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Unexpected Synthesis of a New Highly Fluorocarbon Soluble Phosphite for Biphasic Catalysis

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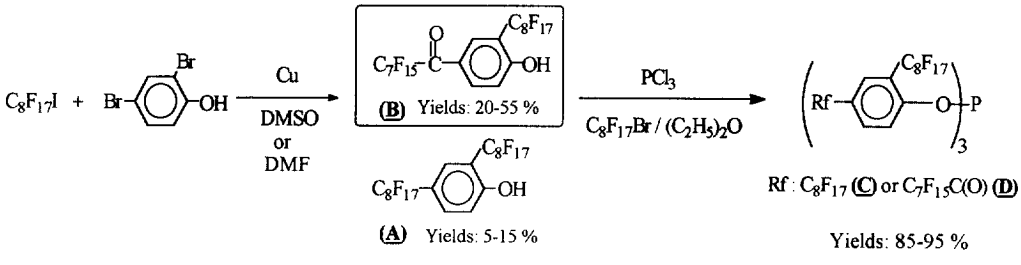
Abstract: The synthesis of tris(4-(1-oxoperfluorooctyl)-2-perfluorooctylphenyl)phosphite and tris(2,4-bis(perfluorooctyl)phenyl)phosphite from commercially available 1-iodoperfluorooctane and 2,4-dibromophenol is described. The stability and the solubility of these new compounds are reported.

Keywords: fluorocarbons, perfluoroalkylated triarylphosphites, copper.

The synthesis and study of new fluorocarbon-soluble catalysts is a growing area of organometallic chemistry and homogeneous catalysis [1]. The growth of this area relies essentially on the synthesis of highly fluorocarbon-soluble ligands, which allow to immobilize the catalysts in the fluorocarbon layer [2]. In this context, we have recently reported a general route for the synthesis of monofluorinated analogues of $P(OPh)_3$ [3]. This synthesis is based on the copper-mediated coupling reaction of 1-iodoperfluorooctane with various monohalophenol derivatives, followed by the reaction of the corresponding phenol with phosphorus trichloride. In this paper, we report that the coupling reaction of 1-iodoperfluorooctane with 2,4-dibromophenol does not lead exclusively to the 2,4-bis(perfluorooctyl)phenol (**A**) but preferentially to an unexpected product: 4-(1-oxoperfluorooctyl)-2-perfluorooctylphenol (**B**). These two phenol derivatives can be easily converted into new highly fluorocarbon-soluble phosphites (**C**) and (**D**) by addition of phosphorus trichloride.



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The copper bronze-catalyzed perfluoroalkylation of 2,4-dibromophenol in dimethylsulfoxide provided a complex mixture composed of 4-bromo-2-perfluorooctylphenol (isolated yields after chromatographic purification: 0-30%, according to the experimental conditions), **A** (5-15%), **B** (20-55%) and unknown products (10-20%). The formation of 2-bromo-4-perfluorooctylphenol, 2-(1-oxoperfluorooctyl)-4-perfluorooctylphenol and 2,4-bis(1-oxoperfluorooctyl)phenol has never been observed under these experimental conditions. Another aprotic solvent such as N,N-dimethylformamide had no significant effect upon the distribution and yield of **B**. The best yields of **B** (55 %) were generally obtained at 125-130°C after 20 hours of reaction. A longer reaction time (48 h or 96 h) or a higher temperature (150°C) decreased the yields of **B** and increased significantly the amount of unknown products. A kinetic analysis of the production of **A** and **B** indicates that **B** is produced from **A** as intermediate. As no product corresponding to the exclusive reaction at the *ortho* position of the hydroxy group of **A** could be detected, it is also clear that the benzyl fluorines at the *para* position are more reactive than those at the *ortho* position. The mechanism of formation of compound **B** from **A** is still unclear. Indeed, to the best of our knowledge, the conversion of perfluoroalkylbenzenes to aryl perfluoroalkyl ketones has never been observed under such conditions and requires generally a prolonged treatment with aqueous hydrobromic acid [4]. The absence of 2-bromo-4-perfluorooctylphenol in all reaction mixtures suggests also that the bromo group at the *ortho* position is more reactive than the bromo group at the *para* position and that **A** is formed from 4-bromo-2-perfluorooctylphenol.

Interestingly, the synthesis of new fluorocarbon-soluble ligands for the fluorous biphase catalysis can be easily achieved from **A** and **B**: addition of phosphorus trichloride to a solution of **A** or **B** gives the new phosphites **C** and **D** in 85-95 % yields. These phosphites appeared more sensitive to hydrolysis and oxidation than the mono perfluoroalkyled triphenylphosphites that we have previously synthesized [3]. For example, when **D** was dissolved in $C_8F_{17}Br$ and heated at 80 °C under an oxygen atmosphere, 10 % of oxide is formed after 2 hours. Under the same conditions, no appreciable decomposition or oxidation occurred with tris(4-perfluorooctylphenyl)phosphite (**E**). Whereas hydrolysis of **E** into H_3PO_3 and the corresponding phenol derivative required 24 hours at 20 °C in a water-tetrahydrofuran mixture (50/50; v/v), the hydrolysis of **D** was complete within 10 minutes at 20 °C in a water-tetrahydrofuran-$C_8F_{17}Br$ mixture (25/50/25; v/v/v). The lower hydrolytic stability of the P-O bond in phosphites **C** and **D** compared to phosphites bearing only one perfluoroalkyl chain is attributed to the strong electronic influence of the perfluoroalkyl solubilizers. As expected, the solubilities of phosphites **C** and **D** in perfluorocarbon solvents are higher than those of phosphites bearing one perfluoroalkyl chain. For instance, the solubility of **D** in $C_8F_{17}Br$ at 20°C is about three times higher than that of **E** (1,750 Kg/L against 0,581 Kg/L). Phosphites **C** and **D** are, at room temperature, very slightly soluble in tetrahydrofuran and insoluble in chloroform, toluene, dimethylsulfoxide and alcanes.

In conclusion, although the copper-catalyzed perfluoroalkylation of 2,4-dibromophenol gives an unexpected product, this reaction can be used to obtain in moderate yields a new potential ligand for coordination chemistry and catalysis in a fluorocarbon/hydrocarbon biphasic medium. Furthermore, the presence of a carbonyl group on this ligand could offer new synthetic opportunities (reduction of the carbonyl group, covalent binding of the ligand to a soluble fluorocarbon support ...)

General procedure for the copper catalyzed perfluoroalkylation of 2,4-dibromophenol.

In a typical experiment, 2,4-dibromophenol (10.75 mmol), $C_8F_{17}I$ (22.57 mmol) and copper (53.82 mmol) were dissolved in 30 ml of anhydrous DMSO, and heated to 125-130°C under nitrogen for 20 h. After cooling to room temperature, water (50 ml) and diethyl ether (50 ml) were added to the reaction mixture. The orange solid was filtered and washed with diethyl ether (50 ml). The organic layer was separated and washed with water (3 × 50 ml), dried over Na_2SO_4 and evaporated in vacuo. The crude product was purified by column chromatography on silica gel with CH_2Cl_2. All products were recristallized from $CHCl_3$. The yields of the isolated products from the reaction crude and their characterization data are listed below:

4-bromo-2-perfluorooctylphenol Yield: 10 % of a white solid, Mp: 52°C, (Rf = 0.74; CH_2Cl_2), ^1H NMR ($CDCl_3$) δ 7.53 (1H, d, J = 9.2 Hz, 5-ArH), 7.52 (1H, s, 3-ArH), 6.87 (1H, d, J = 9,2 Hz, 6-ArH) ^{19}F-{^1H} NMR ($CDCl_3$) δ -81.18 (3F, t, $^3J_{FF}$ = 9.4 Hz, $-CF_3$), -108.88 (2F, t, $^3J_{FF}$ = 14.1 Hz, $-CF_2$- next to 2-C arom), -121.80 (2F, um, $-CF_2$-), -121.98 (2F, um, $-CF_2$-), -122.20 (4F, um, 2 × $-CF_2$-), -123.06 (2F, um, $-CF_2$-), -126.48 (2F, um, $-CF_2$-) ^{13}C-{^1H} NMR ($CDCl_3$) δ 153.95 (s, 1-C arom), 136.91 (s, 5-CH arom), 131.38 (t, $^3J_{CF}$ = 8.2 Hz, 3-CH arom), 120.37 (s, 6-CH arom), 115.77 (t, $^2J_{CF}$ = 22.3 Hz, 2-C arom), 112.89 (s, 4-C arom) + complex signals of $-CF_2$- and $-CF_3$ (105-120) MS (EI) m/z: 592/590 (M^+, 4.9 %), 561/559 ($[C_8F_{17}C_5H_3Br]^+$, 87.3 %), 223/221 (M^+ - C_7F_{15}, 100 %), 194/192 ($[CF_2C_5H_3Br]^+$, 10.2 %), 119 ($C_2F_5^+$, 36.9 %), 69 (CF_3^+, 56.9 %) IRFT (KBr) ν (cm^{-1}): 1484 (m), 1371 (m), 1332 (s), 1307 (m), 1290 (s), 1259 (s), 1229 (vs), 1201 (vs), 1149 (vs), 1135 (vs), 1115 (s), 657 (m).

2,4-bis(perfluorooctyl)phenol (A) Yield: 12 % of a white solid, Mp: 60°C, (Rf = 0.64; CH_2Cl_2), ^1H NMR (THF-d8) δ 7.69 (1H, d, J = 8.4 Hz, 5-ArH), 7.68 (1H, s, 3-ArH), 7.14 (1H, d, J = 8.4 Hz, 6-ArH), 3.00 (1H, s, -OH) ^{19}F-{^1H} NMR (THF-d8) δ -80.97 (6F, t, $^3J_{FF}$ = 9.5 Hz, 2 × $-CF_3$), -108.37 (2F, t, $^3J_{FF}$ = 13.5 Hz, $-CF_2$- next to 2-C arom), -109.70 (2F, t, $^3J_{FF}$ = 13.8 Hz, $-CF_2$- next to 4-C arom), -121.03 (4F, um, 2 × $-CF_2$-), -121.25 (2F, um, $-CF_2$-), -121.59 (8F, um, 4 × $-CF_2$-), -121.83 (2F, um, $-CF_2$-), -122.43 (4F, um, 2 × $-CF_2$-), -125.96 (4F, um, 2 × $-CF_2$-) ^{13}C-{^1H} NMR (THF-d8) δ 161.44 (s, 1-C arom), 133.06 (br s, 5-CH arom), 128.94 (t, $^3J_{CF}$ = 6.5 Hz, 3-CH arom), 119.88 (t, $^2J_{CF}$ = 25.2 Hz, 4-C arom), 118.88 (s, 6-CH arom), 116.10 (t, $^2J_{CF}$ = 23.1 Hz, 2-C arom) + complex signals of $-CF_2$- and $-CF_3$ (105-120)) MS (EI) m/z: 930 (M^+, 4.9 %), 911 (M^+ - F, 7.7 %), 891 (M^+ - 2F - H, 0.9 %), 592 (M^+ - F - C_6F_{13}, 2.0 %), 561 (M^+ - C_7F_{15}, 100 %), 541 (M^+ - F - H - C_7F_{15}, 11.7 %), 223 (M^+ - F - C_6F_{13} - C_7F_{15}, 14.4 %) IRFT (KBr) ν (cm^{-1}): 1331 (s), 1312 (s), 1206 (vs), 1149 (vs), 1116 (s).

4-(1-oxoperfluorooctyl)-2-perfluorooctylphenol (B) Yield: 55 % of a white solid, Mp: 114°C, (Rf = 0.40; CH_2Cl_2), ^1H NMR (THF-d8) δ 8.22 (1H, s, 3-ArH), 8.19 (1H, d, J = 8.7 Hz, 5-ArH), 7.15 (1H, d, J = 8.7 Hz, 6-ArH) ^{19}F-{^1H} NMR (THF-d8) δ -80.83 (6F, t, $^3J_{FF}$ = 10.0 Hz, 2 × $-CF_3$), -108.37 (2F, t, $^3J_{FF}$ = 13.6 Hz, $-CF_2$- next to 2-C arom), -112.49 (2F, t, $^3J_{FF}$ = 12.4 Hz, $-CF_2$- next to CO), -120.53 (2F, um, $-CF_2$-), -120.73 (2F, um, $-CF_2$-), -120.88 (2F, um, $-CF_2$-), -121.15 (2F, um, $-CF_2$-), -121.56 (6F, um, 3 × $-CF_2$-), -122.33 (4F, um, 2 × $-CF_2$-), -125.86 (4F, um, 2 × $-CF_2$-) ^{13}C-{^1H} NMR (THF-d8) δ 180.96 (t, $^2J_{CF}$ = 26.4 Hz, $-\underline{C}O-CF_2$-), 164.56 (s, 1-C arom), 136.88 (s, 5-CH arom), 133.54 (br s, 3-CH arom), 124.08 (s, 4-C arom), 119.18 (s, 6-CH arom), 116.42 (t, $^2J_{CF}$ = 24.1 Hz, 2-C arom) + complex signals of $-CF_2$- and $-CF_3$ (105-120) MS (EI) m/z: 908 (M^+, 0.9 %), 889 (M^+ - F, 7.9 %), 869 (M^+ - 2F - H, 0.9 %), 861 (M^+ - F - CO, 0.5 %), 539 (M^+ - C_7F_{15}, 100 %), 519 (M^+ - F - H - C_7F_{15}, 9.9 %), 143 ($[OC-C_5H_3-CF_2]^+$, 11.5 %), 69 (CF_3^+, 7.3 %) Anal. Calcd for $C_{22}H_4F_{32}O_2$: C, 29.07; H, 0.44 Found: C, 29.23; H, 0.62. IRFT (KBr) ν (cm^{-1}): 3317 (m), 1670 (s), 1587 (s), 1520 (m), 1372 (m), 1323 (s), 1303 (s), 1234 (vs), 1202 (vs), 1145 (vs), 1082 (m), 982 (m), 830 (w), 675 (w).

General procedure for the synthesis of phosphites.

The phenol derivative **A** or **B** (1.87 mmol) was azeotropically distilled with toluene (30 ml, distilled over sodium under N_2) and dissolved in a mixture of 5 ml of ether and 5 ml of $C_8F_{17}Br$ (dried over

CaH_2) to avoid the precipitation of the phosphite as an oil. Triethylamine (1.87 mmol, dried over CaH_2 under N_2) and phosphorus trichloride (0.80 mmol) dissolved in 5 ml of ether were successively added dropwise at 0°C in 0.5 h under N_2 to the stirred solution of phenol derivative. Subsequently the reaction mixture was stirred 2 h at room temperature. The amine salts produced were removed by filtration over dried silica gel under N_2 with further 40 ml of ether. The solvent was removed in vacuo to afford the pure phosphite.

Tris(2,4-bis(perfluorooctyl)phenyl)phosphite (C) Yield: 85 % of a colorless oil, ^{31}P-{^1H} NMR ($C_8F_{17}Br$, unlocked, external H_3PO_4) δ + 124.14 (s) ^1H NMR ($C_8F_{17}Br$, external $CDCl_3$ lock) δ 7.78 (1H, s, 3-ArH), 7.67 (1H, d, J = 8.6 Hz, 5-ArH), 7.38 (1H, d, J = 8.6 Hz, 6-ArH) ^{19}F-{^1H} NMR (CF_2ClCCl_2F, unlocked, external $CFCl_3$) δ -82.11 (18F, um, 6 × -CF_3), -109.17 (6F, um, 3 × -CF_2- next to 2-C arom), -111.46 (6F, um, 3 × -CF_2- next to 4-C arom), -121.74 (6F, um, 3 × -CF_2-), -121.97 (6F, um, 3 × -CF_2-), -122.23 (6F, um, 3 × -CF_2-), -122.59 (30F, um, 15 × -CF_2-), -123.54 (12F, um, 6 × -CF_2-), -127.13 (12F, um, 6 × -CF_2-) ^{13}C-{^1H} NMR (CF_2ClCCl_2F, external $CDCl_3$ lock) δ 159.94 (s, 1-C arom), 132.44 (br s, 5-CH arom), 128.46 (br s, 3-CH arom), 126.57 (t, $^2J_{CF}$ = 24.9 Hz, 4-C arom), 121.49 (t, $^2J_{CF}$ = 23.7 Hz, 2-C arom), 121.04 (s, 6-CH arom) + complex signals of -CF_2- and -CF_3 (105-120) MS (MALDI) m/z: 2752 (M^+), 2733 (M^+ - F) IRFT (deposited on KBr support) ν (cm^{-1}): 1369 (s), 1315 (s), 1287 (vs), 1237 (vs), 1152 (vs), 1115 (vs), 1084 (s).

Tris(4-(1-oxoperfluorooctyl)-2-perfluorooctylphenyl)phosphite (D) Yield: 95 % of a colorless oil, ^{31}P-{^1H} NMR ($C_8F_{17}Br$, unlocked, external H_3PO_4) δ + 123.27 (s) ^1H NMR ($C_8F_{17}Br$, external $CDCl_3$ lock) δ 8.25 (1H, s, 3-ArH), 8.06 (1H, d, J = 8.9 Hz, 5-ArH), 7.44 (1H, d, J = 8.9 Hz, 6-ArH) ^{19}F-{^1H} NMR (CF_2ClCCl_2F, unlocked, external $CFCl_3$) δ -82.13 (18F, um, 6 × -CF_3), -109.25 (6F, um, 3 × -CF_2- next to 2-C arom), -113.84 (6F, um, 3 × -CF_2- next to CO), -121.65 (18F, um, 9 × -CF_2-), -122.27 (6F, um, 3 × -CF_2-), -122.74 (18F, um, 9 × -CF_2-), -123.56 (12F, um, 6 × -CF_2-), -127.18 (12F, um, 6 × -CF_2-) ^{13}C-{^1H} NMR (CF_2ClCCl_2F, external $CDCl_3$ lock) δ 180.43 (t, $^2J_{CF}$ = 27.2 Hz, -CO-CF_2-), 162.21 (s, 1-C arom), 135.50 (br s, 5-CH arom), 132.82 (br s, 3-CH arom), 128.62 (s, 4-C arom), 121.48 (t, $^2J_{CF}$ = 24.9 Hz, 2-C arom), 120.96 (s, 6-CH arom) + complex signals of -CF_2- and -CF_3 (105-120) MS (MALDI) m/z: 2752 (M^+), 2733 (M^+ - F) Anal. Calcd for $C_{66}H_9F_{96}O_6P$: C, 28.78; H, 0.003 Found: C, 28.87; H, < 0.01, IRFT (deposited on KBr support) ν (cm^{-1}): 1720 (m), 1606 (s), 1322 (s), 1235 (vs), 1208 (vs), 1148 (vs), 1115 (s).

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