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# Perfluoroalkylations and perfluorooxaalkylations*. Part 1. Bromoaromatics as substrates in copper-mediated cross-coupling**

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## Abstract

Tribromobenzenes, bromobiphenyl ethers and a bromoterphenyl ether have been used as substrates in copper-mediated cross-coupling reactions with perfluoroalkyl and perfluorooxaalkyl iodides. Excellent yields were obtained from perfluoroalkyl iodides as well as the ether iodides in which the ether oxygen was situated at position 5 or higher. However, ether iodides where the ether oxygen was at the 3-position gave only traces of the cross-coupled product, if any. This difference in reactivity is based on the relative position of the ether linkage to the reaction site and was more pronounced in reactions with aryl bromides than in reactions with aryl iodides.

## Introduction

Among the variety of methods available for fluoroalkylations [1], the reactions of fluoroalkylcopper derivatives with aryl and vinyl halides have been well documented [1a, 2–5]. For substitutions on the aromatic ring, aryl iodides are commonly used. The copper-mediated cross-coupling reaction has been investigated previously in detail in this laboratory and has been extended to certain perflurooxaalkyl iodides as well as some bromoaromatics [1a] and bromoheterocyclic compounds [5]. In previous efforts, it was shown that, with proper control of experimental conditions, it is possible to obtain a variety of perfluoroalkylated products in good to excellent yields, utilizing brominated rather than iodinated substrates.

In continuing these studies we have extended the cross-coupling reaction to include tribromobenzenes as well as brominated diphenyl ethers and a bromoterphenyl ether. These brominated substrates are more readily available than the corresponding iodo analogs.

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*The term 'perfluorooxaalkylation' is used to represent the introduction of a perfluoroalkyl group containing non-terminal oxygen atom(s) and to distinguish the process from 'perfluoroalkoxylation' where a perfluoroalkyl group is attached to the substrate through an oxygen atom.

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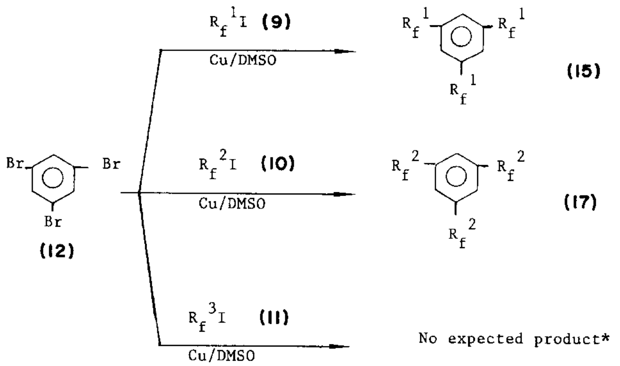
## Results and discussion

As the aliphatic component in these copper-mediated reactions, we have used a perfluoro-n-hexyl iodide (**1**) and 1,6-diiodoperfluorohexane (**2**), as well as three different perfluorooxaalkyl iodides. The cross-coupling reactions involving bromophenyl ethers **3–5** and either **1** or **2** proceeded readily in dimethylsulfoxide (DMSO) providing good to excellent yields of the expected products **6–8** (see Table 1, Exp. 1–4).

The three different perfluorooxaalkyl iodides used in this study differed from each other in the position of the ether linkage relative to the iodine atom. The reactions of these perfluorooxaalkyl iodides (**9–11**) with 1,3,5-tribromobenzene (**12**) are illustrated in Scheme 1. Those perfluorooxaalkyl iodides where the ether oxygen was separated from the iodine atom by four or eight difluoromethylene groups, i.e. $R_f^1I$ (**9**) and $R_f^2I$ (**10**), behaved like perfluoroalkyl iodides in reactions with substrates such as dibromoterphenyl (**4**), 1,3,5-tribromobenzene (**12**) and 1,2,4-tribromobenzene (**13**) giving excellent yields of the cross-coupled products **14–17** (see Scheme 1 and Table 1, Exp. 5–8). However, an iodide $R_f^3I$ (**11**) having only two difluoromethylene groups separating the iodine atom and the ether oxygen behaved quite differently. Thus, compound **11** gave no trisubstitution product on reaction with 1,3,5-tribromobenzene (**12**). On work-up of the reaction mixture, substantial amounts (>80%) of the starting iodide **11** were recovered. By-products formed were **18** and **19** (see Scheme 1) in addition to products of partial substitution and reductive dehalogenation, reaction with DMSO,



**9, 15**: $R_f^1 = (CF_3)_2CFO(CF_2)_4-$

**10, 17**: $R_f^2 = (CF_3)_2CFO(CF_2)_8-$

**11, 18**: $R_f^3 = C_3F_7O[CF(CF_3)CF_2O]_2CF_2CF_2-$

*$R_f^3I$, > 80 GC area %, $R_f^3H$ (18), $C_3F_7OCF(CF_3)CF_2OCF_2CF_2H$ (19), and small amounts of other products (see Table 1, Exp. 9).

Scheme 1.

etc. (Table 1, Exp. 9). Reaction of $R_f^3I$ (**11**) with bromobenzene (**20**) led to similar results (Table 1, Exp. 10). Similar by-products have also been reported in earlier work [3] where aryl iodides were employed as substrates, and by-product formation was explained on the basis of side-reactions involving an intermediate copper complex formed from the aliphatic iodide.

The reason for the unusual behavior of perfluorooxaalkyl iodides of the type $R_f^3I$ (**11**) in these copper-assisted reactions is not clear at present. One possible explanation is that iodides such as **11** do not form a copper complex in DMSO as readily as a perfluoroalkyl iodide or ether iodides such as $R_f^1I$ (**9**) and $R_f^2I$ (**10**). A second possibility is that, once a copper complex is formed from iodides such as **11**, it is stabilized in some fashion, thus inhibiting further reaction with the aromatic substrate. Our results support either of these postulates and it may be that both processes contribute to the lower reactivity of the type $R_f^3I$ (**11**) iodides. For example, in the reaction between **11** and 1,3,5-tribromobenzene (**12**), a longer reaction time was required for the complete disappearance of metallic copper than in the reaction between **12** and **9** or **10**. Furthermore, $>80\%$ of the starting iodide (**11**) was recovered in the reaction between **11** and **12** as well as between **11** and bromobenzene (**20**). The fact that large quantities of **11** were recovered in these reactions, however, does not suggest necessarily that only a small amount of the copper complex is actually formed or that the copper complex from **11** forms slowly. A copper complex could be formed from **11** and could revert back to the starting iodide (**11**) on work-up of the reaction mixture in the presence of air. This is supported by the published work [3] that, on passing dry air through the DMSO solution of the copper complex derived from 1-iodo-3-phenylhexafluoropropane, in which no free iodo compound was present, 65% of the iodide was recovered. This observation suggests that the copper complex formed from the iodide in DMSO is a soluble complex and has iodine (probably as CuI) associated with it, and that the starting iodo compound is regenerated in the presence of air.

Considering the possibility of enhanced stability of the copper complex from $R_f^3I$ (**11**) as compared to that from $R_f^1I$ (**9**) or $R_f^2I$ (**10**), there is no direct evidence other than the observed lack of reactivity of **11** with the substrates 1,3,5-tribromobenzene (**12**) and bromobenzene (**20**). However, in our earlier studies [6, 7], a perfluorooxaalkyllithium compound having similar structural features, i.e. an ether linkage at the 3-position, was shown to possess relatively high stability. The $(CF_3)_2CFOCF_2CF_2Li$ generated from the corresponding iodide, was stable at $-78$ °C in diethyl ether for up to 24 h and reacted smoothly with substrates such as hexafluoroacetone. In contrast, a perfluoroalkyllithium such as $C_6F_{13}Li$ decomposed readily under the same conditions.

Although iodides such as $R_f^3I$ (**11**) fail to undergo the copper-assisted cross-coupling reaction with bromoaromatics in DMSO, they are reported to react with iodoaromatic compounds in DMF [8, 9] giving rise to cross-coupled products. However, the relatively low yields of the products obtained and/or the longer reactions times required to realize reasonable yields, reflect

TABLE 1

Perfluoroalkylations and perfluorooxaalkylations of bromoaromatic compounds[a]

| Exp. | Iodofluoro compounds[b] (mmol) | Bromoaromatic compounds (mmol) | Copper (mmol) | Reaction time (h) | Products, isolated yield (%)[c] |
|---|---|---|---|---|---|
| 1 | n-$C_6F_{13}I$ (48)<br>**(1)** | $(4\text{-}BrC_6H_4)_2O$ (20)<br>**(3)** | 106 | 5 | $[(4\text{-}C_6F_{13})C_6H_4]_2O$, 79<br>**(6)** |
| 2 | n-$C_6F_{13}I$ (48)<br>**(1)** | 1,3-$(3\text{-}BrC_6H_4O)_2C_6H_4$ (20)<br>**(4)** | 106 | 4 | 1,3-$[(3\text{-}C_6F_{13})C_6H_4O]_2C_6H_4$, 88<br>**(7)** |
| 3 | $I(CF_2)_6I$ (9)<br>**(2)** | 4-$BrC_6H_4OC_6H_5$ (21)<br>**(5)** | 38 | 20[d] | $[(4\text{-}C_6H_5O)C_6H_4(CF_2)_3]_2$, 60[e]<br>**(8)** |
| 4 | $I(CF_2)_6I$ (9)<br>**(2)** | 4-$BrC_6H_4OC_6H_5$ (20)<br>**(5)** | 37 | 8 | $[(4\text{-}C_6H_5O)C_6H_4(CF_2)_3]_2$, 50[e]<br>**(8)** |
| 5 | $R_f^1I$ (142)<br>**(9)** | 1,3-$(3\text{-}BrC_6H_4O)_2C_6H_4$ (53)<br>**(4)** | 323 | 4 | 1,3-$[(3\text{-}R_f^1)C_6H_4O]_2C_6H_4$, 89<br>**(14)** |
| 6 | $R_f^1I$ (118)<br>**(9)** | 1,3,5-$Br_3C_6H_3$ (30)<br>**(12)** | 236 | 24 | 1,3,5-$(R_f^1)_3C_6H_3$, 76<br>**(15)** |
| 7 | $R_f^1I$ (120)<br>**(9)** | 1,2,4-$Br_3C_6H_3$ (30)<br>**(13)** | 240 | 5 | 1,2,4-$(R_f^1)_3C_6H_3$, 78<br>**(16)** |
| 8 | $R_f^2I$ (54)<br>**(10)** | 1,3,5-$Br_3C_6H_3$ (15)<br>**(12)** | 108 | 21 | 1,3,5-$(R_f^2)_3C_6H_3$, 72<br>**(17)** |
| 9 | $R_f^3I$ (39)<br>**(11)** | 1,3,5-$Br_3C_6H_3$ (10)<br>**(12)** | 75 | 28 | 1,3,5-$(R_f^3)_3C_6H_3$, 0[f] |

| | | | | | |
|---|---|---|---|---|---|
| 10 | $R_f^3I$ (1.3)<br>**(11)** | $BrC_6H_5$ (1.3)<br>**(20)** | 3 | 20 | $R_f^3C_6H_5$, trace[g] |

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[a] Reaction temperature, 120–135 °C; solvent, DMSO.

[b] $R_f^1 = (CF_3)_2CFO(CF_2)_4-$; $R_f^2 = (CF_3)_2CFO(CF_2)_8-$; $R_f^3 = C_3F_7O[CF(CF_3)CF_2O]_2CF_2CF_2-$.

[c] Yield based on bromoaromatic compounds. By-products were products of partial substitution, reductive dehalogenation and reaction with DMSO.

[d] Reaction temperature, ~80 °C; 2,2′-bipyridine (0.7 mmol) was used as catalyst.

[e] Yield based on $I(CF_2)_6I$.

[f] The starting iodide was recovered in >80% yield based on GC area %. By-products formed in small amounts were, in addition to unknown compounds, $R_f^3H$ (**18**) and its lower homolog $C_3F_7OCF(CF_3)CF_2OCF_2CF_2H$ (**19**), $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C_6H_4Br$, $R_f^3C_6H_4Br$, $R_f^3C_6H_5$, $R_f^3C_6H_4SCH_3$, $CH_3SC_6H_5$ and $(CH_3S)_2C_6H_4$. These were identified by GC/MS methods alone.

[g] $R_f^3I$ was recovered in >80% yield as in Exp. 10. Other products included $R_f^3H$ (**18**), $CH_3SC_6H_5$ and unknown compounds.

the differences in behavior of iodides of type $R_f{}^3I$ (**11**) compared to perfluoroalkyl iodides and ether iodides of the type $R_f{}^1I$ (**9**) and $R_f{}^2I$ (**10**). It is also reported that the iodide $C_8F_{17}OCF_2I$, in which only one difluoromethylene group separates the ether oxygen from the iodine atom, failed to undergo the copper-promoted cross-coupling reaction even with an iodoaromatic substrate like 4-iodobenzil in DMF [9].

From our observations, as well as published information, it may be concluded that perfluorooxaalkyl iodides having the general formula $R_fO(CF_2)_nI$, where $R_f$ is a perfluoroalkyl group and $n=1$ or 2, behave quite differently than those where $n=4$ or 8. We were unable to obtain a suitable iodine having $n=3$ in order to study its behavior.

Generally, it has been recognized that in these copper-assisted cross-coupling reactions, the aryl bromides react at a slower rate than the aryl iodides [1a, 3]. Hence, reactions involving aryl bromides had to be conducted for a relatively longer duration or at higher temperatures than the corresponding aryl iodides in order to achieve complete reaction. It was preferable to conduct these reactions between 120 °C and 135 °C for longer duration in order to suppress competing side-reactions and to obtain high yields. By using a bidentate ligand such as 2,2′-bipyridine [10] as a catalyst, the reaction temperature could be lowered even further. These results and experimental conditions are presented in Table 1.

Further studies are in progress utilizing secondary perfluorooxaalkyl iodides in these copper-assisted reactions.

## Experimental

### *General comments*

All reactions were carried out in oven-dried glassware under an atmosphere of dry nitrogen. Copper bronze was purchased from Gallard Schlesinger Chemical Manufacturing Corporation, New York (USA) and used directly without activation. Solvents dimethylsulfoxide (DMSO, spectrographic grade), diethyl ether (anhydrous) and Freon-113 were used as purchased. All reactants and 2,2′-bipyridine were commercially available except $(CF_3)_2CFO(CF_2)_4I$ ($R_f{}^1I$) (**9**) and $(CF_3)_2CFO(CF_2)_8I$ ($R_f{}^2I$) (**10**) which were obtained from Allied Chemical Co., $C_3F_7O[CF(CF_3)CF_2O]_2CF_2CF_2I$ ($R_f{}^3I$) (**11**) which was received from PCR Inc. and 1,3-(3-$BrC_6H_4O)_2C_6H_4$ (**4**) which was prepared by a reported procedure [11]. Gas chromatographic analyses were performed on a Perkin-Elmer Sigma I or IIB chromatograph using a 2 ft. stainless-steel column (1/4 in. i.d.) packed with 5% Dexsil 400 on 100–120 mesh Supelcoport or 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 obtained on a Finnigan 4021 mass spectrometer using 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 (see Table 2). All temperatures are uncorrected. Most compounds were characterized by a combination of analytical techniques, e.g. IR, GC/MS, NMR and elemental analyses (see Tables 2 and 3).

### *Synthesis of 1,3,5-[$(CF_3)_2CFO(CF_2)_4]_3C_6H_3$ (15) (nc) (see Table 1, Exp. 6)*

A mixture of 1,3,5-$Br_3C_6H_3$ (**12**) (9.45 g, 30 mmol), $(CF_3)_2CFO(CF_2)_4I$ (**9**) (60.3 g, 118 mmol), copper bronze (15.0 g, 236 mmol) and DMSO solvent (70 ml) were placed in a 300 ml three-necked flask fitted with a thermometer, stirrer and a condenser connected to a nitrogen gas inlet. The reaction mixture was heated at ~ 125 °C under dry $N_2$. An exothermic reaction was noted during the course of reaction, and the temperature was controlled between ~125 °C to ~135 °C. Aliquot samples were removed periodically, hydrolyzed with water, extracted with Freon-113 and analyzed by GC methods. After 24 h, the reaction mixture was cooled to room temperature and Freon-113 (80 ml) and water (80 ml) were added. The mixture was stirred and centrifuged. The organic and water layers were decanted from the solid material and separated. The solid residue was extracted with additional Freon-113 ($3 \times 30$ ml). The combined organic solution was washed with water ($3 \times 30$ ml) and dried over $MgSO_4$. GC analysis showed 87% of **15**, and smaller amounts of 3,5-[$(CF_3)_2CFO(CF_2)_4]_2C_6H_3Br$, 1,3-[$(CF_3)_2CFO(CF_2)_4]_2C_6H_4$ and unknown compounds. The solvent was removed by means of rotary evaporator. The crude product (38.8 g) obtained was distilled to yield the desired product (**15**), 28.1 g (yield 76%); b.p. 124 °C/ 0.07 mmHg.

### *Synthesis of 1,2,4-[$(CF_3)_2CFO(CF_2)_4]_3C_6H_3$ (16) (nc) and 1,3,5-[$(CF_3)_2CFO(CF_2)_8]_3C_6H_3$ (17) (nc)*

These compounds were synthesized by the same procedure as outlined above for compound **15** (see Scheme 1 and Table 1, Exp. 7 and 8).

### *Attempted preparation of $R_f^3C_6H_5$ and 1,3,5-$(R_f^3)_3C_6H_3$; ($R_f^3 = C_3F_7O[CF(CF_3)CF_2O]_2CF_2CF_2-$)*

These reactions were conducted in a similar manner as described above for compound **15** (see Scheme 1 and Table 1, Exp. 9 and 10). GC analysis of the reaction mixture indicated the following.

For the reaction of $R_f^3I$ (**11**) and $BrC_6H_5$ (**20**): >80% of the starting iodide (**11**) was recovered. The minor products were $R_f^3C_6H_5$ (traces), $R_f^3H$ (**18**), $CH_3SC_6H_5$ and unknown compounds (traces).

For the reaction of **11** and **12**: again >80% of the starting iodide (**11**) was recovered. The desired trisubstitution product was not formed. The minor products were $R_f^3H$ (**18**), **19**, $R_f^3C_6H_5$, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C_6H_4Br$, $R_f^3C_6H_4Br$, $R_f^3C_6H_4SCH_3$, $CH_3SC_6H_5$, $(CH_3S)_2C_6H_4$ and unknown compounds.

### *Synthesis of [$(4\text{-}C_6H_5OC_6H_4(CF_2)_3]_2$ (8) (see Table 1, Exp. 3)*

Copper bronze (2.38 g, 37.5 mmol), 2,2′-bipyridine (0.11 g, 0.7 mmol), DMSO (30 ml), 4-$BrC_6H_4OC_6H_5$ (**5**) (5.2 g, 20.9 mmol) and $I(CF_2)_6I$ (**2**)

TABLE 2

NMR spectra of some perfluoroalkyl and perfluorooxaalkyl aromatic compounds[a]

| Compounds | $^1$H NMR | $^{19}$F NMR |
|---|---|---|
| 1,3,5-$(R_f^1)_3C_6H_3$[b] **(15)** | 8.13 (s) | −80.8 (b, $3CF_2O$); −81.5 (d, $6CF_3$); −112.2 (b, $3CF_2$); −122.7 (b, $3CF_2$); −125.0 (b, $3CF_2$); −145.9 (b, 3CFO) |
| 1,2,4-$(R_f^1)_3C_6H_3$[b] **(16)** | 8.00 (b, 2H);<br>7.97 (b, 1H) | −81.1 (m, $6CF_3$ and $3CF_2O$); −104.4 (b, $2CF_2$)/ −112.6 (t, $J$=13.6 Hz, $CF_2$); −118.9 and −119.1 (b, $2CF_2$); −112.6 (b, $CF_2$); −125.0 ($CF_2$); −125.6 (b, $2CF_2$); −145.9 (m, 3CFO) |
| $[(4\text{-}C_6H_5O)C_6H_4(CF_2)_3]_2$[c] **(8)** | A. 7.66 (d); B. 7.46 (m);<br>C. 7.25 (tt); D. 7.14 (om) | −108.9 (um, $2CF_2$); −120.8 (um, $2CF_2$); −121.3 (um, $2CF_2$) |
| $[(4\text{-}C_6F_{13})C_6H_4]_2O$ **(6)** | 7.59 (d, J=11.33 Hz)<br>7.12 (d, J=11.33 Hz) | −81.6 (t, $J$=10.0 Hz, $CF_3$); −110.5 (t, $J$=14.5 Hz, $CF_2$); −121.8 (b, $CF_2$); −122.1 (b, $CF_2$); −123.2 (b, $CF_2$); −126.6 (b, $CF_2$) |

[a] $^1$H NMR (300 MHz), chemical shifts (ppm/TMS); $^{19}$F NMR (282.3 MHz), chemical shifts (ppm/Freon-113 or $CFCl_3$); s=singlet, b=broad, d=doublet, t=triplet, tt=triplet of triplets, m=multiplet, om=overlapping multiplets, um=unresolved multiplets.

[b] $R_f^1=(CF_3)_2CFO(CF_2)_4$.

[c]

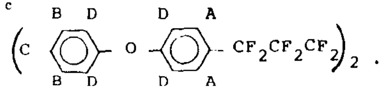

TABLE 3

Physical properties and analysis of perfluoroalkyl- and perfluorooxaalkyl-substituted aromatic compounds

| Compounds | MS (*m/e*) | B.p. (°C/mmHg) (m.p.) | Elemental analysis (Calc./Found) | | |
|---|---|---|---|---|---|
| | | | %C | %H | %F |
| 1,3,5-$(R_f^1)_3C_6H_3$[a] | 895 $[M-C_3F_7O(CF_2)_3]^{+b}$; | 124/0.07 | 26.36 | 0.25 | 69.49 |
| **(15)** | | | 26.02 | 0.29 | 69.31 |
| | 375 $[C_6H_3(C_2F_4)_3]^+$ | | | | |
| 1,2,4-$(R_f^1)_3C_6H_3$[a] | 895 $[M-C_3F_7O(CF_2)_3]^{+b}$; | 126/0.06 | 26.36 | 0.25 | 69.49 |
| **(16)** | | | 26.31 | 0.25 | 68.97 |
| | 375 $[C_6H_3(C_2F_4)_3]^+$ | | | | |
| 1,3,5-$(R_f^2)_3C_6H_3$[c] | 375 $[C_6H_3(C_2F_4)_3]^{+b}$ | 188/0.01 | 25.59 | 0.17 | 71.62 |
| **(17)** | | (45) | 25.28 | 0.20 | 71.56 |
| $[(4\text{-}C_6H_5O)C_6H_4(CF_2)_3]_2$[d] | 638 $[M^+]$; | 227/0.03 | 56.44 | 2.84 | 35.71 |
| **(8)** | 219 $[C_6H_5OC_6H_4CF_2]^+$ | (97) | 56.27 | 2.71 | 36.15 |
| $[(4\text{-}C_6F_{13})C_6H_4]_2O$ | 806 $[M^+]$; | 139/0.45 | 35.75 | 1.00 | 61.26 |
| **(6)** | 787 $[M-F]^+$ | (59) | 35.57 | 1.06 | 60.87 |
| 1,3-$[(3\text{-}C_6F_{13})C_6H_4O]_2C_6H_4$ | 898 $[M^+]$; | 161/0.03 | 40.11 | 1.35 | 54.98 |
| **(7)** | 879 $[M-F]^+$ | | 39.84 | 1.41 | 54.31 |
| 1,3-$[(3\text{-}R_f^1)C_6H_4O]_2C_6H_4$[a] | 695 $(M-C_3F_7O(CF_2)_3]^{+b}$ | 170/0.03 | 37.30 | 1.17 | 55.31 |
| **(14)** | | | 37.13 | 1.25 | 54.92 |

[a] $R_f^1=(CF_3)_2CFO(CF_2)_4$.

[b] The parent ion peak (>1000) was beyond the limit of the spectrometer used. However, the fragmentation peaks were consistent with the structure.

[c] $R_f^2=(CF_3)_2CFO(CF_2)_8$.

[d] Previously prepared [12] as an isomeric mixture of $[(C_6H_5OC_6H_4(CF_2)_3]_2$.

(5.1 g, 9.2 mmol) were placed in a 250 ml three-necked flask, equipped with a stirrer, thermometer and a nitrogen gas inlet. The reaction mixture was heated under a nitrogen atmosphere at ~80 °C. After 24 h, the reaction mixture was cooled to room temperature and diethyl ether (120 ml) and water (80 ml) were added. The mixture was stirred and then centrifuged. The diethyl ether and water layers were decanted from the solid material and separated. The solid was extracted with additional amounts of diethyl ether ($2 \times 30$ ml). The organic solutions were combined, washed with $H_2O$ ($2 \times 30$ ml) and dried over $MgSO_4$. GC/MS analysis indicated 94% of $[(4\text{-}C_6H_5O)C_6H_4(CF_2)_3]_2$ (**8**), some $(4\text{-}C_6H_5O)C_6H_4(CF_2)_6H$, traces of $(4\text{-}C_6H_5O)C_6H_4I$ and unknown compounds. Distillation yielded the desired product, 3.52 g, (yield 60%); b.p. 277 °C/0.03 mmHg and m.p. 97 °C.

Another reaction was carried out without the catalyst, 2,2′-bipyridine, at ~125 °C to ~135 °C for 8 h (Table 1, Exp. 4). The reaction mixture was worked-up in a similar manner as described above. GC/MS analysis showed 82% of the desired product (**8**), and smaller amounts of $(4\text{-}C_6H_5O)C_6H_4(CF_2)_6H$, $(4\text{-}C_6H_5O)C_6H_4I$ and unknown compounds.

Compound **8** or its isomer(s) have been prepared earlier [12] by the thermal reaction of biphenyl ether with 1,6-diiodoperfluorohexane. The product had a boiling point of 220 °C/0.02 mmHg but the exact nature of the isomer(s) was not determined.

### *Synthesis of* $[(4\text{-}C_6F_{13})C_6H_4]_2O$ *(**6**) (nc) (see Table 1, Exp. 1)*

To a well-stirred mixture of copper bronze (6.72 g, 106 mmol), $(4\text{-}BrC_6H_4)_2O$ (**3**) (6.56 g, 20 mmol) and DMSO (60 ml) under a nitrogen atmosphere at ~ 125 °C was added dropwise $n\text{-}C_6F_{13}I$ (**1**) (21.4 g, 48 mmol) over a period of 50 min. 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 methods. After stirring at ~ 125 °C for 5 h, the yield of the expected product was maximized. GC analysis showed 97% of $[(4\text{-}C_6F_{13})C_6H_4]_2O$ (**6**), and minor amounts of $(4\text{-}C_6F_{13})C_6H_4OC_6H_4Br$ and unknown compounds. The reaction mixture was cooled to room temperature and diethyl ether (100 ml) and water (50 ml) were added. The mixture was stirred and then centrifuged. The diethyl ether and water layers were decanted from the solid material and separated. The solid was extracted with additional amounts of diethyl ether ($2 \times 50$ ml). The organic layers were combined, washed with water ($2 \times 80$ ml) and dried over $MgSO_4$. On evaporation of the solvent, a crude product (14.3 g, 97 GC area %) was obtained and subsequently distilled to yield **6** (b.p. 139 °C/0.45 mmHg, m.p. 59 °C, 12.7 g or 79% yield).

### *Synthesis of* $1,3\text{-}[(3\text{-}C_6F_{13})C_6H_4O]_2C_6H_4$ *(**7**) (nc)*

The reaction was carried out in the same manner as described above for compound **6** (see Table 1, Exp. 2). GC/MS analysis of the crude product showed 94% of the desired product (**7**) and minor amounts of $(3\text{-}C_6F_{13})C_6H_4OC_6H_4Br$, $(3\text{-}C_6F_{13})C_6H_4OC_6H_5$ and $(3\text{-}C_6F_{13})C_6H_4OC_6H_4OC_6H_4SCH_3$. Isolated yield of **7** was 88%.

### *Synthesis of 1,3-[(3-$R_f^1$)$C_6H_4O$]$_2C_6H_4$ (14) ($R_f^1 = (CF_3)_2CFO(CF_2)_4-$) (nc)*

This compound was synthesized by the same procedure as described for compound **15** (see Table 1, Exp. 6) except that the molar ratio of reactants, reaction time and work-up procedure were different. The reaction mixture was worked-up as for $[(4\text{-}C_6F_{13})C_6H_4]_2O$ (**6**) (see Table 1, Exp. 5).

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## References

1 (a) G. J. Chen and C. Tamborski, *J. Fluorine Chem., 43* (1989) 207; (b) G. E. Carr, R. D. Chambers, T. F. Holmes and D. G. Parker, *J. Chem. Soc., Perkin Trans. 1,* (1988) 921, and references therein.

2 J. Burdon, P. L. Coe, C. R. Marsh and J. C. Tatlow, *Chem. Commun.,* (1967) 1259.

3 V. C. R. McLoughlin and J. Thrower, *Tetrahedron, 25* (1969) 5921.

4 J. Burdon, P. L. Coe, C. R. Marsh and J. C. Tatlow, *J. Chem. Soc., Perkin Trans. 1,* (1972) 639.

5 G. J. Chen and C. Tamborski, *J. Fluorine Chem., 46* (1990) 137.

6 K. K. Sun, C. Tamborski and K. C. Eapen, *J. Fluorine Chem., 17* (1981) 457.

7 L. S. Chen, G. J. Chen and C. Tamborski, *J. Fluorine Chem., 26* (1984) 341.

8 A. K. Ankudinov and R. M. Ryazonova, *J. Org. Chem., USSR, 8* (1972) 217.

9 K. J. L. Paciorek, S. R. Masuda,, J. G. Shih and J. H. Nakahara, *J. Fluorine Chem., 53* (1991) 233.

10 F. G. A. Stone and R. West (eds.), *Adv. Organomet. Chem., 12* (1974) 227.

11 M. R. Unroe and F. C. Hedberg, *US Air Force Tech. Rep. AFWAL-TR-85-4040* (1985).

12 I. L. Knunyants, V. V. Shokina, P. M. Krasuskaya and S. P. Khrlakyan, *Izv. Akad. Nauk SSSR, Ser. Khim., 7* (1967) 1520.