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POLYFLUOROALKYLATION OF BROMOAROMATIC COMPOUNDS VIA PERFLUORO-  
ALKYL COPPER INTERMEDIATES

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SUMMARY

Cross coupling reactions between various perfluoroalkyl iodides, copper and mono and dibromobenzenes, as well as mono and dibromobenzenes containing functional groups e.g., OH, CO<sub>2</sub>H, CO<sub>2</sub>R, NO<sub>2</sub>, NH<sub>2</sub>, OCH<sub>3</sub> and C(O)CH<sub>3</sub> have produced perfluoroalkyl substituted aromatic compounds in good to excellent yields. From certain bromo arenes, by-products were obtained, indicating competing reactions. These reactions may be due to the slower rate of cross coupling between a carbon-bromine bond and the perfluoroalkylcopper intermediate as compared to the cross coupling reaction involving a carbon-iodine bond with the perfluoroalkylcopper intermediate.

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## INTRODUCTION

Fluoroalkylation of aromatic compounds by means of free radicals and by organometallics, and  $SF_4/HF$  fluorination of fluoroketones have been previously reported [1-6]. One of the earliest methods, reported by McLoughlin and Thrower [7], provided a convenient method for the introduction of perfluoroalkyl groups onto an aromatic substrate through the reaction between an aromatic iodide, perfluoroalkyl iodide and copper in an aprotic solvent. By this process, mono perfluoroalkylation of aromatics gave yields in many instances of 60 - 70%. This procedure was also adaptable to iodoaromatics containing functional groups e.g. OH,  $CO_2H$ ,  $CO_2R$ ,  $NH_2$ ,  $NO_2$  and  $OCH_3$ . Since the functional groups did not seem to interfere in the perfluoroalkylation process, this method was reported to provide a convenient means of synthesis for a variety of mono perfluoroalkylated aromatic compounds.

We have studied this reaction in more detail and have extended it to include the perfluoroalkylation of bromoaromatic compounds. Mono and di-bromoaromatic compounds were perfluoroalkylated via a cross coupling reaction to produce good to excellent yields of unsubstituted and functionally substituted aromatic compounds. Because of the broader availability of bromoaromatic compounds over the iodoaromatic compounds, this process of perfluoroalkylation offers the possibility of synthesizing considerably more mono and polyperfluoroalkylated aromatic compounds.

## DISCUSSION

Three different experimental procedures were used, Method A (in situ method) where all the reactants were placed together and heated between 125° to 135°C; Method B, the perfluoroalkyl iodide was slowly added to a heated (125° to 130°C) mixture of bromoaromatic and copper and Method C, the bromoaromatic was added to a preformed perfluoroalkylcopper intermediate. The solvent of choice in all the reactions was dimethylsulfoxide (DMSO). With but a few exceptions, the solvent did not enter into the reaction with the aromatic substrate. On one occasion, some CH<sub>3</sub>S-substituted aromatics were identified as minor by-products (Exp. 16, Table 2). Compared to perfluoroalkylation of iodoaromatics, the bromoaromatics were perfluoroalkylated at slower rates, as would be expected and reported earlier [7]. A competition reaction (see Table 1) between one mole equivalent each of C<sub>6</sub>F<sub>13</sub>I, C<sub>6</sub>H<sub>5</sub>I, C<sub>6</sub>H<sub>5</sub>Br, and two mole equivalents of copper showed the faster rate of reaction for the aryl iodide.

TABLE 1

Competition reaction

TIME, hr.	PERCENT C <sub>6</sub> H <sub>5</sub> I REACTED*	PERCENT C <sub>6</sub> H <sub>5</sub> Br REACTED*
2	77	8
3	80	9
19	83	15

\*using an internal GC standard

The percentage of  $C_6H_5I$  and  $C_6H_5Br$  which actually reacted may be somewhat different since the  $CuBr$  and  $CuI$  formed in the reaction may undergo some halogen exchange reactions with the aromatic bromide and/or iodide. There is some evidence of such halogen-halogen exchange in Experiment 6 (see Table 2).

Under comparable conditions, perfluoroalkylation of iodobenzene occurred at a faster rate and provided a cleaner reaction mixture than bromobenzene. In situ reactions (Method A) between  $C_6H_5I$  and  $FC(CF_3)_2O(CF_2)_8I$  gave a 99.3% yield (GC area %) of the perfluoroalkylated product with ~ 0.7% of a disubstituted product (see Exp. 1, Table 2 with  $C_6H_5Br$  for comparison). Similarly,  $m-IC_6H_4OH$  gave 96% of the mono perfluoroalkylated product with approximately 4% of an unknown mixture of by-products (see Exp. 8, Table 2 with  $m-BrC_6H_4OH$  for comparison). Similarly,  $p-IC_6H_4OH$  gave 92% of fluorinated product and 8% of a mixture of unknown by-products (see Exp. 7, Table 2 with  $p-BrC_6H_4OH$  for comparison).

Aliquot samples were removed and analyzed by gas chromatography during the perfluoroalkylations. Some reactions were completed in 2 - 4 h depending on the reactivity of the bromoaromatic compound. The data shown in Table 2 is a summary of the perfluoroalkylation of various bromoaromatic compounds. For complete substitution of the aryl bromide usually an excess of the perfluoroalkyl iodide and copper was required. The copper was an industrial grade, 'copper bronze' and did not need activation. Gas chromatographic analysis of the reaction mixtures indicated some losses on work-up. In some cases, depending

on the bromoaromatic, competing reactions produced minor quantities of by-products, causing some difficulty in isolation of the principal product using fractional distillation. These by-products originate from a number of possible competing reactions e.g. 1) reductive dehalogenation [7,8], 2) multiple perfluoroalkylation beyond the number of carbon-bromine bonds present [9], 3) partial substitution in the case of the dibromoaromatic compounds and to a lesser extent 4) solvent interaction with the aromatic products. Results of the competing reactions can be seen in Table 2. As an example (Exp. 1) the reaction of  $C_6H_5Br$  with a slight excess (5 mole %) of  $FC(CF_3)_2O(CF_2)_8I$  gave a 78% yield of the expected monosubstituted product in addition to 11% of a mixture of disubstituted products and 11% of unreacted  $C_6H_5Br$ . On addition of more perfluoroalkyl iodide and copper and an additional 17.5 hours of reaction time, the yield of the monosubstituted product increased to 86 percent at the expense of the unreacted  $C_6H_5Br$ . Surprisingly, the yield of the disubstituted product was not increased. It is quite possible that, since the cross coupling reaction was slow, some of the perfluoroalkyl iodide or perfluoroalkylcopper intermediate may have decomposed to perfluoroalkyl free radicals which may be the source of the second perfluoroalkylation. It has been previously reported [3,5,6] that long chain perfluoroalkyl iodides on thermal degradation yielded free radicals capable of perfluoroalkylating aromatic compounds to yield a mixture of o, m and p-isomers. Polyperfluoroalkylation beyond the number of carbon halogen bonds present in the starting aromatic compound has also been noted by other investigators [3,6,9]. The mode of polysubstitution has not yet been clearly defined though free radical formation and attack on the aromatic compounds seems plausible.

TABLE 2  
Perfluoroalkylation of bromoaromatic compounds

Exp.	Method <sup>a</sup>	R <sub>f</sub> OR <sub>f</sub> <sup>b</sup> or R <sub>f</sub> I (mmol)		ArBr (mmol)	Cu (mmol)	Reaction		Products (% yield <sup>c,d</sup> )
		R <sub>f</sub> OR <sub>f</sub>	R <sub>f</sub> I			Time (h)		
1	A	R <sub>f</sub> OR <sub>f</sub>	(31.5)	C <sub>6</sub> H <sub>5</sub> Br (30.0)	(63.0)	4.5	C <sub>6</sub> H <sub>5</sub> Br	11 <sup>d</sup>
		n = 8					R <sub>f</sub> OR <sub>f</sub> C <sub>6</sub> H <sub>5</sub>	78 <sup>d</sup>
								(R <sub>f</sub> OR <sub>f</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>
	addi- tional	R <sub>f</sub> OR <sub>f</sub>	(5.6)	-----	(11.0)	(17.5)	R <sub>f</sub> OR <sub>f</sub> C <sub>6</sub> H <sub>5</sub>	74 <sup>c</sup> , 86 <sup>d</sup>
		total (37.1)			total (74.0)	total 22	(R <sub>f</sub> OR <sub>f</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	12 <sup>d</sup>
2	A	R <sub>f</sub> OR <sub>f</sub>	(58.0)	o-Br-C <sub>6</sub> H <sub>4</sub> (20.0)	(124)	7.5	R <sub>f</sub> OR <sub>f</sub> C <sub>6</sub> H <sub>5</sub>	5 <sup>d</sup>
		n = 4					o-(R <sub>f</sub> OR <sub>f</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	44 <sup>c</sup> , 74 <sup>d</sup>
								(R <sub>f</sub> OR <sub>f</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>3</sub>
						m + p (R <sub>f</sub> OR <sub>f</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	9 <sup>d</sup>	

3	B	$C_6F_{13}$ (52.0)	$o\text{-Br}_2C_6H_4$ (20.0)	(100)	3.5	$C_6F_{13}C_6H_5$ $o\text{-}(C_6F_{13})_2C_6H_4$ $m + p (C_6F_{13})_2C_6H_4$ $C_6F_{13}C_6H_4Br$ $(C_6F_{13})_3C_6H_3$	--- --- --- --- ---	$3^d$ $61^d$ $11^d$ $6^d$ $11^d$
4	A	$R_fOR_f$ (66.0) $n = 4$	$m\text{-Br}_2C_6H_4$ (25.0)	(136)	24	$R_fOR_fC_6H_5$ $m\text{-}(R_fOR_f)_2C_6H_4$	--- 78 <sup>c</sup> , 89 <sup>d</sup>	$4^d$ 89 <sup>d</sup>
5	A	$R_fOR_f$ (36.0) $n = 8$	$p\text{-Br}_2C_6H_4$ (15.0)	(77.0)	45	$R_fOR_fC_6H_5$ $p\text{-}(R_fOR_f)_2C_6H_4$	--- 83 <sup>c</sup>	$3^d$ 93 <sup>d</sup>

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(Continued)

TABLE 2 (cont.)

Exp.	Method <sup>a</sup>	R <sub>f</sub> OR <sub>f</sub> I <sup>b</sup> or		ArBr (mmol)	Cu (mmol)	Reaction		Products (% yield <sup>c,d</sup> )
		R <sub>f</sub> I (mmol)	R <sub>f</sub> I (mmol)			Time (h)		
6	A	R <sub>f</sub> OR <sub>f</sub> (31.0)	p-BrC <sub>6</sub> H <sub>4</sub> I (30.0)	(63.0)	16		C <sub>6</sub> H <sub>5</sub> Br(1 <sup>d</sup> ); C <sub>6</sub> H <sub>5</sub> I(1 <sup>d</sup> );	
		n = 8					C <sub>6</sub> H <sub>4</sub> Br <sub>2</sub> (10 <sup>d</sup> ); C <sub>6</sub> H <sub>4</sub> R <sub>f</sub> OR <sub>f</sub> (3 <sup>d</sup> ); C <sub>6</sub> H <sub>4</sub> Br(R <sub>f</sub> OR <sub>f</sub> )(37 <sup>d</sup> ); (R <sub>f</sub> OR <sub>f</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> (25 <sup>d</sup> ); C <sub>6</sub> H <sub>4</sub> BrI(7 <sup>d</sup> ); (R <sub>f</sub> OR <sub>f</sub> )C <sub>6</sub> H <sub>4</sub> I (16 <sup>d</sup> )	
7	A	R <sub>f</sub> OR <sub>f</sub> (33.0)	---	(69.0)	addi- tional		R <sub>f</sub> OR <sub>f</sub> C <sub>6</sub> H <sub>5</sub> --- 14 <sup>d</sup>	
		n = 8			8		p-(R <sub>f</sub> OR <sub>f</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> 63 <sup>c</sup> , 82 <sup>d</sup>	
7	A	R <sub>f</sub> OR <sub>f</sub> (37.5)	p-BrC <sub>6</sub> H <sub>4</sub> OH (30.0)	(75.0)	21		p-BrC <sub>6</sub> H <sub>4</sub> OH --- 10 <sup>d</sup>	
		n = 8					p-R <sub>f</sub> OR <sub>f</sub> C <sub>6</sub> H <sub>4</sub> OH --- 57 <sup>d</sup> unknowns --- 22 <sup>d</sup>	



8	C	C <sub>6</sub> F <sub>13</sub> (36.0)	m-BrC <sub>6</sub> H <sub>4</sub> OH (30)	(76.0)	4.5	m-BrC <sub>6</sub> H <sub>4</sub> OH m-C <sub>6</sub> F <sub>13</sub> C <sub>6</sub> H <sub>4</sub> OH unknowns	--- 28 <sup>c</sup> , ---	11 <sup>d</sup> 57 <sup>d</sup> 32 <sup>d</sup>
9	A	R <sub>F</sub> OR <sub>F</sub> (38.5) n = 8	m-BrC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H (30.0)	(78.0)	11	C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> H m-F <sub>13</sub> OR <sub>F</sub> C <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H unknowns	--- 50 <sup>c</sup> , ---	9 <sup>d</sup> 74 <sup>d</sup> 15 <sup>d</sup>
10	B	C <sub>6</sub> F <sub>13</sub> (36.0)	p-BrC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> (30.0)	(82.0)	4	p-C <sub>6</sub> F <sub>13</sub> C <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	93 <sup>c</sup>	99 <sup>d</sup>
11	A	C <sub>8</sub> F <sub>17</sub> (37.5)	m-BrC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> (30.0)	(75.0)	4	m-BrC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> m-C <sub>8</sub> F <sub>17</sub> C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> (C <sub>8</sub> F <sub>17</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> OCH <sub>3</sub>	--- 64 <sup>c</sup> , ---	2 <sup>d</sup> 86 <sup>d</sup> 11 <sup>d</sup>

(Continued)

TABLE 2 (cont.)

Exp.	Method <sup>a</sup>	R <sub>F</sub> -OR <sub>F</sub> I <sup>b</sup> or R <sub>F</sub> I (mmol)		ArBr (mmol)	Cu (mmol)	Reaction		Products (% yield <sup>c,d</sup> )	
						Time (h)			
12	A	C <sub>8</sub> F <sub>17</sub>	(39.0)	m-Br <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	(30.0)	(82.0)	22	m-C <sub>8</sub> F <sub>17</sub> C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> unknowns	68 <sup>c</sup> , 81 <sup>d</sup> -- 19 <sup>d</sup>
13	B	C <sub>6</sub> F <sub>13</sub>	(36.0)	p-BrC <sub>6</sub> H <sub>4</sub> C(O)CH <sub>3</sub> (30.0)	(82.0)	(82.0)	2.5	p-C <sub>6</sub> F <sub>13</sub> C <sub>6</sub> H <sub>4</sub> C(O)CH <sub>3</sub>	91 <sup>c</sup> 99 <sup>d</sup>
14	B	C <sub>6</sub> F <sub>13</sub>	(35.0)	2,4-Br <sub>2</sub> C <sub>6</sub> H <sub>3</sub> OCH <sub>3</sub> (15.0)	(82.0)	(82.0)	22	C <sub>6</sub> F <sub>13</sub> C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> 2,4-(C <sub>6</sub> F <sub>13</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> OCH <sub>3</sub>	--- 5 <sup>d</sup> 86 <sup>c</sup> , 94 <sup>d</sup>
15	B	C <sub>6</sub> F <sub>13</sub>	(36.0)	2,4-Br <sub>2</sub> C <sub>6</sub> H <sub>3</sub> NH <sub>2</sub> (15.0)	(82.0)	(82.0)	20	C <sub>6</sub> F <sub>13</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub> 2,4-(C <sub>6</sub> F <sub>13</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> NH <sub>2</sub> (C <sub>6</sub> F <sub>13</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>2</sub> NH <sub>2</sub>	--- 2 <sup>d</sup> 60 <sup>c</sup> 83 <sup>d</sup> --- 12 <sup>d</sup>

16	C	$C_6F_{13}$ (78.0)	1-Br $C_{10}H_7$ (60.0) (156)	22	$C_{10}H_8$	---	2 <sup>d</sup>
			(1-bromonaphthalene)		$C_{10}H_7Br$	---	14 <sup>d</sup>
					$C_{10}H_7SCH_3$	---	4 <sup>d</sup>
					1- $C_6F_{13}C_{10}H_7$	51 <sup>c</sup> ,	68 <sup>d</sup>
					unknowns	---	12 <sup>d</sup>
17	B	$C_6F_{13}$ (36.0)	1-Br $C_{10}H_7$ (30.0) (72)	3.5	$C_{10}H_8$	---	---
					$C_{10}H_7Br$	---	5 <sup>d</sup>
					1- $C_6F_{13}C_{10}H_7$	62 <sup>c</sup> ,	78 <sup>d</sup>
					unknowns	---	17 <sup>d</sup>

a Method A - in situ

B -  $R_fI$  added to ArX + Cu at 125-130°C

C - ArX added to preformed  $R_fCu$

b  $R_fOR_f = FC(CF_3)_2(CF_2)_n$

c isolated

d GC area %

In the o-dibromobenzene experiments (Exp. 2, Table 2) the presence of m- and p-disubstituted products as well as trisubstituted products may be an indication of substituent migration as also noted by Leroy *et al.* [10].

The hydroxy substituent in m- and p-bromophenols seems to cause (Exp. 7 and 8, Table 2) lower yields of the m- and p-perfluoroalkylated phenols as compared to the iodo analogs. In these two experiments, higher yields of a complex mixture of unidentified products were detected by GC analysis. The  $-\text{CO}_2\text{H}$  (Exp. 9, Table 2),  $-\text{OCH}_3$  (Exp. 11, Table 2 [9]) and  $-\text{NO}_2$  (Exp. 12, Table 2 [9]) substituted bromobenzenes gave very good yields of the perfluoroalkylated products. Exceptionally high yields of products were obtained from the bromo-arenes containing the  $-\text{C}(\text{O})\text{CH}_3$  (Exp. 13, Table 2) and  $-\text{CO}_2\text{C}_2\text{H}_5$  groups (Exp. 10, Table 2). The products were the only ones detected by GC analysis of the reaction mixtures.

The perfluoroalkylation reactions have been extended to dibromobenzene compounds containing  $-\text{OCH}_3$  (Exp. 14, Table 2) and  $-\text{NH}_2$  (Exp. 15, Table 2), to give excellent yields of diperfluoroalkylated products.

We have thus been able to provide perfluoroalkylated aromatic compounds, both functionally and non-functionally substituted, from a variety of readily available bromoaromatic compounds. This study has been extended to tribromobenzenes as well as to mono and polybrominated heterocyclic compounds. The results will be published in forthcoming communications.

## EXPERIMENTAL

All reactions were carried out in an atmosphere of dry nitrogen with the usual precaution for vigorous exclusion of moisture and air. Copper-bronze was purchased from Gallard Schlesinger Chemical Manufacturing Corporation, New York (U.S.A.) and was used directly without activation. Dimethylsulfoxide (DMSO), spectrographic grade, was used as purchased from Aldrich Chemical Company, Inc. (U.S.A). Gas chromatographic analyses were performed on a Perkin Elmer Sigma IIB gas chromatograph with a two-foot five percent Dexsil 400 on 100-120 mesh Supelcoport packed column or a Sigma I gas chromatograph with a six-foot, ten percent SE-30 on 80-100 mesh Supelcoport packed column. For separation of difficult mixtures of components, a SPB-1, 30 m. x 0.25 mm (ID) fused silica capillary column was used. The GC/MS analyses were performed on a Finnigan 4021 mass spectrometer using either chemical ionization or electron impact mode. Infrared spectra were recorded on a Perkin Elmer 683 spectrometer. NMR spectra were performed on an NT-300 spectrometer with TMS as internal reference for  $^1\text{H}$ . The  $^1\text{H}$  NMR data given in Table 5 shows in certain compounds small percentages of isomeric impurities. Since the purity of the starting bromides was not determined (except for o-dibromobenzene) it is possible that the impurities arose from other species present in the starting materials. Most compounds were characterized by a combination of analytical techniques e. g. IR, GC/MS, NMR and combustion analyses (see Table 3). All temperatures are uncorrected. Yields of products are reported as isolated yield or GC area % or both (see Table 2). Three experimental procedures were used, methods A, B, and C.

TABLE 3  
Analyses of perfluoroalkyl substituted aromatic compounds

Compound <sup>a</sup>	M.S.	m.p. (b.p., °C/mmHg)	Combustion Data (Calc'd/Found)		
			% C	% H	Other
$C_6H_4R_2OR_f$ (nc) n = 8	662 (M+)	--- (71/0.05)	30.83/30.88	0.76/0.86	-
$o-C_6H_4(R_fOR_f)_2$ (nc) n = 4	846 (M+)	--- (83/0.1)	28.39/28.08	0.48/0.48	-
$m-C_6H_4(R_fOR_f)_2$ (nc) n = 4	846 (M+)	43-45 (68-70/0.03)	28.39/28.20	0.48/0.51	67.36/67.58 (F)
$p-C_6H_4(R_fOR_f)_2$ (nc) n = 8	1246 (M+) <sup>b</sup> 711 (CF <sub>2</sub> C <sub>6</sub> H <sub>4</sub> R <sub>f</sub> OR <sub>f</sub> )	63-64 (153-155/0.05)	26.98/26.62	0.32/0.42	-
$p-R_fOR_fC_6H_4OH$ (nc) n = 8	678 (M+)	--- (103-105/0.06)	30.11/30.18	0.74/0.69	-
$m-C_6F_{13}C_6H_4OH$ (nc)	412 (M+)	--- (61-62/0.3)	34.97/34.65	1.22/1.21	-

$m\text{-R}_f\text{OR}_f\text{C}_6\text{H}_4\text{CO}_2\text{H}^c$ (nc)	706 (M+)	124-125	30.61/30.23	0.71/0.77	-
$n = 8$					
$p\text{-C}_6\text{F}_{13}\text{C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_5$ (nc)	468 (M+)	29-30 (80-81/0.1)	38.48/38.58	1.94/1.95	-
$m\text{-C}_6\text{F}_{17}\text{C}_6\text{H}_4\text{OCH}_3$ (nc)	526 (M+)	--- (63-65/0.03)	34.24/33.87	1.34/1.30	-
$m\text{-C}_8\text{F}_{17}\text{C}_6\text{H}_4\text{NO}_2$ (nc)	541 (M+)	53-54 (80-81/0.07)	31.07/31.01	0.75/0.80	2.59/2.73 (N)
$p\text{-C}_6\text{F}_{13}\text{C}_6\text{H}_4\text{COCH}_3$ (nc)	438 (M+)	47-49 (68/0.03)	38.37/37.89	1.61/1.61	-
$2,4\text{-}(\text{C}_6\text{F}_{13})_2\text{C}_6\text{H}_3\text{OCH}_3$ (nc)	744 (M+)	--- (88-89/0.03)	30.57/30.56	0.81/0.83	-
$2,4\text{-}(\text{C}_6\text{F}_{13})_2\text{C}_6\text{H}_3\text{NH}_2$ (nc)	729 (M+)	--- (89-90/0.03)	29.65/29.55	0.69/0.73	1.92/2.38 (N)
$1\text{-C}_6\text{F}_{13}\text{C}_{10}\text{H}_7$ (nc)	446 (M+)	--- (83-84/0.15)	43.07/43.57	1.58/1.67	-

<sup>a</sup>  $\text{R}_f\text{OR}_f = \text{CF}(\text{CF}_3)_2\text{O}(\text{CF}_2)_n$ ,  $n = 4$  or  $8$       <sup>b</sup> Parent ion peak (1246+) was beyond limit of spectrometer, however, fragmentation peaks were consistent with structure.      <sup>c</sup> Compound purified by recrystallization from  $\text{Et}_2\text{O}$  and hexane. On distillation, compound decomposed.

Method A: Synthesis of  $\text{FC}(\text{CF}_3)_2\text{O}(\text{CF}_2)_8\text{C}_6\text{H}_5$ 

Into a 250 ml three-necked flask with a thermometer, stirrer and a condenser with a nitrogen gas inlet, was added copper bronze powder (4.0 g., 63 mmol.),  $\text{FC}(\text{CF}_3)_2\text{O}(\text{CF}_2)_8\text{I}$  (22.43 g, 31.5 mmol) bromobenzene (4.71 g, 30 mmol) and DMSO (40 ml). The reaction mixture, under a nitrogen atmosphere, was heated to ~ 125°C (carefully monitored). An exothermic reaction was noted during the course of reaction and the temperature was controlled between ~ 125 - 135°C. Aliquot samples were removed periodically, hydrolyzed with water and extracted with  $\text{CFCl}_2\text{CClF}_2$  and analyzed by GC. After heating at ~ 125°C for 2.5 h and 4.5 h; GC analyses showed 11% of bromobenzene, 78% of expected mono-substituted product ( $\text{C}_6\text{H}_5\text{R}_f\text{OR}_f$ ) and 11% of di-substituted product ( $\text{C}_6\text{H}_4(\text{R}_f\text{OR}_f)_2$ , two isomers). Additional perfluoroalkylether iodide (4.0 g, 5.6 mmol) and copper bronze (0.7 g, 11 mmol) were added and the reaction mixture was heated again at ~ 125°C for an additional 17.5 h. The GC analysis showed no bromobenzene, 86% of  $\text{C}_6\text{H}_5\text{R}_f\text{OR}_f$ , 12% of  $\text{C}_6\text{H}_4(\text{R}_f\text{OR}_f)_2$  and 2% of unknown compounds. The reaction mixture was cooled to room temperature and  $\text{CFCl}_2\text{CClF}_2$  (80 ml) and water (40 ml) were added. The mixture was stirred and then centrifuged. The  $\text{CFCl}_2\text{CClF}_2$  and DMSO layers were decanted from the solid material and separated. The solid was extracted with additional  $\text{CFCl}_2\text{CClF}_2$  (2 x 30 ml). The organic solutions were combined, washed with  $\text{H}_2\text{O}$  (2 x 60 ml) and dried over  $\text{MgSO}_4$ . On evaporation of the solvent, a crude product (22.9 g) was obtained and subsequently distilled to yield  $\text{C}_6\text{H}_5\text{R}_f\text{OR}_f$  (b.p. 71°C/0.05 mmHg, 14.75 g, 74% yield) (See Table 2, Exp. 1).



Method B: Synthesis of 2,4-(C<sub>6</sub>F<sub>13</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OCH<sub>3</sub>

To a well-stirred mixture of copper bronze powder (5.21 g 82 mmol), 2,4-Br<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OCH<sub>3</sub> (3.99 g, 15 mmol) and DMSO (50 ml) under a nitrogen atmosphere at ~ 125°C was added n-C<sub>6</sub>F<sub>13</sub>I (15.72 g, 35.2 mmol) dropwise over a period of one hour. An exothermic reaction was noted and the rate of addition was controlled so that the temperature did not exceed 135°C. Aliquot samples were removed periodically, hydrolyzed and analyzed by GC. After stirring at ~ 125°C for 22 h, the yield of the expected product was maximized. The reaction mixture was worked up as for Method A, except using diethyl ether instead of CFC1<sub>2</sub>CClF<sub>2</sub>. The crude product (11.4 g) was distilled to yield the desired product in 86% yield (see Exp. 14, Table 2).

Method C: Synthesis of 1-perfluoro-n-hexylnaphthalene

To a suspension of copper bronze powder (9.92 g, 156 mmol) in DMSO (100 ml) at ~ 125°C was added n-C<sub>6</sub>F<sub>13</sub>I (34.79 g, 78.0 mmol) dropwise over 70 min. After the reaction was judged to be completed (1.4 h, tan color slurry), 1-bromonaphthalene (12.43 g, 60 mmol) was added. The mixture was heated for 22 h at ~ 120°C. Aliquots were removed from the reaction mixture periodically, hydrolyzed with water, extracted with diethyl ether and analyzed by GC. The results are listed in Table 4.

TABLE 4

Reaction of 1-bromonaphthalene and  $n\text{-C}_6\text{F}_{13}\text{Cu}$ 

Reaction time (h)	Unreacted		Products (GC area %)		
	$1\text{-BrC}_{10}\text{H}_8$	$\text{C}_{10}\text{H}_8$	$\text{C}_{10}\text{H}_7\text{SCH}_3$	$1\text{-C}_6\text{F}_{13}\text{C}_{10}\text{H}_7$	Others*
2.5	25	-	2	68	5
4.5	19	-	3	72	6
22.0	14	2	4	68	12

\*unidentified products

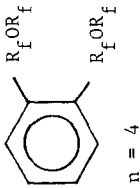
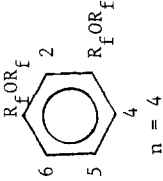
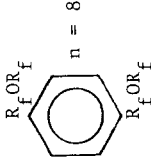
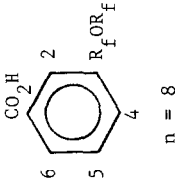
The reaction mixture was worked up as for Method A, except using diethylether instead of  $\text{CFCl}_2\text{CClF}_2$ . The crude residue (24.5 g) was distilled to yield 1-perfluoro-n-hexylnaphthalene (13.56 g, b.p.  $83\text{-}84^\circ\text{C}/0.15\text{ mmHg}$ , 51% yield) (Table 2, Exp. 16).

Another reaction was carried out by Method B for a shorter reaction time. The results are shown in Table 2, Exp. 17. The by-product,  $\text{C}_{10}\text{H}_7\text{SCH}_3$ , due to solvent reaction, was absent.

Reaction between 1,2-dibromobenzene, copper and  $\text{FC}(\text{CF}_3)_2\text{O}(\text{CF}_2)_4\text{I}$

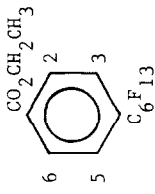
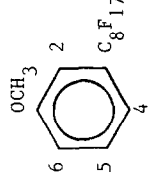
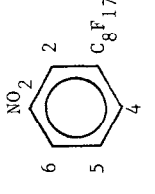
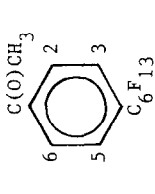
The reaction was carried out using copper bronze powder (7.87 g, 124 mmol), 1,2-dibromobenzene containing no isomers (4.72 g, 20 mmol),  $\text{FC}(\text{CF}_3)_2\text{O}(\text{CF}_2)_4\text{I}$  (29.62 g, 57.9 mmol) and DMSO (50 ml) (Method A) and heating the reaction mixture at  $\sim 125^\circ\text{C}$  for 7.5 h. The crude product (18.7 g) was analyzed by GC and the results are listed in Table 2 (Exp. 2). The crude residue was distilled to yield fraction 1) 4.1 g, b.p.  $80\text{-}85^\circ\text{C}/0.1\text{ mmHg}$ , 24% yield which by GC/MS was a mixture of o,m, and p- $\text{C}_6\text{H}_4(\text{R}_f\text{OR}_f)_2$ . The GC area % of this mixture was 72% -ortho, 23% -meta and 5% -para isomers. The second fraction 2) was pure o- $\text{C}_6\text{H}_4(\text{R}_f\text{OR}_f)_2$  (7.44 g, b.p.  $83^\circ\text{C}/0.10\text{ mmHg}$ , 44% yield).

TABLE 5  
 NMR spectra<sup>a</sup> of some perfluoroalkyl substituted aromatic compounds

Compound <sup>b</sup>	<sup>1</sup> H NMR	Comments
 $n = 4$	7.60 to 7.85(m) (A <sub>2</sub> B <sub>2</sub> pattern)	< 0.3% of another isomer
 $n = 4$	7.63(t) (H <sub>5</sub> ) 7.83 (overlapping d and s) (H <sub>2</sub> , H <sub>4</sub> , H <sub>6</sub> )	no evidence of other isomer
 $n = 8$	7.90(s)	< 3% of another isomer
 $n = 8$	7.64(t) (H <sub>5</sub> ), 7.85(d) (H <sub>4</sub> ), 8.35(c) (H <sub>6</sub> ), 8.40(s) (H <sub>2</sub> )	< 1% of another isomer

(Continued)

TABLE 5 (cont.)

Compound <sup>b</sup>	<sup>1</sup> H NMR	Comments
	1.40(t)(CH <sub>3</sub> ), 4.42(q)(CH <sub>2</sub> O) 7.67(d)(H <sub>3</sub> , H <sub>5</sub> ), 8.19(d)(H <sub>2</sub> , H <sub>6</sub> )	no evidence of other isomer
	3.75(s)(CH <sub>3</sub> ), 7.03(d)(H <sub>4</sub> ), 7.13(s)(H <sub>2</sub> ), 7.16(d)(H <sub>6</sub> ), 7.33(t)(H <sub>5</sub> )	no evidence of other isomer
	7.19(t)(H <sub>5</sub> ), 7.96(d)(H <sub>4</sub> ), 8.50(m)(H <sub>2</sub> , H <sub>6</sub> )	~ 2% of another isomer
	2.79(s)(CH <sub>3</sub> ), 7.87(d)(H <sub>3</sub> , H <sub>5</sub> ) 8.24(d)(H <sub>2</sub> , H <sub>6</sub> )	no evidence of other isomer

	<p>3.90(s)(CH<sub>3</sub>), 7.11(d)(H<sub>6</sub>), 7.73(d)(H<sub>5</sub>), 7.76(s)(H<sub>3</sub>)</p>	<p>2-3% of another isomer</p>
	<p>4.52(s)(NH<sub>2</sub>), 6.70(d)(H<sub>6</sub>), 7.45(d)(H<sub>3</sub>), 7.58(s)(H<sub>3</sub>)</p>	<p>~ 5% of another isomer</p>
	<p>7.22(t)(H<sub>3</sub>), 7.30(t)(H<sub>6</sub> or H<sub>7</sub>), 7.39(t)(H<sub>6</sub> or H<sub>7</sub>), 7.61(d)(H<sub>8</sub>), 7.70(d)(H<sub>4</sub> and H<sub>5</sub>), 8.25(d)(H<sub>2</sub>)</p>	<p>~ 3% of another isomer probably the 2-isomer</p>

<sup>a</sup> <sup>1</sup>H NMR (300 MHz), chemical shifts (ppm/TMS), s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet  
<sup>b</sup> R<sub>f</sub>OR<sub>f</sub> = CF(CF<sub>3</sub>)<sub>2</sub>O(CF<sub>2</sub>)<sub>n</sub> n = 4 or 8

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