The treatment of **17** with an alkoxide produced no perfluoroalkyl ether, but a decomposition of **17** occurred.[3b] However, **17** reacted with arenethiols and alkanethiols in the presence of a base in dichloromethane to give perfluoroalkyl aryl and alkyl sulfides in good yields.[3b,13] **17** smoothly reacted with phenol in the presence of a base to afford a mixture of *o*-, *m*-, and *p*-Rf-phenyls **25** in a 55% yield with a ratio of 4.1 : 1 : 4.6, but not an ether, RfOPh[3b,14] (Eq. 15). With phenols having bulky substituents, **17** gave the perfluoroalkyl ethers along with the *C*-perfluoroalkylated phenols.[15] As mentioned above, **3** reacted only at the oxygen site of the phenoxide anion, but **3** reacted with the anion of phenol having an electron-donating substituent to give a small amount of *C*-RfCH2-phenol in addition to *O*-RfCH2-phenol.[16] Whereas **3** reacted with aniline derivatives at the nitrogen sites to give *N*-RfCH2-anilines or *N*-RfCH2-anilinium triflates,[10] **17** underwent a displacement at the aromatic ring to give a mixture of *o*- and *p*-Rf–aniline derivatives.[3b,14] **17** showed a higher reactivity than **3** as follows: **3** did not react with alkenes such as styrene and butadiene, while **17** reacted smoothly with them to give Rf-alkenes in good yields, and **17** reacted much more smoothly with aromatic compounds than **3**.[3b,10,14]



(15)

25

As a whole, the reaction pattern of **3**, **11**, and **17** agrees with the bond strength order mentioned before. Namely, RfCH2–I and Rf–I bonds of **3** and **17** are easily broken and the cleavage of the corresponding bonds of **11** is difficult. The above results also reveal that the pattern depends not only on the nature of the iodine compounds but also on the reactants. The remarkable difference between **3** and **17** might finally be attributed to the easy formation of $RfCH_2^+$ compared to Rf^+ cations, or to the high electron deficiency at the iodine sites of **17** due to the high electronegativity of the Rf groups, compared to that of **3**.

The predominant fluoroalkylation of **3** at the O- and N-sites of phenols and anilines and the preferential reaction of **17** at the C-sites may suggest that, while **3** could be directly attacked by nucleophiles at highly positively polarized CH2 carbon sites, the reactions of **17** might be initiated preferably by a one-electron transfer[17] from the nucleophiles to the iodine sites, resulting in the homolytic fission of Rf–I bonds, because of the difficulty in the formation of Rf^+ species.

In conclusion, the presented results show that the properties and reactivity of the trivalent iodine compounds vary to a remarkable degree depending on the static or dynamic properties of the fluoro-alkyl or -alkenyl groups bonding to the iodine atoms.

Experimental

General. Melting points were uncorrected. ^1H NMR spectra were recorded with a Varian XL-100 NMR spectrometer, a Varian EM 390 NMR spectrometer, or a Bruker AM-400 NMR spectrometer with tetramethylsilane as an internal standard. ^{19}F NMR spectra were measured with a Varian XL-100 NMR spectrometer or a Hitachi R-20B NMR spectrometer. ^{19}F NMR chemical shifts were reported in ppm upfield from trichlorofluoromethane as an internal standard. IR spectra were measured on a Jasco A-202 diffraction grating infrared spectrometer. Mass spectra were recorded on a Hitachi RMU-6MG spectrometer at 70 eV and 100 °C.

Materials. 1,1,1-Trifluoro-2-iodoethane is commercially available. Other 1-iodo-1*H*,1*H*-perfluoroalkanes and 1-iodo-1*H*,1*H*,ω*H*-perfluorododecane were prepared from 1*H*,1*H*- and 1*H*,1*H*,ω*H*-perfluoro-1-alkanols, respectively, according to the reported method.[18] Diiodide **8** was similarly prepared from the corresponding diol. 2,3,3,3-Tetrafluoro-2-trifluoromethyl-1-propanol was prepared by the reduction with lithium aluminium hydride from perfluoroisobutyric acid which was prepared from 2-iodoperfluoropropane according to the reported method.[19]

(Polyfluoroalkyl)aryliodonium salts 3, 4, 5, 6, and 7. General Procedure; Into a mixture of 82 ml of trifluoroacetic anhydride and 0.7 ml of trifluoroacetic acid was dropwise added 6.45 ml of 60% aq hydrogen peroxide with stirring under cooling on an ice bath. After stirring for additional 10 min, 1-iodopolyfluoroalkane (143 mmol) was added into the mixture. The reaction mixture was stirred for 1 day at 0 °C to room temperature, and evaporated up to dryness to give almost quantitatively 1-[bis(trifluoroacetoxy)iodo]polyfluoroalkane **2** as a white solid. An arene (189 mmol) and a sulfonic acid (122 mmol) were added into a mixture of 122 mmol of **2** in 150 ml of 1,1,2-trichloro-1,2,2-trifluoroethane at 0 °C and it was stirred for 1 day at 0 °C. The reaction mixture was evaporated up to dryness and the resulting solid was washed with chloroform to give pure crystals of an iodonium salt. For further purification the crystals were recrystallized from acetonitrile or acetonitrile–ether at room temperature. **3a**: 88% yield; mp 88—89 °C (decomp); ^{1}H NMR (CD_3CN) δ=4.80 (2H, q, J=10 Hz, CH_2), 7.40—7.90 (3H, m, ArH), 8.00—8.30 (2H, m, ArH); ^{19}F NMR (CD_3CN) 61.5 (3F, t, J=10 Hz, CF_3), 77.9 (3F, s, CF_3S); IR (KBr), 3060, 3040, 2970, 1565, 1470, 1440, 1400, 1280, 1240, 1195, 1170, 1120, 1040, 985, 840, 760, 730, 680, 650, 620 cm^{-1}; MS m/z 204 (PhI$^+$, 100%). Found: C, 25.03; H, 1.51%. Calcd for $C_9H_7F_6IO_3S$: C, 24.79; H, 1.62%. **3b**: 72% yield; mp 130 °C (decomp); ^{1}H NMR (acetone-d_6) δ=5.20 (2H, t, J=18 Hz, CH_2), 7.46—7.96 (3H, m, ArH), 8.26—8.50 (2H, m, ArH); ^{19}F NMR (acetone-d_6) 77.3 (3F, s, CF_3S), 82.7 (3F, m, CF_3), 106.5 (2F, t, J=18 Hz, CF_2); IR (KBr), 3040, 2980, 1570, 1480, 1445, 1410, 1340, 1220, 1180, 1050, 1015, 995, 920, 790, 735, 710, 680, 650, 630, 575, 520 cm^{-1}; MS m/z 204 (PhI$^+$, 100%). Found: C, 24.78; H, 1.19%. Calcd for $C_{10}H_7F_8IO_3S$: C, 24.70; H, 1.45%. **3c**: 70% yield; mp 133 °C (decomp); ^{1}H NMR (CD_3CN) δ=4.80 (2H, t, J=18 Hz, CH_2), 7.60—7.95 (3H, m, ArH), 8.10—8.30 (2H, m, ArH); ^{19}F NMR (CD_3CN) 80.8 (3F, s, CF_3S), 82.6 (3F, t, J=15 Hz, CF_3), 107.2 (2F, m, CF_2), 128.1 (2F, m, CF_2); IR (KBr) 3070, 3050, 1570, 1480, 1440, 1410, 1350, 1250, 1180, 1110, 1030, 960, 930, 770, 740, 680, 650, 580, 510 cm^{-1}; MS m/z 204 (PhI$^+$, 100%). Found: C, 24.39; H, 1.24%. Calcd for $C_{11}H_7F_{10}IO_3S$: C, 24.64; H, 1.32%. **3d**: 77% yield; mp 151 °C (decomp); ^{1}H NMR (CD_3CN) δ=4.88 (2H, d, J=18 Hz, CH_2), 7.46—7.94 (3H, m, ArH), 8.06—8.30 (2H, m, ArH); ^{19}F NMR (CD_3CN) 74.3 (6F, d, J=8.5 Hz, CF_3), 77.6 (3F, s, CF_3S), 167.3 (1F, m, F); IR (KBr) 3100, 3080, 3040, 2980, 1580, 1570, 1475, 1440, 1410, 1330, 1300, 1280, 1240, 1170, 1140, 1020, 990, 965, 915, 800, 770, 730, 720, 675, 650, 630, 570, 540, 515 cm^{-1}. Found: C, 24.67; H, 1.43%. Calcd for $C_{11}H_7F_{10}IO_3S$: C, 24.54; H, 1.32%. **3e**: 89% yield; mp 142—143 °C (decomp); ^{1}H NMR (CD_3CN) δ=4.83 (2H, t, J=18 Hz, CH_2), 7.40—7.80 (3H, m, ArH), 8.05—8.25 (2H, m, ArH); ^{19}F NMR (CD_3CN) 78.0 (3F, s, CF_3S), 80.6 (3F, t, J=10 Hz, CF_3), 102.8 (2F, m, CF_2), 120.8 (8F, m, CF_2), 124.9 (2F, m, CF_2); IR (KBr) 3070, 3000, 1480, 1450, 1410, 1370, 1250, 1100, 1060, 1030, 1010, 890, 770, 750, 710, 640, 520 cm^{-1}; MS m/z 204 (PhI$^+$, 40%), 69 (CF_3^+, 100%). Found: C, 24.38; H, 0.85%. Calcd for $C_{15}H_7F_{18}IO_3S$: C, 24.48; H, 0.96%. **4**: 72% yield; mp 103—104 °C (decomp); ^{1}H NMR (CD_3CN) δ=4.77 (2H, q, J=10 Hz, CH_2), 7.33 (2H, dd, J=9, 9 Hz, ArH), 8.20 (2H, dd, J=9, 4.5 Hz, ArH); ^{19}F NMR (CD_3CN) 61.1 (3F, t, J=10 Hz, CF_3), 77.5 (3F, s, CF_3S), 102.8 (1F, bs, ArF); IR (KBr) 3050, 2980, 1583, 1490, 1261, 1180, 1035, 825, 650, 645, 578, 525 cm^{-1}. Found: C, 23.68; H, 1.16%. Calcd for $C_9H_6F_7IO_3S$: C, 23.81; H, 1.33%. **5**: 95% yield; mp 107 °C (decomp); ^{1}H NMR (CD_3CN) δ=4.83 (2H, t, J=18 Hz, CH_2), 7.40—7.90 (3H, m, ArH), 8.10—8.30 (2H, m, ArH); ^{19}F NMR (CD_3CN) −38.5 (1F, s, FSO_2), 80.3 (3F, t, J=10 Hz, CF_3), 103.2 (2F, m, CF_2), 120.8 (6F, m, CF_2), 122.0 (2F, m, CF_2), 125.5 (2F, m, CF_2); IR (KBr) 3070, 3000, 1480, 1440, 1400, 1370, 1280, 1220, 1140, 1100, 1070, 1010, 990, 740, 710, 670, 590 cm^{-1}; MS m/z 510 ($C_7F_{15}CH_2I^+$, 1.3%), 204 (PhI$^+$, 100%). Found: C, 24.24; H, 0.96%. Calcd for $C_{14}H_7F_{16}IO_3S$: C, 24.51; H, 1.03%. **6**: 49% yield; mp 90—91 °C (decomp); ^{1}H NMR (acetone-d_6) δ=5.16 (2H, t, J=18 Hz, CH_2), 5.30 (broad peak, OH), 7.40—7.80 (3H, m, ArH), 8.20—8.40 (2H, m, ArH); ^{19}F NMR (DMSO-d_6) 80.0 (3F, t, J=10 Hz, CF_3), 120.5 (2F, m, CF_2), 121.6 (4F, m, CF_2), 122.2 (2F, m, CF_2), 122.8 (2F, m, CF_2), 125.6 (2F, m, CF_2); IR (KBr) 3450, 3080, 3050, 2970, 1580, 1480, 1460, 1410, 1370, 1320, 1210, 1150, 1100, 1050, 1010, 890, 730, 710, 660, 590, 530 cm^{-1}; MS m/z 510 ($C_7F_{15}CH_2I^+$, 25%), 204 (PhI$^+$, 100%). Found: C, 23.73; H, 1.25%. Calcd for $C_{14}H_{10}F_{15}IO_5S$ (as monohydrate): C, 23.95; H, 1.44%. **7**: 85% yield; mp 157—158 °C; ^{1}H NMR (CD_3CN) δ=4.92 (2H, t, J=18 Hz, CH_2), 6.52 (1H, dd, J=51.0, 4.8 Hz, CF_2H), 7.5—8.32 (5H, m, ArH); ^{19}F NMR (CD_3CN) 78.1 (3F, s, CF_3), 103.1 (2F, m, CF_2) 120.2—123.1 (14F, m, CF_2), 128.7 (2F, m, CF_2), 137.8 (2F, d, J=51 Hz, CF_2H); MS m/z 204 (PhI$^+$, 36%), 69 (CF_3^+, 100%). Found: C, 24.80; H, 0.89%. Calcd for $C_{18}H_8F_{23}IO_3S$: C, 24.90; H, 0.93%.

The NMR data of the intermediate bis(trifluoroacetates) **2** are as follows. **2a**: ^{1}H NMR ($CDCl_3$) δ=4.92 (q, J=9 Hz, CH_2); ^{19}F NMR ($CDCl_3$) 62.9 (3F, t, J=9 Hz, CF_3CH_2), 73.4 (6F, s, CF_3). **2b**: ^{1}H NMR ($CDCl_3$) δ=4.93 (t, J=15 Hz, CH_2); ^{19}F NMR ($CDCl_3$) 74.1 (6F, s, CF_3CO), 83.8 (3F, s, CF_3), 109.8 (2F, t, J=15 Hz, CF_2). **2c**: ^{1}H NMR (CD_3CN) δ=5.03 (t, J=16.5 Hz, CH_2); ^{19}F NMR (CD_3CN) 74.3 (6F, s, CF_3CO), 80.3 (3F, s, CF_3), 105.4 (2F, s, CF_2), 125.3 (2F, s, CF_2). **2d**: ^{1}H NMR (CD_3CN) δ=5.25 (d, J=16.5 Hz, CH_2); ^{19}F NMR (CD_3CN) 72.8 (6F, s, CF_3CO), 75.0 (6F, d, J=8.5 Hz, CF_3), 169.5 (1F, m, F). **2e**: ^{1}H NMR (CD_3CN) δ=5.13 (t, J=18 Hz, CH_2); ^{19}F NMR (CD_3CN) 74.3 (6F, s, CF_3CO), 81.0 (3F, s, CF_3), 104.3 (2F, m, CF_2), 120.8 (8F, m, CF_2), 124.5 (2F, m, CF_2).

(1*H*,1*H*,5*H*,5*H*-Perfluoropentane-1,5-diyl)bisphenylbisiodonium Triflate 9. The procedure was the same as for **3—7** except for the use of double the quantity of trifluoroperacetic acid, benzene, and triflic acid. **9**: 96% yield; mp 113—114 °C (decomp); ^{1}H NMR (CD_3CN) δ=4.80 (4H, t, J=18 Hz, CH_2), 7.40—7.90 (6H, m, ArH), 8.00—8.20 (4H, m, ArH); ^{19}F NMR (CD_3CN) 78.0 (6F, s, CF_3), 102.6 (4F, m, CF_2CH_2), 120.9 (2F, s, CF_2); IR (KBr) 3080, 1580, 1480, 1440, 1430, 1410, 1260, 1180, 1040, 890, 740, 660, 640, 530 cm^{-1}; MS m/z 432 [$ICH_2(CF_2)_3CH_2I^+$, 1.4%], 204 (PhI$^+$, 100%). Found: C, 25.63; H, 1.60%. Calcd for $C_{19}H_{14}F_{12}I_2O_6S_2$: C, 25.81; H, 1.60%.

Dehydrofluorination of 3b, 3c, and 3e. General Procedure; Into a solution of 1 mmol of **3** in 7 ml of acetonitrile was added 1 mmol of sodium hydride (50% in oil) at 0 °C with stirring under argon atmosphere. The reaction mixture was stirred for 30 min, filtered with celite, and evaporated up to dryness. The resulting solid was recrystallized from 1,2-dichloroethane. **11b**: 80% yield; mp 127—128 °C; ^{1}H NMR (acetone-d_6) δ=7.50—7.90 (3H, m, ArH), 8.20—8.50 (2H, m, ArH), 8.20 (1H, d, J=33 Hz, vinyl proton); ^{19}F NMR (acetone-d_6) 71.3 (3F, d, J=10 Hz, CF_3), 77.6 (3F, s, CF_3S), 99.8 (1F, dq, J=33, 10 Hz, vinyl F); IR (KBr) 3100, 1680, 1475, 1455, 1340, 1270, 1250, 1220, 1170, 1160, 1040, 1020, 990, 820, 740, 720, 675, 650, 630 cm^{-1}; MS m/z 240 (CF_3CF=CHI^+, 100%), 226 ($PhOTf^+$, 40%), 204 (PhI^+, 19%). Found: C, 25.49; H, 1.10%. Calcd for $C_{10}H_6F_7IO_3S$: C, 25.77; H, 1.30%. **11c**: 86% yield; mp 144 °C; ^{1}H NMR (acetone-d_6) δ=7.33—8.10 (3H, m, ArH), 8.20—8.70 (2H, m, ArH), 8.26 (1H, d, J=33 Hz, vinyl proton); ^{19}F NMR (acetone-d_6) 78.0 (3F, s, CF_3S), 83.1 (3F, dt, J=6, 2 Hz, CF_3), 96.2 (1F, dtq, J=33, 14.5, 6 Hz, vinyl F), 120.1 (2F, dq, J=14.5, 2 Hz, CF_2); IR (KBr) 3070, 3040, 1680, 1570, 1475, 1445, 1325, 1315, 1275, 1250, 1230, 1180, 1090, 1040, 1020, 995, 730, 670, 650, 630 cm^{-1}; MS m/z 367 (C_2F_5CF=$CHIPh^+$, 1.4%), 290 (C_2F_5CF=CHI^+, 100%), 226 ($PhOTf^+$, 52%), 204 (PhI^+, 25%). Found: C, 25.15; H, 1.10%. Calcd for $C_{11}H_6F_9IO_3S$: C, 25.60; H, 1.17%. **11e**: 87% yield; mp 128—130 °C; ^{1}H NMR (acetone-d_6) δ=7.50—7.96 (3H, m, ArH), 8.32 (1H, d, J=33 Hz, vinyl proton), 8.30—8.50 (2H, m, ArH); ^{19}F NMR (acetone-d_6) 78.0 (3F, s, CF_3S), 80.5 (3F, m, CF_3), 95.0 (1F, m, vinyl F), 116.0 (2F, m, CF_2), 121.3 (2F, m, CF_2), 122.1 (4F, m, CF_2), 125.6 (2F, m, CF_2); IR (neat) 3130, 3080, 1670, 1590, 1570, 1475, 1450, 1370, 1250, 1200, 1180, 1145, 1090, 1030, 990, 950, 920, 850, 800, 790, 760, 740, 720, 680, 650, 640 cm^{-1}; MS m/z 567 ($C_6F_{13}CF$=$CHIPh^+$, 10%), 490 ($C_6F_{13}CF$=CHI^+, 32%), 226 ($PhOTf^+$, 100%), 204 (PhI^+, 40%). Found: C, 24.97; H, 0.75%. Calcd for $C_{15}H_6F_{17}IO_3S$: C, 25.16; H, 0.84%.

Thermolysis of 3e. The crystals of **3e** was heated at 140—145 °C for 10 min under atmospheric pressure. The decomposition products were separated by column chromatography on silica gel with pentane as an eluent. The structural assignment of the products **13** and **14** was carried out by the comparison with authentic samples.

Thermolysis of 11e. The crystals of **11e** was heated at 200 °C under pressure of 180 mmHg (1 mmHg=133.322 Pa) by using a glass tube oven. The decomposition products **15** and **16** condensed at the cooled part of the glass tube and their yields were determined by ^{19}F NMR technique. Each of the products was isolated by the usual method. **15**: 79% yield, oil, ^{1}H NMR ($CDCl_3$) δ=6.63 (1H, J=31 Hz, vinyl proton); ^{19}F NMR ($CDCl_3$) 81.6 (3F, s, CF_3), 103.3 (1F, m, CF), 116.7 (2F, m, CF_2), 122.7 (2F, m, CF_2), 123.4 (4F, m, CF_2), 126.9 (2F, m, CF_2); IR (neat) 3120, 1670, 1370, 1320, 1300, 1240, 1200, 1150, 1125, 1090, 1040, 1020, 840, 795, 735, 710, 655 cm^{-1}; MS m/z 490 (M^+). **16**: 76% yield, oil, ^{1}H NMR ($CDCl_3$) δ=7.10—7.70 (5H, m); ^{19}F NMR ($CDCl_3$) 73.1 (s, CF_3); IR (neat) 3080, 1605, 1590, 1490, 1420, 1250, 1210, 1140, 1070, 1020, 910, 880, 780, 760, 730, 680, 620, 600 cm^{-1}; MS m/z 226 (M^+).

Reaction of 11b with Sodium Phenoxide. Under argon atmosphere, 0.667 mmol of sodium hydride (50% in oil) was added into a solution of 0.667 mmol of phenol in 2 ml of dichloromethane and the mixture was stirred for 5 min. **11b** (0.606 mmol) was added and the mixture was stirred for 30 min at 0 °C. Then the reaction mixture was filtered with celite and evaporated up to dryness. The resulting solid was recrystallized from dichloromethane–diethyl ether–pentane to give **22** in a 42% yield. **22**: mp 86—87 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ=6.94—7.00 (2H, m, ArH), 7.20—7.63 (6H, m, ArH), 7.43 (1H, s, vinyl proton), 7.90—7.96 (2H, m, ArH); ^{19}F NMR ($CDCl_3$) 66.8 (3F, s, CF_3), 78.8 (3F, s, CF_3S); IR (KBr) 3100, 1640, 1590, 1490, 1440, 1320, 1280, 1250, 1210, 1160, 1060, 1030, 990, 860, 790, 730, 635 cm^{-1}; MS m/z 314 [$CF_3(PhO)C$=CHI^+]. Found: C, 35.35; H, 1.95%. Calcd for $C_{16}H_{11}F_6IO_4S$: C, 35.58; H, 2.05%.

Reaction of 11b with Sodium 2-Phenylethoxide. The procedure was similar to the above case. The crude product was recrystallized from ethyl acetate–pentane to give **23** as a mixture of E- and Z-isomers in a 32% yield. **23**: mp 62—63 °C (a 88:12 or 12:88 mixture of E- and Z-isomers); ^{1}H NMR (400 MHz, $CDCl_3$) A:B component=88:12, A component; δ=3.07 (2H, t, J=6.7 Hz, benzyl protons), 4.44 (2H, td, J=6.8, 0.7 Hz, allyl protons), 6.91 (1H, s, vinyl proton), 7.74—7.80 (2H, m, ArH), B component; δ=3.06 (2H, t, J=6.4 Hz, benzyl protons), 4.23 (2H, t, J=6.5 Hz, allyl protons), 6.74 (1H, s, vinyl proton), 7.98—8.02 (2H, m, ArH), A+B component; δ=7.15—7.62 (m, ArH); ^{19}F NMR ($CDCl_3$) A:B component=88:12, A component; 66.0 (3F, s, CF_3), 78.8 (3F, s, CF_3S), B component; 65.2 (3F, s, CF_3), 78.8 (3F, s, CF_3S); IR (KBr) 3080, 1620, 1560, 1500, 1470, 1440, 1325, 1270, 1250, 1190, 1160, 1090, 1050, 1030, 990, 730, 700, 660, 630 cm^{-1}. Found: C, 37.93; H, 2.65%. Calcd for $C_{18}H_{15}F_6IO_4S$: C, 38.04; H, 2.66%.

Reaction of 11b with Sodium *p*-*t*-Butylbenzenethiolate. In analogy with that described above, **11b** was treated with sodium *p*-*t*-butylbenzenethiolate in dichloromethane at 0 °C for 1 h, which was prepared in situ from *p*-*t*-butylbenzenethiol and sodium hydride. The usual post-treatment and then thin-layer chromatography gave **24** and **25** in 16 and 32% yields, respectively. **24**: A 78:22 mixture of Z- and E-isomers; oil, ^{1}H NMR ($CDCl_3$) Z-isomer; δ=1.40 (9H, s, *t*-Bu), 6.38 (1H, d, J=31.5 Hz, vinyl proton), 6.85—7.30 (3H, m, ArH), 7.56—7.75 (2H, m, ArH), E-isomer; δ=1.40 (9H, s. *t*-Bu), 6.48 (1H, d, J=19.5 Hz, vinyl proton), 6.85—7.35 (3H, m, ArH), 7.56—7.75 (2H, m, ArH); ^{19}F NMR ($CDCl_3$) Z-isomer; 72.1 (3F, d, J=13 Hz, CF_3), 131.6 (1F, dq, J=31.5, 13 Hz, vinyl F), E-isomer; 68.7 (3F, d, J=10 Hz, CF_3), 128.2 (1F, dq, J=19.5, 10 Hz, vinyl F); IR (KBr) 3090, 2980, 2880, 1500, 1350, 1240, 1190, 1140, 1060, 1010, 840 cm^{-1}; MS m/z 278 (M^+). Found: C, 56.01; H, 5.15%. Calcd for $C_{13}H_{14}F_4S$: C, 56.10; H, 5.07%. **25**: A 86:14 mixture of two isomers A and B; bp 230 °C/5 mmHg (using a glass tube oven); ^{1}H NMR ($CDCl_3$) δ=1.31 (18H, s, *t*-Bu), 7.20—7.50 (8H, m, ArH), 7.78 (1H, bs, vinyl proton); ^{19}F NMR ($CDCl_3$) A isomer; 64.1 (s, CF_3), B isomer; 56.6 (s, CF_3); IR (KBr) 3100, 2980, 2920, 2890, 1570, 1495, 1460, 1400, 1365, 1270, 1250, 1200, 1160, 1130, 1010, 960, 840, 825, 710, 650 cm^{-1}; MS m/z 424 (M^+). Found: C, 66.00; H, 6.78%. Calcd for $C_{23}H_{27}F_3S_2$: C, 65.05; H, 6.41%.

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