

PERFLUOROALKYLATION OF AROMATIC COMPOUNDS WITH $R_fI(Ph)OSO_2CF_3$

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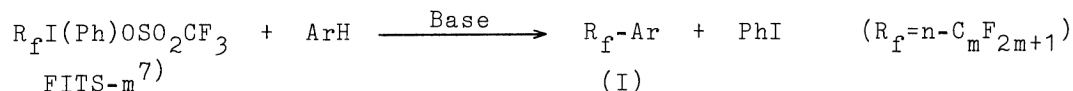
Perfluoroalkylation of various aromatic compounds with perfluoroalkylphenyliodonium trifluoromethanesulfonate (FITS) under mild conditions was described. The reactivity of other perfluoroalkyliodonium salts was also examined.

Direct perfluoroalkylations of aromatic compounds have been carried out by thermal or photochemical reactions of iodoperfluoroalkanes,¹⁾ perfluoroalkane-sulfonyl chlorides,²⁾ or perfluoroalkylcoppers.³⁾ They require high temperature or irradiation for a long period. A new perfluoroalkylating agent has been desired, which can easily give perfluoroalkyl compounds directly from aromatic compounds under mild conditions. Recently it was reported that perfluoroalkyl-p-tolyliodonium chloride reacted with aniline derivatives to give p-perfluoroalkylaniline derivatives.⁴⁾ However, the yields were low and there were no data on the reactivity with other aromatic compounds.

In the previous work, we succeeded in perfluoroalkylating various carbanions with perfluoroalkylphenyliodonium trifluoromethanesulfonate (FITS).^{5,6)} In a course of our studies on the reactivity of FITS as a cationic perfluoroalkylating agent, we examined the reaction with aromatic compounds.

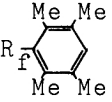
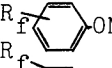
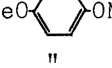
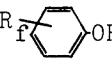
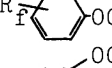
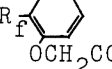
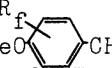
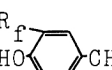
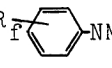
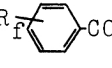
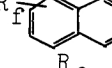
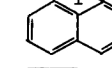
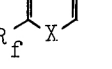
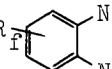
It was found that FITS smoothly reacted with a series of aromatic compounds in the presence of an equivalent amount of pyridine or its derivative as a very weak base in an appropriate solvent to afford perfluoroalkylaromatic compounds in moderate to high yields and iodobenzene was liberated in an almost quantitative yield (Scheme 1). The results and reaction conditions are summarized in Table 1.

Scheme 1.



In the case of the aromatic compounds with high π -electron density such as anthracene, phenol, dimethylaniline, furan, thiophene, or pyrrole, the reaction proceeded smoothly at 0°C to room temperature. The reaction with dimethylaniline gave p-isomer as a main product, while that with phenol or its derivatives gave o-isomers abundantly. In furan, thiophene, pyrrole, or anthracene, there was obtained one isomer exclusively in a good yield. The treatment of FITS with 2(1H),3(4H)-quinoxalinedione gave a small amount of 5- and 6-perfluoroalkyl-2(1H),3(4H)-quinoxalinediones. However it is interesting that FITS was treated with the sodium salt of the quinoxalinedione obtained by use of sodium methylsulfinylmethide to afford

Table 1. Reaction of FITS-m with aromatic compounds.

Run	Product (I) ^{a)}	Isomer {mp(°C)} ^{b)}	Yield ^{c)} (%)	FITS-m	$\frac{ArH^d)}{FITS}$	Base ^{e)} (1 eq)	Solv.	Temp. (°C)	Time (min)
1	R _f -Ph		97(81) _{m=6}		large excess	A	PhH	reflux	60
2		{58-59}	32	8	1.5	A	CH ₃ CN	60	7
3		4:1:2 (o:m:p)	61(30)	2	0.92	B	CH ₂ Cl ₂	reflux	30
4			58	3	1.1	B	CH ₂ Cl ₂	r.t.	15
5	"		74	3	1.2	A	CH ₃ CN	r.t.	10
6		4.1:1:4.6 (o:m:p)f)	55(26)	8	1.1	A	CH ₂ Cl ₂	r.t.	10
7		1.3:1:1.2 (o:m:p)g)	(45)	10	1.1	B	(CH ₂ Cl) ₂	reflux	210
8		{76-77}	57	8	1	A	CH ₃ CN	57	10
9	"		68	8	2	A	CH ₃ CN	64	10
10	"		(44)	8	1.5	A	CH ₂ Cl ₂	r.t.	60
11		3.8:1 (o:m)h)	45	10	1.5	B	(CH ₂ Cl) ₂	reflux	120
12		{76.5-77}	52(48)	8	1.5	A	CH ₃ CN	r.t.	10
13		1:2.7 (o:p)	(37)	8	2.1	-	CH ₃ CN	reflux	60
14		(1:1:1.3) (o:m:p)	54(35)	8	1.1	A	CH ₃ CN	r.t.	60
15		4:1 (α:β)	82	8	2.1	A	CH ₃ CN	60	5
16		{84-87}	(63)	3	1	B	CH ₂ Cl ₂	0	60
17		(X=O)	87	8	2	B	CH ₂ Cl ₂	r.t.	30
18	"	(X=S)	73(40)	8	1.1	A	CH ₂ Cl ₂	r.t.	15
19	"	(X=NH)	92	8	1.1	B	CH ₂ Cl ₂	r.t.	30
20		1:2 (5-:6-)	(8)	2	0.91	-	DMF	45	720 ⁱ⁾
21	"		(49)	2	0.91	C	DMF	r.t.	720 ⁱ⁾

a) All products showed spectral data (¹H- and ¹⁹F-NMR, IR, Mass) and elementary analysis in agreement with the assigned structure. b) Melting points of new compounds. c) Yields were determined by GLC. Values in parentheses are isolated yields. The products were isolated by means of column-chromatography (Run 1, 7, 10, 12, 14, and 16), GL-chromatography (Run 3, 6, 13, and 18), or fractional crystallization (Run 20 and 21). As the perfluoroalkyl compounds have high volatility, the large difference between GLC yields and isolated ones is due to loss of the products during the operation of isolation, particularly by GL-chromatography. d) Molar ratio. e)-i) See below in Table 2.

the same ones in rather good yields (Run 20 and 21 in Table 1). On the other hand, the reaction with π -electron-deficient aromatic compounds such as methyl benzoate occurred in acetonitrile at 82°C in the presence of pyridine.

Similarly to FITS, perfluoroalkylphenyliodonium sulfate (FIS)⁶⁾ reacted with various aromatic compounds to give the products (Scheme 2). The results and reaction conditions are shown in Table 2. As a whole, the reactivity of FIS is

Scheme 2.

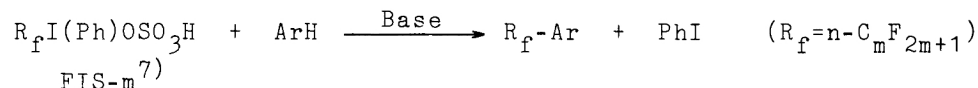
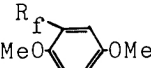



Table 2. Reaction of FIS-m with aromatic compounds.

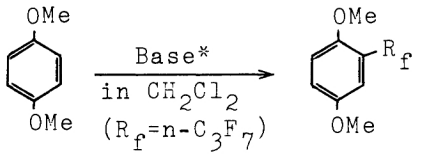
Run	Product (I) ^{a)}	Yield ^{c)} (%)	FIS-m	$\frac{\text{ArH}}{\text{FIS}}$ ^{d)}	Base ^{e)} (eq)	Solv.	Temp. (°C)	Time (min)
22 ^{j)}	R _f -Ph	70	m=6	large excess	A(2.0)	PhH	reflux	90
23 ^{j)}	"	75	6	"	—	PhH	reflux	20
24		63	3	1.1	B(1.0)	CH ₂ Cl ₂	reflux	20
25		57	8	1.1	A(2.0)	CH ₂ Cl ₂	r.t.	20
26	"	60	8	1.1	A(2.0)	CH ₃ CN	60	60

a)-d) See below Table 1. e) A=pyridine; B=2,6-di-*t*-butyl-4-methylpyridine; C=sodium methylsulfinylmethide. f) {54-54.5:oil:71-73} g) {74-77:67-69:85-86} h) {59-61:78-82} i) The reaction completed essentially within one hour. j) *n*-Tridecafluorohexyliodobenzene was obtained in 5 and 16% yields in Run 22 and 23, respectively.

somewhat lower than that of FITS. It is due to the difference in the strength of the leaving groups. It appears that the lower yields in FIS are in some part owing to its poor solubility. FITS has relatively considerable solubility in organic solvents.

The high reactivity of FITS or FIS compared to perfluoroalkyl-*p*-tolyliodonium chloride was demonstrated by the next experiments.

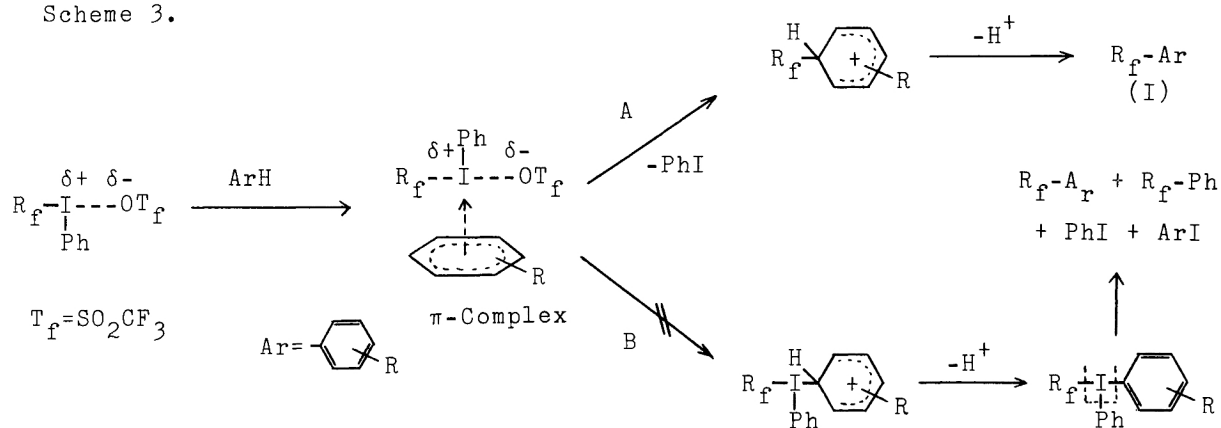
Table 3.

	Reagent	Yield(%)	Temp.	Time(min)
	FITS-3	58	r.t.	15
	FIS-3	63	reflux	20
	R _f I(<i>p</i> -Tolyl)Cl	6	reflux	30

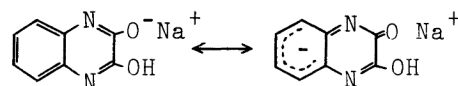
*2,6-Di-*t*-butyl-4-methylpyridine

The following scheme is proposed as a reaction mechanism (Scheme 3). The formation of the π -complex of the iodonium salt with an aromatic compound is assumed as the first step. There are two routes (A and B) from the complex. Route B will give R_f-Ph and/or ArI along with R_f-Ar and PhI. It is excluded because of no formation of R_f-Ph and ArI in the reaction. Accordingly it may be concluded that the

Scheme 3.



reaction proceeds through Meisenheimer complex of Route A. The high proportion of o- and p-substitutions in the isomer distribution of the products from the aromatic compounds with π -electron-donating groups is in support of the proposed mechanism. The easy formation of o-isomers in the case of phenol or its derivatives can be explained as follows. In the π -complex, there is some contribution of the oxygen atom by the coordination of its lone pair electrons to the positively polarized iodine atom. It brings about some proximity of the perfluoroalkyl group to o-position. In the case of the quinoxalinedione, the high reactivity of its sodium salt can be accounted for by ready formation of the π -complex at the benzene ring due to some increase of π -electron density. On the other hand, the significant formation of o- and p-isomers in the reaction with methyl benzoate suggests that the reaction with π -electron-deficient aromatic compounds is accompanied by the free-radical reaction of $R_f\cdot$ generated from the homogeneous cleavage of R_f-I bond in FITS.



Since FITS has the highest reactivity to various aromatic compounds as mentioned above, it is expected that FITS serves as a useful reagent for the preparation of a wide range of perfluoroalkylaromatic compounds.

References

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- 2) J.R.Mattson, USP 1,180,400.
- 3) P.L.Coe and N.E.Milner, *J. Fluorine Chem.*, **2**, 167 (1972/73).
- 4) L.M.Yagupolskii, I.I.Maletina, N.V.Kondratenko, and V.V.Orda, *Synthesis*, 835 (1978).
- 5) T.Umemoto and Y.Kuriu, to be submitted for publication.
- 6) FITS-10: mp 162-166°C, FITS-8: dec 149-151°C, FITS-6: dec 120-123°C, FITS-3: dec 124.5-127°C, FITS-2: dec 116-120°C, FIS-8: mp 114-118°C, FIS-6: mp 107-108°C, FIS-3: mp 109-111°C.
- 7) The letter m means the number of carbons in the perfluoroalkyl group.

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