

Perfluoroalkylations and perfluorooxaalkylations. Part 2. Copper-mediated cross-coupling of secondary perfluorooxaalkyl iodides and aryl halides [1]*

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Abstract

The first successful application of the copper-mediated cross-coupling reaction using secondary perfluorooxaalkyl iodides and iodoaromatic substrates is described. The yields of the cross-coupled products are optimized by careful choice and control of the experimental conditions. The by-products formed are identified and their probable mode of formation is discussed.

Introduction

Since its original disclosure by McLoughlin and Thrower [2], the interaction of iodoalkanes, iodoaromatic compounds and copper in polar aprotic solvents, has received considerable attention. The reaction has been extended to include bromoaromatics [3] and bromoheterocyclic compounds [4] as substrates. As the aliphatic component, perfluoroalkyl iodides and perfluorooxaalkyl iodides have been successfully used to obtain a variety of substituted aromatic and heterocyclic compounds [1–6].

Almost all the aliphatic iodides used in the earlier studies were primary iodides. The only secondary iodide utilized in these cross-coupling reactions, as far as is known to the authors, was perfluoroisopropyl iodide which was used in the initial study [2]. No secondary perfluorooxaalkyl iodides have been reported as used in these cross-coupling reactions. In our previous work [1], primary perfluorooxaalkyl iodides showed a difference in reactivity depending on the position of the ether oxygen relative to the iodine atom. Perfluorooxaalkyl iodides in which the ether oxygen was separated from the iodine atom by four or eight difluoromethylene groups appeared to behave like perfluoroalkyl iodides and gave the cross-coupled products in high yields, even when the substrates were the less reactive aryl bromides. However, those perfluorooxaalkyl iodides in which the ether oxygen was separated from the iodine

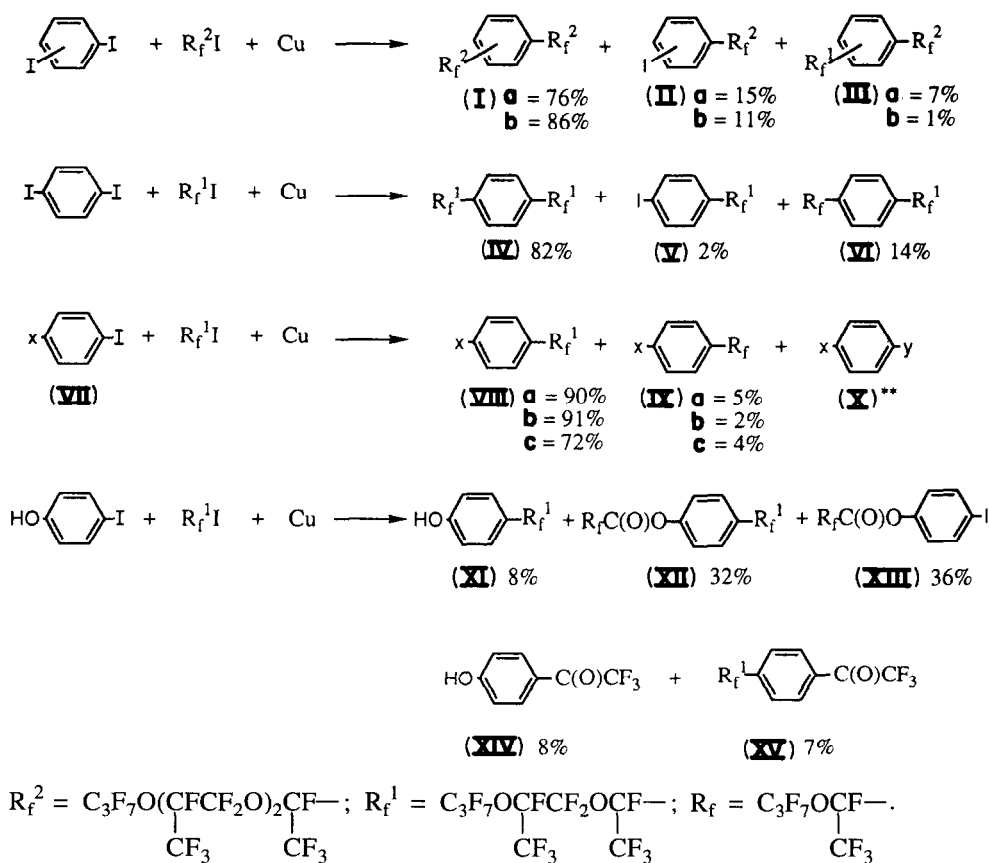
atom by only two difluoromethylene groups gave fair yields of cross-coupled products with aryl iodides, but only after long reaction times, and very little cross-coupled product with aryl bromides, suggesting decreased reactivity [1, 6] relative to the materials with more carbon atoms between the ether oxygen and the iodine atom. A primary iodide with only one difluoromethylene group separating the iodine atom and the ether oxygen gave none of the expected cross-coupled product with iodobenzil [6]. Thus it was of interest to investigate how a secondary ether iodide would behave. The secondary iodides studied in this work, R_f^2I and R_f^1I (Scheme 1), were derived from oligomers of hexafluoropropylene oxide (HFPO) and had one $CF(CF_3)$ unit separating the ether oxygen from the iodine atom. Our studies using different substrates as well as optimization of the reaction conditions are described here.

Experimental

All reactions were conducted in oven-dried glassware under an atmosphere of dry nitrogen. Copper bronze was purchased from Gallard Schlesinger Chemical Manufacturing Corporation, New York and was used without activation. The secondary iodides were prepared by modification of reported procedures [7, 8]. The solvents used were from the Aldrich Chemical Company and were anhydrous, except dimethyl sulfoxide (DMSO, spectrographic grade) and hexamethyl phosphoramide (HMPA) which were used as received. Hexafluorobenzene and the oligomeric HFPO acid fluorides were

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I, II, III: a = *m*-; b = *p*-; VII, VIII, IX: a, x = F; b, x = H; c, x = OCH₃; X: a, x = F, y = CF₃CF₂-; b, x = F, y = CF₃C(O)-.

**Formed only in reactions using DMF and DMAC (see Table 2).

Scheme 1. Substitution products from aromatic iodides. The percentages shown are GC area %.

from PCR Inc., FL. Gas chromatographic analyses were performed on a Perkin-Elmer Sigma I or IIB chromatograph using either a 2 ft. stainless-steel column (1/4 in. i.d.) packed with 5% Dexsil 400 on 100–200 mesh Supelcoport or a 6 ft. stainless-steel column (1/4 in. i.d.) packed with 10% SE-30 on 80–100 mesh Supelcoport. The GC/MS analyses were performed on a Finnigan 4021 mass spectrometer in either a chemical ionization or electron impact mode. Infrared spectra were recorded on a Perkin-Elmer 683 spectrometer. NMR spectra were obtained on an NT-300 spectrometer. All temperatures are uncorrected.

Preparation of C₃F₇O[CF(CF₃)CF₂O]₂CF(CF₃)I (R_f²I)

Iodine (10.2 g, 40.2 mmol) was added at room temperature to a suspension of Cs₂CO₃ (13.0 g, 39.9 mmol) in anhydrous diglyme (30 ml) maintained under a nitrogen atmosphere. A mild exotherm which raised the temperature to c. 35 °C was noticed. Hexafluoropropylene oxide (HFPO) tetramer acid fluoride, [R_f²C(O)F], (25.0 g, 37.7 mmol) was added to the above mixture at c. 35 °C over 10 min. The temperature of

the reaction mixture increased to c. 45 °C during this addition. The reaction mixture was then heated to c. 70 °C. Aliquot samples were removed periodically, hydrolyzed with water and analyzed by gas chromatography. After about 4 h at 70 °C, the reaction mixture showed the expected product, R_f²I (90%), a by-product, R_f²H (7%) and minor amounts of unknown products. The reaction mixture was cooled to room temperature and hydrolyzed with water (100 ml). The organic layer was separated, treated with sodium bisulfite solution to remove iodine and washed with water (3 × 100 ml). The crude product obtained was dried with anhydrous MgSO₄ and distilled to obtain 22.7 g of R_f²I (97% pure), yield 81%, b.p. 80–81 °C/25 mmHg. The IR spectrum was consistent with the proposed structure. MS (EI) *m/e*: 501 (C₃F₇OC₃F₆OC₃F₆)⁺; 335 (C₃F₆OC₃F₆)⁺; 227 (C₂F₄I)⁺; 169 (C₃F₇)⁺; 127 (I)⁺; 119 (C₂F₅)⁺; 100 (C₂F₄)⁺; 69 (CF₃)⁺.

Preparation of C₃F₇OCF(CF₃)CF₂OCF(CF₃)I (R_f¹I)

This compound was prepared in the same manner as described above for the preparation of R_f²I. IR and

MS analyses were consistent with the structure. R_f^1I was obtained in 70% yield (98% pure), b.p. 72–74 °C/100 mmHg (lit. value [7], b.p. 145 °C).

Synthesis of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C_6H_4F$ (VIIIa) (nc)

Copper bronze (2.40 g, 37.8 mmol) was placed in a 100 ml three-necked flask fitted with a thermometer, stirrer and a water condenser connected to a nitrogen gas bypass. The secondary iodide $C_3F_7OCF(CF_3)CF_2OCF(CF_3)I$ (R_f^1I) (10.1 g, 17.5 mmol), 4-fluoroiodobenzene (VIIa) (2.96 g, 13.3 mmol), 2,2'-bipyridine (0.20 g, 1.28 mmol) DMSO (5.4 g, 69.2 mmol) and hexafluorobenzene (28 ml) were added to the copper powder. The reaction mixture was heated with stirring to 50 °C and maintained at that temperature for a total period of 6 d. A sample analyzed by GC at the end of 3 d showed 86% of the expected product VIIIa and 12% of the unreacted substrate VIIa, in addition to other minor products. At the end of 6 d, the yield of product VIIIa had increased only slightly to 90% while 5% of VIIa remained unreacted. The reaction was terminated at this stage. The reaction mixture was allowed to cool to ambient temperature and a mixture of $CFCl_2CF_2Cl$ (20 ml) and water (50 ml) added. The mixture was stirred and then centrifuged to separate the solids. The solid part was extracted with additional amounts (2×20 ml) of $CFCl_2CF_2Cl$. The organic layer was separated from the combined liquid part and washed again with water (2×30 ml) and dried over anhydrous $MgSO_4$. On evaporation of the solvent, the crude product (7.9 g) was obtained. Distillation gave the pure product (4.99 g). Isolated yield 69%, b.p. 102 °C/45 mmHg.

The procedure described above is typical for the perfluorooxaalkylation of substituted benzenes using secondary iodides derived from HFPO oligomers. A similar procedure was applied to substrates containing other functional groups such as p - x - C_6H_4I where x = H, OH, OCH_3 and I, as well as *meta*-diiodobenzene. These reactions and results are shown in Scheme 1 and in Table 1.

Results and discussion

The two secondary perfluorooxaalkyl iodides (R_f^2I and R_f^1I) (see Scheme 1) used in this study were derived from HFPO oligomeric acid fluorides and were prepared by a modification of known methods [7, 8]. Initially, R_f^2I was allowed to react with 1,3,5-tribromobenzene in DMSO in order to form the corresponding tri(perfluorooxaalkyl)benzene. After 24 h reaction in the presence of copper benzene at 120–135 °C, no substitution product was obtained. The reaction mixture consisted of unreacted tribromobenzene and products

of reductive dehalogenation such as *m*-dibromobenzene and bromobenzene. In addition, R_f^2I , R_f^1I and R_fH were also present, apparently formed by a combination of hydrogen abstraction by the copper complex and unzipping of the oligomer chain. Minor amounts of products derived from reaction of the copper complex with the solvent were also formed.

Although 1,3,5-tribromobenzene did not undergo the cross-coupling reaction with secondary iodides, aryl iodides did. The most promising experimental conditions for the cross-coupling of aryl iodides with secondary iodides were arrived at by an elaborate study which involved screening a number of different solvents, varying the molar ratios of reactants and studying the reaction at different temperatures, with and without the use of a catalyst, 2,2'-bipyridine. The development of optimum reaction conditions is discussed below and summarized in Table 2. In order to evaluate the best conditions for the cross-coupling of secondary iodides, 4-fluoroiodobenzene (VIIa) was selected as the substrate and R_f^1I as the aliphatic iodide. Using the optimum reaction conditions developed, it was found that 4-fluoroiodobenzene (VIIa) reacted with R_f^1I , providing high yield (90%, based on GC area) of the expected product, VIIIa (see Table 1). Interestingly, iodobenzene (VIIb) reacted equally well with R_f^1I to yield the desired product VIIIb in 91% yield (based on GC area).

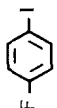
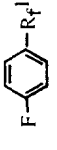
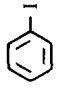
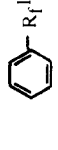
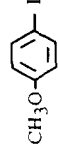
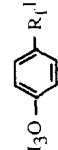
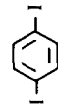
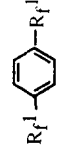
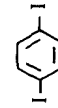
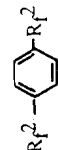
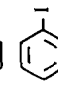
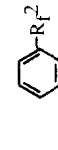
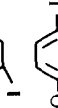
Effect of solvent

From previous work [2], it is known that a suitable polar aprotic solvent must be present for the cross-coupling reaction with primary iodides to succeed. DMSO and DMF are commonly used and DMSO is generally preferred. Even small amounts of DMSO in an inert diluent such as hexafluorobenzene are effective [2]. When the cross-coupling reaction between VIIa and R_f^1I was conducted at 120 °C using DMSO alone as the solvent, only traces of the substitution product, VIIIa, were formed in 3 h. However, the R_f^1I had completely disappeared while about 75% of VIIa remained unreacted. At 60 °C, the results were similar, except that there was still some R_f^1I present after 5 h. When DMF was used as the solvent, substantial amounts of 4-fluoro(pentafluoroethyl)benzene (Xa) were formed. Reactions using diglyme or hexafluorobenzene alone as solvents were also not successful (see Experiments 1–6, Table 2). However, hexafluorobenzene containing small amounts of DMSO, DMF or DMAC gave more encouraging results when secondary iodides are used.

Effect of ligand and catalyst

In Part 1 [1], we reported the beneficial effect of 2,2'-bipyridine in these copper-assisted cross-coupling reactions, when used in catalytic amounts. Hence,

TABLE 1. Formation and characterization of perfluorooxaalkylbenzenes^a

Aryl iodide	Aliphatic iodide ^b	Time of reaction (d)	Product ^b	Yield (%) ^c		B.p. (°C/mmHg)	MS (EI)	Elemental analysis (%)			
				A	B			C	H	F	F
	R _f ¹ I	6	 F- 	90	69	102/45	546 (M) ⁺	30.79 30.58	0.74 0.68	62.61 63.59	
	R _f ¹ I	3		91	73	98/50	528 (M) ⁺	31.84 31.40	0.95 0.86	61.15 60.58	
	R _f ¹ I	3	 CH ₃ O- 	72	40	214 ^g	558 (M) ⁺	32.28 32.08	1.26 1.16	57.86 57.95	
	R _f ¹ I	4	 R _f ¹ - 	82	55	233 ^g	909 ^e (M-CF ₃) ⁺	27.01 26.59	0.41 0.37	66.03 65.18	
	R _f ² I	7	 R _f ² - 	86	53	99/0.04	959 ^e (M-C ₃ F ₇ OC ₃ F ₆ O) ⁺	25.67 25.37	0.31 0.29	66.70 67.29	
	R _f ² I	7	 R _f ² - 	76	60	280 ^g	959 ^e (M-C ₃ F ₇ OC ₃ F ₆ O) ⁺	25.67 25.47	0.31 0.32	66.70 66.04	
	R _f ¹ I	2	 HO- 	8 ^f	-	-	544 (M) ⁺	-	-	-	-

^aThe reactions were conducted in C₆F₆ as solvent at 50 °C and in the presence of copper bronze, DMSO (ligand) and 2,2'-bipyridine (catalyst) in the molar ratio, aliphatic iodide/aryl iodide/Cu/DMSO/catalyst/solvent = 1:0.9:2.2:4:0.07:15.

^bSee Scheme 1.

^cA = GC area %; B = isolated yield.

^dIsolated by preparative GC.

^eMolecular ion peaks > 1000 amu were beyond the limit of the spectrometer. Fragmentation was consistent with structure.

^fNot isolated. By-products were **XII** (32%), **XIII** (36%); **XIV** (8%) and **XV** (7%).

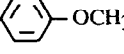
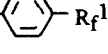
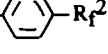
^gBoiling point determined by Differential Scanning Calorimetry (DSC).

TABLE 2. Optimization of yield in the reaction $\text{I}-\text{C}_6\text{H}_4-\text{F}$ (**VIIa**) + $\text{R}_f^1\text{I} \longrightarrow \text{R}_f^1-\text{C}_6\text{H}_4-\text{F}$ (**VIIIa**)

Expt. No.	Molar ratio of reactants ^a		Solvent ^d	Conditions		Yield of VIIIa (GC area %)	Remarks, by-products (GC area %)
	x (ligand) ^b	y (catalyst) ^c		Temp. (°C)	Time (h)		
1	–	none	DMSO	120	3	traces	R_f^1I completely consumed ^e
2	–	none	DMSO	60	5	traces	
3	–	none	DMF	120	48	none	Xa (94%)
4	–	0.07	DMF	60	17	none	Xa (95%)
5	–	none	Diglyme	120	96	none	R_f^1I completely consumed
6	–	none	C_6F_6	60	4	none	R_f^1I decreased with time VIIa (99%)
7	6.0 (DMSO)	0.07	C_6F_6	60	22	72	IXa (10%), VIIa (17%) ^f
8	6.0 (DMF)	0.07	C_6F_6	60	41	70	IXa (3%), Xb (8%), Xa (2%), VIIa (17%)
9	6.0 (DMAC)	0.07	C_6F_6	60	77	62	IXa (5%), Xb (8%), Xa (5%), VIIa (14%)
10	6.0 (HMPA)	0.07	C_6F_6	60	20	6	R_f^1I completely consumed VIIa (93%)
11	6.0 (CH_3CN)	0.07	C_6F_6	60	18	none	VIIa (99%)
12	1.0 (DMSO)	0.07	C_6F_6	60	4	29	VIIa (69%) ^f
13	2.0 (DMSO)	0.07	C_6F_6	60	6	45	VIIa (51%) ^f
14	4.0 (DMSO)	0.07	C_6F_6	60	4	13	VIIa (87%)
15	4.0 (DMSO)	0.07	C_6F_6	60	29	76	IXa (5%), VIIa (18%) ^f
16	8.0 (DMSO)	0.07	C_6F_6	60	28	61	IXa (19%), VIIa (18%) ^f
17	4.0 (DMSO)	0.07	C_6F_6	80	4	58	IXa (5%), VIIa (36%) ^f
18	4.0 (DMSO)	none	C_6F_6	80	4	16	VIIa (84%)
19	4.0 (DMSO)	none	C_6F_6	80	10	47	VIIa (43%), IXa (2%) ^h
20	4.0 (DMSO)	0.07	C_6F_6	50	4	8	VIIa (92%)
21	4.0 (DMSO)	0.07	C_6F_6	50	71	86	VIIa (12%), IXa (2%)
22	4.0 (DMSO)	0.07	C_6F_6	50	144	90	VIIa (5%), IXa (5%)

^a $\text{R}_f^1\text{I}/\text{VIIa}/\text{Cu}/\text{ligand}/\text{catalyst} = 1:0.9:2.2:x:y$.^bDMSO = Me_2SO ; DMF = $\text{HC}(\text{O})\text{NMe}_2$; DMAC = $\text{MeC}(\text{O})\text{NMe}_2$; HMPA = $(\text{Me}_2\text{N})_3\text{PO}$.^c2,2'-Bipyridine.^dSolvent was used in excess, $\sim 15\times$ molar excess with respect to R_f^1I .^eGave 20% $\text{F}-\text{C}_6\text{H}_4-\text{SMe}$.^fSmall amounts of fluorobenzene, $\text{F}-\text{C}_6\text{H}_4-\text{SMe}$ and other unidentified products were present.^gAbout 5% of fluorobenzene present.^hAbout 8% of products described in footnote f above.

TABLE 3. NMR spectra of some secondary perfluoroalkylether-substituted aromatic compounds^a

Compounds ^b	¹ H NMR δ (ppm)	¹⁹ F NMR δ (ppm)
	7.49 (um, <i>ortho</i> Hs); 7.00 (um, <i>meta</i> and <i>para</i> Hs)	–79 to –82.5 (AB, 2CF ₂ O); –80.2 (m, CF ₃ on CF); –81.7 (at, CF ₃ terminal); –84.7 (d, CF ₃ near ring); –129.8 (ts, CF ₂ next to CF ₃); –130.6 (tp, CF α to ring); –145.3 (m, CF in midchain)
	7.39 (dd, <i>meta</i> Hs to OCH ₃); 6.57 (dd, <i>ortho</i> Hs to OCH ₃); 3.16 (ts, OCH ₃)	–79 to –82.2 (AB, 2CF ₂ O); –80.2 (m, CF ₃ on CF); –81.7 (ut, CF ₃ terminal); –84.8 (s, CF ₃ near ring); –129.3 (td, CF α to ring); –129.8 (ts, CF ₂ next to CF ₃); –145.3 (m, CF in midchain)
	7.26 (dt, <i>meta</i> Hs to F); 6.61 (dt, <i>ortho</i> Hs to F)	–80.5 (p, CF ₃ on CF); –80.35 to –81.61 (nq, 2CF ₂ O); –81.80 (ut, CF ₃ terminal); –84.89 (d, CF ₃ near ring); –107.4 (m, F on ring); –129.7 (dd, CF α to ring); –129.9 (d, CF ₂ next to CF ₃); –145.3 (m, CF in midchain)
	7.75 (tod, Hs on ring)	–78 to –83 (AB, 4CF ₂ O); –80.6 (m, 2CF ₃ on CF); –82.6 (m, 2CF ₃ terminal); –85.0 (dd, 2CF ₃ near ring); –130.2 (d, 2CF ₂ next to CF ₃); –131.8 (tp, 2CF α to ring); –145.7 (M, 2CF in midchain)
	7.75 (tod, Hs on ring)	–79.6 to –83.2 (AB, 6CF ₂ O); –80.5 (tom, 4CF ₃ on CF); –82.1 (s, 2CF ₃ terminal); –84.7 (s, 2CF ₃ near ring); –130.2 (s, 2CF ₂ next to CF ₃); –131 (tod, 2CF α to ring); –145.4 (m, 4CF in chain)
	7.9 to 8.1 (om, Hs on ring)	–79 to –81 (um, 4CF ₃ on CF and 4CF ₂ O in midchain); –81.8 (sb, 2CF ₃ and 2CF ₂ O terminal); –84.7 (b, 2CF ₃ near ring); –129.9 (s, 2CF ₂ next to CF ₃); –130.3 (m, 2CF α to ring); –145.0 (m, 4CF in chain)

^a ¹H NMR (300 MHz), chemical shifts (ppm/TMS); ¹⁹F NMR (282.3 MHz), chemical shifts (ppm/CFC1₃ or Freon-113); AB = multiple AB patterns, at = asymmetric triplet, b = broad, d = doublet, dd = doubled doublet, dt = doubled triplet, m = multiplet, nq = nonequivalent quartet, om = overlapping multiplets, p = pentet, s = singlet, sb = singlet on broad base, td = two doublets, tod = two overlapping doublets, tom = two overlapping multiplets, tp = two peaks, ts = two singlets, um = unresolved multiplet, ut = unsymmetrical triplet.

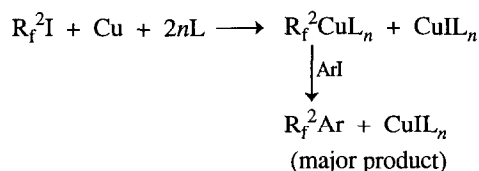
^b R_f¹ = CF₃CF₂CF₂OCF(CF₃)CF₂OCF(CF₃)–; R_f² = CF₃CF₂CF₂O[CF(CF₃)CF₂O]₂CF(CF₃)–.

2,2'-bipyridine was used as a catalyst in most of the reactions studied in the present work. As complexing ligands for the organocopper intermediates formed in these reactions, DMSO, DMF, acetonitrile, *N,N*-dimethylacetamide (DMAC) and hexamethylphosphoramide (HMPA) were used. Approximately 6.0 mol equiv. of these ligands, with respect to R_f¹I, were used with excess of hexafluorobenzene as solvent. As can be seen from Experiments 7–11, Table 2, DMSO and DMF gave the highest yields of the product **VIIIa** at 60 °C. In DMSO, however, the reaction proceeded faster than in DMF. Thus, DMSO was selected for further study. Studies with varying amounts of DMSO (Experiments 7, 12–16, Table 2) revealed that a molar ratio of 4:1 DMSO/R_f¹I gave the highest yield (76%). The effect of the catalyst (2,2'-bipyridine) is seen clearly in Experiments 17 and 18 (Table 2) conducted at 80 °C. After 4 h reaction, the yield of the product, **VIIIa**, increased from 16% to 58% when 2,2'-bipyridine was used as the catalyst.

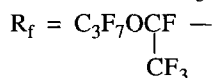
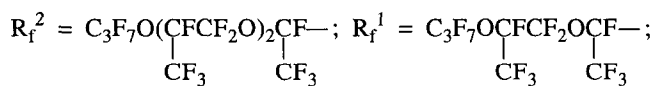
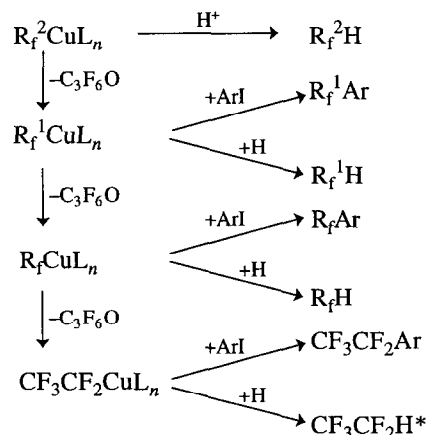
Effect of time and temperature

For the cross-coupling of R_f¹I and 4-fluoroiodobenzene (**VIIa**), the effect of temperature is seen by comparison of Experiments 20, 14 and 17 in Table 2. At temperatures of 50 °C, 60 °C and 80 °C after 4 h, the yields of the cross-coupled product, **VIIIa**, were 8%, 13% and 58%, respectively. However, decomposition of the starting iodide, R_f¹I, was greater at higher temperatures. From Table 2 at a given temperature, it can be seen that using similar reaction conditions, longer reaction times gave improved yields (Experiments 14, 15, 20, 21 and 22) with the best yield resulting from the reaction conducted at 50 °C for 144 h (Experiment 22).

The optimum conditions (based on maximum yield and purity of product) developed for the cross-coupling of R_f¹I and 4-fluoroiodobenzene (**VIIa**) were reaction at 50 °C in the molar ratio aliphatic iodide/aryl iodide/Cu/DMSO/2,2'-bipyridine/C₆F₆ = 1:0.9:2.2:4.0:0.07:15. These conditions were applied to the other iodoaromatic substrates studied as well as R_f²I, and the reactions were conducted for extended periods of time until the



By-product formation



L = ligand (DMSO); n = 2, 3

*Not detected.

Scheme 2. Probable mode of formation of products from R_f^2I .

concentration of the expected product reached a maximum. The results obtained are presented in Table 1. The NMR spectra of the substituted aromatic compounds prepared are presented in Table 3.

The optimum experimental conditions were also applied to reactions using 1,3,5-tribromobenzene and 2,4,6-triiodoanisole in an attempt to prepare trisubstituted materials. Employing these conditions, the reaction of R_f^2I with the tribromobenzene at 50 °C for 2 d gave the perfluorooxaalkyl dibromobenzene as the major product (42%) and c. 10% of the disubstituted bromobenzene. These results may be compared with the reaction of R_f^2I and 1,3,5-tribromobenzene conducted in DMSO alone at 120–135 °C, described earlier, in which no substitution product was formed. The reaction of R_f^2I with 1,3,5-tribromobenzene when conducted in C_6F_6 with DMF instead of DMSO, at 65 °C for 6 d, gave *m*- $R_f^2C_6H_4Br$ as the major product (44%) in addition to perfluorooxaalkyl dibromobenzene (18%) and *m*-(R_f^2) C_6H_4 (19%). Reaction of 2,4,6-triiodoanisole and R_f^2I under the optimum conditions, gave (after 4 d) 2,4-bis(perfluorooxaalkyl)anisole (57%) as

the major product. These products were identified only by MS and the indicated yields are in GC area %. In all these reactions additional products were present, formed by partial substitution and/or reductive dehalogenation. Trisubstitution was not achieved with either of these substrates.

In the present study using oligomeric secondary iodides, one consistent observation was the loss of the monomer units or unzipping of the oligomer chain, which accounted for some of the by-products formed. A probable mode of by-product formation is indicated in Scheme 2, although the exact mechanism is not understood. Similar unzipping has also been reported in an earlier study [6]. Our studies clearly demonstrate that it is possible to use secondary perfluorooxaalkyl iodides in cross-coupling reactions with the iodoaromatic substrates shown in Scheme 1. Carefully controlled experimental conditions are essential to realize a good yield of the desired products. However, when either tribromobenzene or triiodoanisole were used in place of the iodoaromatic substrates shown in Scheme 1, only mono- and di-substitution products were obtained and in low yields.

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