Photoinduced Electron Transfer Reactions of Pentafluoroiodobenzene with Aromatic Compounds

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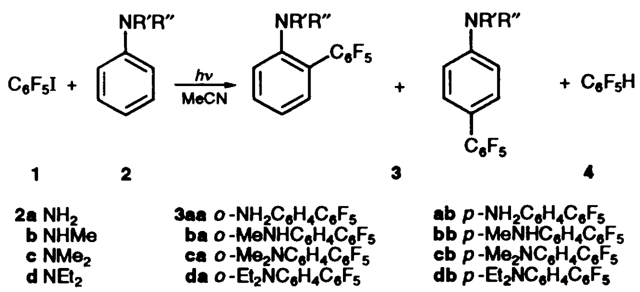
Irradiation of pentafluoroiodobenzene with anilines, pyrroles, indoles, imidazoles, aromatic ethers, or phenols results in the formation of pentafluorophenylated products. A photoinduced electron-transfer mechanism is proposed.

Since Bunnett reported the $S_{RN}1$ reaction of phenyl iodide with potassium amide,[1] the reactions of aryl halides with phosphonate anion,[2] carbanions,[3] aryl amides,[4] and phenoxide anions,[5] have been studied extensively.[6] Similar reactions failed to occur with perfluorophenyl halides (C_6F_5X, X = I, Br and Cl), however, simple nucleophilic substitution at the *para-* or *ortho*-positions occurring instead.[7] Pentafluoroiodobenzene **1** underwent cleavage of the C–I bond when treated with metals to give organometallic reagents.[8] It has also been reported[9] that irradiation of **1** with benzene or toluene for an extended period (150 h) could afford coupling products. Recently, a palladium-catalyzed reaction of **1** with alkynes has been described in which the corresponding coupling products were formed.[10] Earlier we studied the reaction of perfluoroalkyl iodides both with a variety of nucleophiles[11] and with electron-rich aromatic compounds, reactions which occur by a photoinduced electron-transfer(PET) mechanism.[12] Herein we report the results for irradiation-induced reactions between **1** and various aromatic compounds.

Results and Discussion

Irradiation of **1** with anilines **2** in acetonitrile for 10–16 h gave a mixture of *o*- and *p*-pentafluorophenylanilines **3** in good yield in addition to small amount of pentafluorobenzene **4** (Scheme 1).



Scheme 1

The reaction temperature, *ca.* 80 °C, was a result of the irradiation; however, at this temperature without irradiation no reaction took place, an indication that irradiation was essential. No *meta*-substituted products or dipentafluorophenylated products were detected. The reaction results are listed in Table 1.

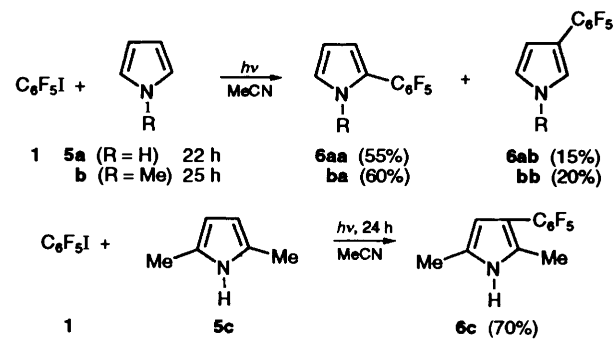
From the results recorded in the Table it was clear that the yield of the reaction was markedly dependent upon the molar ratio of **1** and **2**; *e.g.*, the total yield of **3aa** and **3ab** was 70% for a 1:4 ratio of **1** and **2a** while it was only 35% for a 1:1 ratio. The reaction also proceeded in DMF (see entries 9 and 11, Table 1) with an increase in the amount of **4** formed.

Similarly, the reaction of **1** with aza-aromatic compounds gave the corresponding coupling products. Thus, photolysis of **1** and an excess of pyrroles **5** in acetonitrile gave compounds **6** in high yields (Scheme 2) Neither **4** nor *N*-pentafluorophenylated compounds were produced in the reaction. Compounds **8** were formed in a similar fashion upon irradiation of a mixture of **1** with indoles **7** (Scheme 3).

Table 1 Photoinduced reaction of pentafluoroiodobenzene **1** and anilines **2** in acetonitrile

Entry	2(2:1)[a]	Time (h)	Products[b] (%)	C_6F_5H 4[c] (%)	Other (%)
1	**2a** (1:1)	12	**3aa** (24) **3ab** (11)	0	
2	**2a** (2:1)	12	**3aa** (37) **3ab** (20)	0	
3	**2a**	12	**3aa** (42) **3ab** (25)	0	
4	**2a** (4:1)	12	**3aa** (43) **3ab** (27)	0	
5[d]	**2a** (10:1)	12	**3aa** (43) **3ab** (32)	0	
6[e]	**2a**	12	**3aa** (16) **3ab** (10)	—	
7[f]	**2a**	12	**3aa** (12) **3ab** (7)	—	
8[g]	**2a**	12	**3aa** (10) **3ab** (7)	—	
9[h]	**2a**	10	**3aa** (49) **3ab** (25)	6	
10	**2b**	16	**3ba** (52) **3bb** (29)	4	**2a** (4)
11[h]	**2b**	13	**3ba** (50) **3bb** (30)	10	**2a** (9)
12	**2c**	10	**3ca** (48) **3cb** (25)	14	**2b** (14)
13	**2d**	13	**3da** (46) **3db** (27)	10	(8)

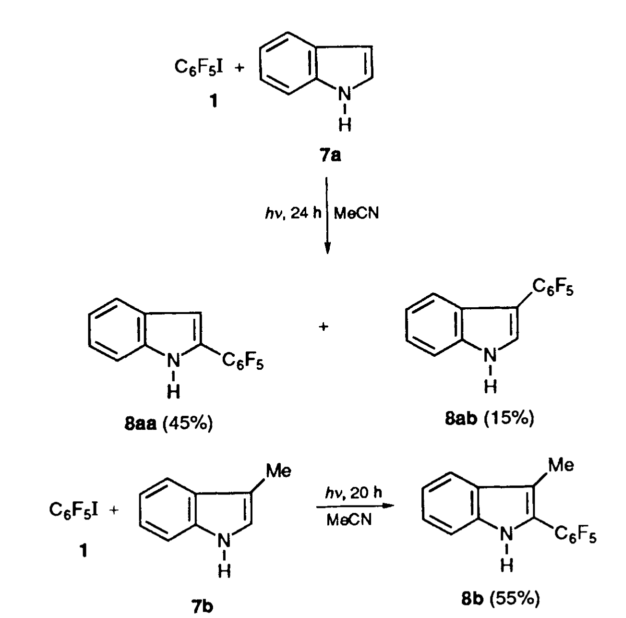
[a] **2**:**1** = 3:1 unless otherwise noted. [b] Isolated yields based on **1**. [c] Determined by ^{19}F NMR. [d] Without MeCN. [e] 20 mol% of *p*-DNB was added. [f] 20 mol% of Bu^t_2NO was added. [g] 20 mol% of HQ was added. [h] Proceeded in DMF.



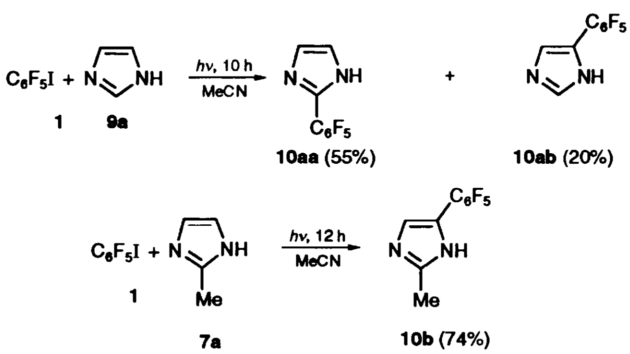
Scheme 2

Neither reaction gave benzene ring substituted products. Although earlier work showed that irradiation of **1** and imidazole **9** in methanol gave only low yields (38%) of pentafluorophenylated products,[13] we found that replacement of the methanol by acetonitrile greatly increased the yields of the reaction (Scheme 4).

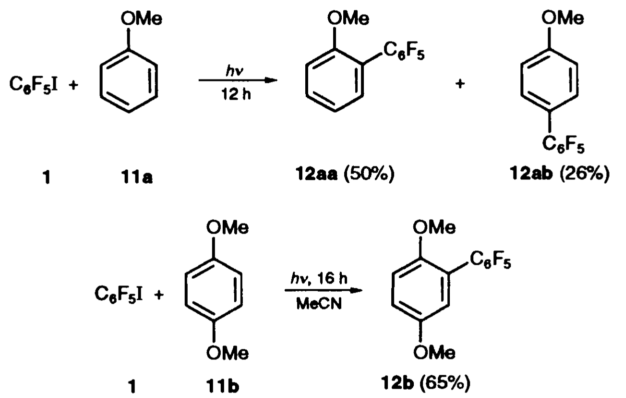
Anisole **11a** and 1,4-dimethoxybenzene **11b** reacted with **1** when the mixtures were irradiated to give compounds **12** in high yields (Scheme 5). The former reaction proceeded with **11a** in excess without extra solvents, no *m*-pentafluorophenylated derivative being produced, whereas the latter proceeded in acetonitrile. Phenols **13a–d** also underwent similar reactions.



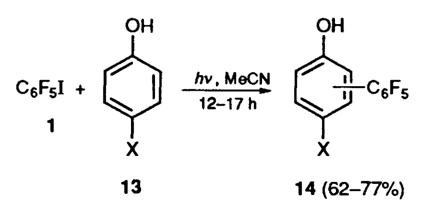
Scheme 3



Scheme 4



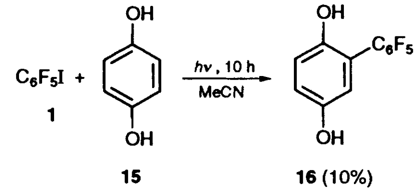
Scheme 5



13a	H	14aa	2-C_6F_5 (50%)	ab 4-C_6F_5 (25%)
b	Me	ba	2-C_6F_5 (47%)	bb 3-C_6F_5 (30%)
c	Cl	ca	2-C_6F_5 (48%)	cb 3-C_6F_5 (12%)
d	NO_2	d	2-C_6F_5 (62%)	

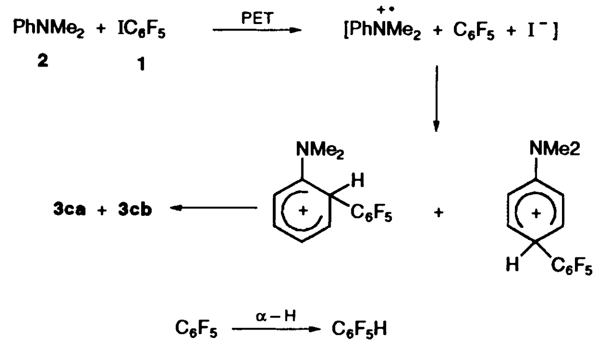
Scheme 6

Thus, irradiating a solution of **1** and **13** (1 : 3) in acetonitrile gave **14** in good yields together with traces of **4** (Scheme 6). The UV-induced reaction of **1** with **13d** in the presence of triethylamine in acetonitrile gave **14d**; under similar conditions, but in the absence of triethylamine, **14d** was obtained in only very low yield (< 5%). Similarly, hydroquinone (HQ) **15** reacted with **1** to give compound **16** in very low yield (Scheme 7). In order to



Scheme 7

elucidate the reaction mechanism, inhibition studies were carried out. For example, the presence of single-electron transfer (SET) scavengers, *p*-dinitrobenzene (DNB) and Bu^t_2NO or a free radical inhibitor, hydroquinone, in the reaction systems significantly suppressed the reaction of **1** and **2** (see entries 6–8 in Table 1); the low yield of the reaction of **1** with **15** might be ascribed to the inhibition of HQ. Addition of tetrachloromethane to the reaction mixture of **1** and **2** resulted in the formation of chloropentafluorobenzene **17**, proof of the existence of pentafluorophenyl radicals. These results seem to point to the involvement of a photoinduced electron-transfer mechanism (PET) in the reaction (see Scheme 8 using **2c** as an example). The charge-transfer from **2** to **1** was initiated by a

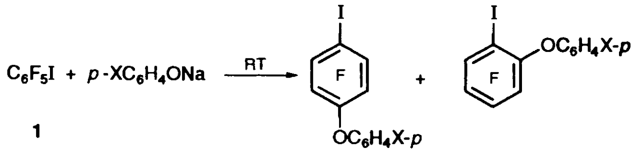


Scheme 8

UV-generated radical cation of **2** and a pentafluorophenyl radical. The latter attacks the benzene ring of $\mathbf{2}^{+\cdot}$ to give **3** or abstracts hydrogen atom from the methyl group of $\mathbf{2}^{+\cdot}$ to afford **4**.* The absence of **4** in the reaction of **1** with **2a** can be understood in terms of the absence of abstractable hydrogen in **2a**. In fact, it was found that **2a**, **2b** or *N*-ethylaniline were formed, which clearly demonstrates that hydrogen abstraction occurs from the alkyl groups,[15] in the reactions of **2b**, **2c** and **2d**.

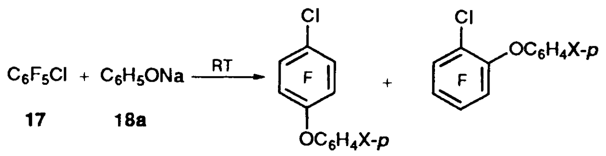
A recent and remarkable synthesis of biphenyl derivatives from phenoxides and naphthoxides by an $S_{RN}1$ mechanism,[6] a reaction, earlier, considered impossible [16] is worth mentioning. In contrast with the UV irradiated reactions of 1 and phenols, the corresponding reactions with sodium phenoxides **18** gave, by simple nucleophilic substitution mainly biphenyl ethers **19aa**, **19ba**, **19ca**, or **19da** in high yields; small amounts of compounds **19ab**, **19bb**, **19cb**, or **19db** (detected by ^{19}F NMR spectra), were also obtained. Such reactions took place both with and without UV irradiation, even at room temperature.

* We have found that a similar reaction also takes place upon UV irradiation of pentafluorophenyl perfluoroalkanesulfonates and aromatic compounds such as anilines, phenols and pyrroles.[14]



18a (X = H) 30 min **19aa** (98%) **ab** (2%)
b (X = Me) 45 min **ba** (97%) **bb** (3%)
c (X = Cl) 10 min **ca** (96%) **cb** (4%)
d (X = NO_2) 12 h (at 85 °C) **da** (80%) **db** (2%)

Scheme 9



20a (88%) **20b** (2%)

Scheme 10

A similar product mixture was also obtained in the reaction of chloropentafluorobenzene **17** with sodium phenoxide at room temperature both with and without UV irradiation.

These results clearly demonstrate that unlike its reactions with aryl halides, **1** undergoes simple nucleophilic substitution with phenoxide rather than a PET or ET reaction; the reason for this is explained in terms of the high electrophilicity of **1** and its analogues.

Experimental

All m.p.s are uncorrected. IR spectra were obtained on a Schimadzu-440 model instrument as KBr pellets for solid samples and as films for liquid samples. ^1H NMR spectra were recorded on a FX-90Q model instrument or a XL-200 model instrument using TMS or chloroform as an internal standard. ^{19}F NMR were recorded on EM-360 model instrument at 56.4 MHz using CF_3CO_2H as an external standard and chemical shifts in ppm were positive upfield. Mass spectra were obtained on a Finnigan-4041 model instrument. Silica gel (40 μm) was used for column chromatography.

Photoinduced Reaction of Pentafluoroiodobenzene **1** *and Anilines* **2**.—*Typical procedure*. Under a N_2 atmosphere, a stirred solution of **1** (1.47 g, 5 mmol), **2c** (1.82 g, 15 mmol) and acetonitrile (15 cm^3) in a Pyrex flask, connected to a solid CO_2 cooler, was exposed to a medium-pressure mercury lamp (450 W) at a distance of 8 cm for 10 h; GC showed that *ca.* 14% of pentafluorobenzene **3** was formed. The mixture was concentrated under reduced pressure and the residue was extracted with ether (40 cm^3). The ether solution was then washed with 5% aqueous $NaHCO_3$, dried ($MgSO_4$) and evaporated; excess of **2c** was then distilled off *in vacuo*. The oily residue was subjected to column chromatography using light petroleum–ether (5:1) as eluent to give 2-dimethylamino-2′,3′,4′,5′,6′-pentafluorobiphenyl **3ca** (0.75 g, 52%) and 4-dimethylamino-2′,3′,4′,5′,6′-pentafluorobiphenyl **3cb** (0.42 g, 29%). Under similar conditions, chloropentafluorobenzene (5%), identified by GC, was formed when tetrachloromethane (2 cm^3) was added to the reaction mixture: **3ca** oil (Found: C, 58.5; H, 3.4; N, 4.75; F, 33.1. Calc. for $C_{14}H_{10}F_5N$: C, 58.53; H, 3.52; N, 4.88; F, 33.07%); ν_{max} 2960, 1620, 1550, 1425, 1340, 995 and 780; δ_H[$^2H_6$]acetone) 2.64 (6 H, s), 7.05 (2 H, m), 7.40 (1 H, m) and 7.65 (1 H, m); δ_F[$^2H_6$]acetone 62.4 (2 F, d), 80.8 (1 F, t) and 87.2 (2 F, t) *m/z* 288 (M$^+$ + 1, 15%), 287 (M$^+$, 99%), 286 (100%), 271 (13%), 143 (36%) and 43 (11%); **3cb**, m.p., 158 °C (lit.,[17] 158–160 °C); ν_{max}/cm^{-1} 2960, 1615, 1510, 1490, 1320, 1230, 1065, 820 and 780 δ_H([$^2H_6$]acetone) 2.72 (6 H, s), 6.92 (2 H, d, *J* 8.5) and 7.62 (2 H, d, *J* 8.5); δ_F([$^2H_6$]acetone) 60.2 (2 F, d), 80.0 (1 F, t) and 86.4 (2 F, t) *m/z* 288 (M$^+$ + 1, 16%), 287 (M$^+$, 84%), 286 (100%), 271 (14%), 243 (12%) and 143 (31%).

2-*Amino-2′,3′,4′,5′,6′-pentafluorobiphenyl* **3aa** and 4-*Amino-2′,3′,4′,5′,6′-pentafluorobiphenyl* **3ab**. **3aa**, m.p., 86–88 °C (Found: C, 55.6; H, 2.3; N, 5.3; F, 36.6; Calc. for $C_{12}H_6F_5N$: C, 55.61; H, 2.34; N, 5.41; F, 36.65%)ν_{max}/cm^{-1} 3400, 3050, 1650, 1500, 1425, 1360, 1260, 1010, 990 and 820; δ_H 3.40 (2 H, w), 7.10 (2 H, m), 7.38 (1 H, m) and 7.62 (1 H, m); δ_F($CDCl_3$) 65.0 (2 F, d), 85.6 (1 F, t) and 88.2 (2 F, t); *m/z* 260 (M$^+$ + 1, 14%), 259 (M$^+$, 100%) and 240 (24%). **3ab**, m.p., 134 °C (lit.,[16] 135–136 °C; δ_H($CDCl_3$) 3.60 (2 H, w), 6.74 (2 H, d, *J* 8.0) and 7.68 (2 H, d, *J* 8.0); δ_F($CDCl_3$) 61.2 (2 F, d), 80.4 (1 F, t) and 87.5 (2 F, t); *m/z* 260 (M$^+$ + 1, 86%), 259 (M$^+$, 100%) and 240 (12%).

2,3,4,5,6-*Pentafluoro-2-methylaminobiphenyl* **3ba** *and* 2,3,4,5,6-*pentafluoro-4′-methylaminobiphenyl* **3bb**. **3ba**, m.p., 75–77 °C. Found: C, 57.1; H, 2.8; N, 5.01; F, 34.4. Calc. for $C_{13}H_8F_5N$: C, 57.14; H, 2.96; N, 5.13; F, 34.77%) ν_{max}/cm^{-1} 3420, 1605, 1585, 1490, 1310, 1245, 980 and 865; δ_H($CDCl_3$) 2.45 (3 H, s), 3.21 (1 H, w), 6.99–7.14 (2 H, m), 7.40 (1 H, m) and 7.68 (1 H, m); δ_F($CDCl_3$) 63.2 (2 F, d), 82.4 (1 F, t) and 88.4 (2 F, t); *m/z* 274 (M$^+$ + 1, 17%), 273 (M$^+$, 100%), 258 (25%) and 106 (44%). **3bb**, m.p., 142 °C (Found: C, 57.0; H, 2.9; N, 5.0; F, 34.5. Calc. for: $C_{13}H_8F_5N$: C, 57.14; H, 2.96; N, 5.13; F, 34.77%), ν_{max}/cm^{-1} 3450, 1510, 1325, 1300, 1245, 990 and 865; δ_H($CDCl_3$) 2.60 (3 H, s), 3.42 (1 H, w), 6.92 (2 H, d, 8.0) and 7.60 (2 H, d, 8.0); δ_F($CDCl_3$) 60.5 (2 F, d), 81.7 (1 F, t) and 88.0 (2 F, t); *m/z* 274 (M$^+$ + 1, 64%) and 273 (M$^+$, 100%).

2-*Diethylamino-2′,3′,4′,5′,6′-pentafluorobiphenyl* **3da** *and* 4-*diethylamino-2′,3′,4′,5′,6′-pentafluorobiphenyl* **3db**. **3da**, m.p., 60–62 °C. (Found: C, 60.6; H, 4.12; N, 4.3; F, 30.0. Calc. for $C_{16}H_{14}F_5N$: C, 60.94; H, 4.48; N, 4.44; F, 30.13%; ν_{max}/cm^{-1}). 2960, 2870, 1605, 1505, 1485, 1390 and 985; δ_H([$^2H_6$]acetone) 1.34 (6 H, t, *J* 7.0), 2.68 (4 H, q, *J* 7.0), 7.14 (2 H, m), 7.36 (1 H, m) and 8.57 (1 H, m); ([$^2H_6$]acetone) 62.0 (2 F, d), 80.1 (1 F, t) and 87.4 (2 F, t); *m/z* 316 (M$^+$ + 1, 16%), 315 (M$^+$, 37%), 301 (14%), 300 (100%) and 272 (38%). **3db**, m.p., 158–160 °C (Found: C, 60.7; H, 4.3; N, 4.4; F, 30.05. Calc. for $C_{16}H_{14}F_5N$: C, 60.94; H, 4.48; N, 4.44; F, 30.13%); ν_{max}/cm^{-1}: 2960, 1620, 1545, 1460, 1350, 980 and 870; *J*([$^2H_6$]acetone) 1.38 (6 H, t, *J* 7.0), 2.70 (4 H, q, *J* 7.0), 6.90 (2 H, d, *J* 8.0) and 7.42 (2 H, d, *J* 8.0); δ([$^2H_6$]acetone) 60.2 (2 F, d), 79.4 (1 F, t) and 87.2 (2 F, t); *m/z* 316 (M$^+$ + 1, 48%), 315 (M$^+$, 100%), 301 (23%), 300 (69%) and 272 (42%).

Photoinduced Reaction of Pentafluoroiodobenzene **1** *and Pyrroles* **5**.—Under a N_2 atmosphere, a mixture of **1** (1.47 g, 5 mmol), **5b** (1.05 g, 15 mmol) and acetonitrile (10 cm^3) was irradiated for 25 h as above. After work-up, 1-methyl-2-pentafluorophenylpyrrole (0.74 g, 60%) **6ba** and of 1-methyl-3-pentafluorophenylpyrrole **6bb** (0.25 g, 20%) were obtained. (The isomers were differentiated according to their m.p.s and yields: **6ba** has a lower m.p. because of its weaker polarity and in a higher yield since C_6F_5 group prefers to attack C-2 of pyrrole **5**). The isomers **6aa**/**6ab** were differentiated similarly. **6ba**, m.p. 87–88 °C (Found: C, 53.5; H, 2.2; N, 5.5; F, 38.2. Calc. for $C_{11}H_5F_5N$: C, 53.45; H, 2.45; N, 5.67; F, 38.43%). ν_{max}/cm^{-1} 1510, 1495, 1410, 1360, 1280, 1120 and 990; (δ[$^2H_6$]acetone) 2.95 (3 H, s), 5.61 (2 H, m) and 6.33 (1 H, m); δ_F([$^2H_6$]acetone) 63.3 (2 F, d), 81.5 (1 F, t) and 88.6 (2 F, t); *m/z* 248 (M$^+$ + 1, 15%), 247 (M$^+$, 100%), 246 (31%) and 205 (22%). **6bb**, m.p., 94–96 °C (Found: C, 53.25; H, 2.4; N, 5.5; F, 38.4%). Calc. for $C_{11}H_6F_5N$: C, 53.45; H, 2.45; N, 5.67; F, 38.43%). ν_{max}/cm^{-1} 1550, 1480, 1235, 1175, 1060, 985 and 800; δ_H([$^2H_6$]acetone) 3.47 (3 H, s), 6.20 (2 H, m) and 6.95 (1 H, m); δ_F([$^2H_6$]acetone) 67.0 (2 F, d), 80.8 (1 F, t) and 89.2 (2 F, t); *m/z* 248 (M$^+$ + 1, 18%), 247 (M$^+$, 100%), 205 (12%) and 123 (13%).

2-Pentafluorophenylpyrrole **6aa** *and 3-pentafluorophenylpyrrole* **6ab**. **6aa**, m.p., 79–81 °C (Found: C, 51.3; H, 1.7; N, 5.9; F, 40.5. Calc. for $C_{10}H_4F_5N$: C, 51.51; H, 1.73; N, 6.01; F, 40.75%); ν_{max}/cm^{-1} 3450, 1560, 1450, 1250, 1120, 985, 875 and 790; δ_H([$^2H_6$]acetone) 8.67 (1 H, w), 6.24 (1 H, m), 6.62 (1 H, m) and 7.01 (1 H, m); δ_F([$^2H_6$acetone) 62.4 (2 F, d), 82.4 (1 F, t) and 88.2 (2 F, t); *m/z* 234 (M^+ + 1, 22%), 233 (M^+, 100%), 205 (31%), 187 (29%) and 116 (11%). **6ab**, m.p., 94–95 °C (Found: C, 51.2; H, 1.5; N, 5.9; F, 40.8. Calc. for $C_{10}H_4F_5N$: C, 51.51; H, 1.73; N, 6.01; F, 40.75%) ν_{max}/cm^{-1} 3500, 1560, 1450, 1400, 1295, 1085, 995 and 875; δ_H([$^2H_6$]acetone) 8.69 (1 H, w), 6.40 (2 H, m) and 7.04 (1 H, m); δ_F([$^2H_6$] acetone) 64.2 (2 F, d), 79.1 (1 F, t), 88.0 (2 F, t); *m/z* 234 (M^+ + 1, 35%) and 233 (M^+, 100%).

2,5-Dimethyl-3-pentafluorophenylpyrrole **6c**. M.p. 104 °C. (Found: C, 55.3; H, 3.3; N, 5.2; F, 36.1. Calc. for $C_{12}H_8F_5N$: C, 55.17; H, 3.09; N, 5.36; F, 36.37%); ν_{max}/cm^{-1} 3450, 2900, 1535, 1515, 1490, 1410, 1320, 1135, 1055, 985, 840 and 780; δ_H($CDCl_3$) 2.15 (3 H, s), 2.26 (3 H, s), 5.91 (1 H, s) and 7.86 (1 H, s); δ_F($CDCl_3$) 64.1 (2 F, d), 81.7 (2 F, t) and 86.3 (2 F, t); *m/z* 261 (M^+, 100) and 246 (10%).

Reaction of **1** *with Indoles* **7** *and Imidazoles* **9**.—These reactions were conducted in a manner similar to that for **1** with **5**.

2-Pentafluorophenylindole (**8aa**) *and 3-pentafluorophenylindoles* **8ab**. **8aa**, m.p., 125–128 °C; ν_{max}/cm^{-1}; 3450, 1555, 1500, 1490, 1340, 1330, 1230, 1155, 1065, 1010, 980, 975 and 800; δ($CDCl_3$) 7.08–7.48 (4 H, m), 7.65 (1 H, m) and 8.80 (1 H, w); δ_P($CDCl_3$) 64.7 (2 F, d), 77.8 (1 F, t) and 84.2 (2 F, t); *m/z* 282 (M^+ + 1, 15%), 283 (M^+, 100), 255 (5%), 142 (12%), 90 (19%) and 69 (7%); **8ab**, m.p., 138–140 °C (Found: C, 59.4; H, 2.0; N, 4.8; F, 33.4. Calc. for $C_{14}H_6F_5N$: C, 59.37; H, 2.14; N, 4.95; F, 33.54%), ν_{max}/cm^{-1} 3350, 1620, 1545, 1485, 1410, 1335, 1320, 1235, 1095, 980, 840 and 805; δ_H($CDCl_3$) 7.12–7.40 (4 H, m), 8.40 (1 H, s) and 8.49 (1 H, s); δ_F($CDCl_3$) 62.9 (2 F, d), 80.4 (1 F, t) and 85.5 (2 F, t); *m/z* 284 (M^+ + 1, 17%), 283 (M^+, 100%), 255 (12%), 237 (19%), 143 (10%), 142 (13%), 107 (18%) 57 (34%) and 43 (79%).

3-Methyl-2-pentafluorophenylindole **8b**. M.p., 124–126 °C (Found: C, 60.45; H, 2.6; N, 4.8; F, 31.8. Calc. for $C_{15}H_8F_5N$: C, 60.61; H, 2.72; N, 4.71; F, 31.96%); ν_{max}/cm^{-1} 3450, 1515, 1495, 1360, 1330, 1240, 1170, 1145, 1075, 1045 and 990; δ($CDCl_3$) 2.26 (3 H, s), 7.10–7.39 (3 H, m), 7.64 (1 H, d) and 8.09 (1 H, s); δ_F($CDCl_3$) 62.0 (2 F, d), 76.3 (1 F, t), and 84.0 (2 F, t) *m/z* 297 (M^+, 100%), 296 (11%), 276 (10%) and 130 (21%).

2-Pentafluorophenylimidazole **10aa** *and 4-pentafluorophenylimidazole* **10ab**–**10aa**, m.p., 202–204 °C (lit.,[13] m.p. 204–205 °C); ν_{max}/cm^{-1} 3360, 1530, 1510, 1350, 1300, 1245, 1150, 1075, 1020, 975 and 900; δ([$^2H_6$]acetone) 7.56 (2 H, s) and 8.01 (1 H, s); δ_F([$^2H_6$]acetone) 66.0 (2 F, d), 80.0 (1 F, t) and 87.7 (2 F, t); *m/z* 235 (M^+ + 1, 17%), 234 (M^+, 100%), 207 (16%), 206 (11%), 180 (31%), 179 (25%), 161 (24%) and 43 (59%). **10ab**, m.p. 169–171 °C (lit.,[13] m.p. 170–172 °C); ν_{max}/cm^{-1} 1510, 1485, 1350, 1300, 1190, 1075, 1045, 940, 820 and 770; δ_H([$^2H_6$]acetone) 7.29 (1 H, s), 7.60 (1 H, s) and 8.19 (1 H, s); δ_F([$^2H_6$]acetone) 66.4 (2 F, d), 84.0 (1 F, t) and 88.8 (2 F, t); *m/z* 235 (M^+ + 1, 16%), 234 (M^+, 100%), 233 (12%), 207 (18%), 180 (41%), 179 (27%), 130 (10%) and 41 (12%).

4-Methyl-2-pentafluorophenyl-imidazole **10b** M.p., 174–176 °C (Found: C, 48.3; H, 2.0; N, 11.3; F, 38.0. Calc. for $C_{10}H_5F_5N_2$: C, 48.39: H, 2.03; N, 11.29; F, 38.28%); ν_{max}/cm^{-1} 3400, 1640, 1585, 1545, 1420, 1360, 1330, 1235, 1145, 1085, 1020, 1010, 985, 930, 820 and 795; δ_H($CDCl_3$): 2.53 (3 H, s), 7.28 (1 H, s) and 7.43 (1 H, s); δ_F($CDCl_3$) 64.3 (2 F, d), 79.6 (1 F, t) and 84.5 (2 F, t); *m/z* 249 (M^+ + 1, 44%), 248 (M^+, 14%), 148 (16%), 137 (15%), 123 (14%), 121 (101%), 97 (96%) and 44 (100%).

Photoinduced Reaction of Pentafluoroiodobenzene **1** *and Anisole* **11a**.—Under a N_2 atmosphere, a stirred mixture of **1** (1.47 g, 5 mmol) and **11a** (10 cm^3) in a Pyrex flask was irradiated with a medium-pressure mercury lamp (450 W) at a distance of 8 cm for 12 h. After this, the anisole was distilled off and the residue was directly subjected to column chromatography on silica gel using ether–light petroleum (1:5) as eluent to give 2,3,4,5,6-pentafluoro-2′-methoxybiphenyl **12aa** (0.69, 50%) and 2,3,4,5,6-pentafluoro-4′-methoxybiphenyl **12ab** (0.36g, 26%). **12aa**, m.p. 47–48 °C (lit.,[18] 46–47.5 °C); ν_{max}/cm^{-1} 1650, 1510, 1440, 1300, 1180, 1025, 945 and 760; δ([$^2H_6$]acetone) 3.32 (3 H, s), 7.01–7.48 (4 H, m); δ_F([$^2H_6$]acetone) 68.5 (2 F, d), 82.7 (1 F, t) and 88.6 (2 F, t); *m/z* 275 (M^+ + 1, 24%), 274 (M^+, 78%), 259 (14%), 231 (100%) and 205 (27%). **12ab**, m.p., 123 °C (lit.,[19] m.p. 123–124 °C); ν_{max}/cm^{-1} 1650, 1600, 1520, 1430, 1250, 1060, 990 and 860; δ_H([$^2H_6$]acetone) 3.30 (3 H, s), 6.99 (2 H, d, *J* 8.0) and 7.48 (2 H, d, *J* 8.0); δ_F([$^2H_6$]acetone) 64.4 (2 F, d), 82.5 (1 F, t) and 88.6 (2 F, t); *m/z* 275 (M^+ + 1, 17%), 274 (M^+, 100%), 259 (20%), 231 (62%) and 205 (17%).

Photoinduced Reaction of Pentafluoroiodobenzene **1** *and* 1,4-*Dimethoxybenzene* **11b**.—Under a N_2 atmosphere, a stirred solution of **1** (1.47 g, 5 mmol) and **11b** (2.76 g, 20 mmol) in acetonitrile (15 cm^3) was exposed to a medium pressure mercury lamp (450 W) at a distance of 8 cm for 16 h. The mixture was then concentrated under reduced pressure and the oily residue extracted with ether (60 cm^3). The extracts were washed with water (10 cm^3 × 3), dried ($MgSO_4$) and concentrated under reduced pressure. The oily residue was subjected to column chromatography as above to give pentafluoro-2′,5′-dimethoxy-2,3,4,5,6-biphenyl **12b** (1.00 g, 65%), m.p. 62 °C (Found: C, 55.3; H, 2.9; F, 31.0. Calc. for $C_{14}H_9F_5O_2$: C, 55.27; H, 2.99; F, 31.23%); ν_{max}/cm^{-1} 2960, 1655, 1470, 1230, 1180, 1045, 990 and 720; δ_H([$^2H_6$]acetone) 3.82 (3 H, s), 3.92 (3 H, s), 7.08 (2 H, m) and 7.35 (1 H, m); δ_F([$^2H_6$]acetone) 64.6 (2 F, d), 81.2 (1 F, t) and 87.2 (2 F, t); *m/z* 305 (M^+ + 1, 17%), 304 (M^+, 100), 261 (29%), 138 (95%) and 123 (99%).

Photoinduced Reaction of Pentafluoroiodobenzene **1** *and Phenols* **13**.—*Typical procedure*. Under a N_2 atmosphere, a stirred solution of **1** (1.47 g, 5 mmol) and **13a** (1.88 g, 20 mmol) in acetonitrile (15 cm^3) was irradiated with a medium-pressure mercury lamp (450 W) at a distance of 8 cm for 12 h. Acetonitrile and unchanged phenol were distilled off under *in vacuo* and the oily residue was directly chromatographed on silica gel using ether–light petroleum (1:3) as eluent to give 2-pentafluorophenylphenol **14aa** (0.65 g, 50%) and 4-pentafluorophenylphenol **14ab** (0.33 g, 25%); **14aa** and **14ab** were distinguished by m.p. **14aa** has the lower m.p. because of intramolecular hydrogen bonding between the OH and F; **14ba/14bb** and **14ca/14cb** were distinguished similarly. **14aa**, m.p., 32 °C; ν_{max}/cm^{-1} 3350, 1600, 1520, 1250, 1225, 1055, 980 and 855; δ_H($CDCl_3$) 6.62–6.95 (4 H, m) and 8.15 (1 H, w); δ_F($CDCl_3$) 64.0 (2 F, d), 81.9 (1 F, t) and 88.5 (2 F, t); *m/z* 261 (M^+ + 1, 11%), 260 (M^+, 100%), 241 (14%), 231 (14%), 213 (15%) and 182 (9%); **14ab**, m.p., 208–10 °C; ν_{max}/cm^{-1} 3340, 1605, 1490, 1265, 1245, 985 and 820 δ_H($CDCl_3$) 6.75 (2 H, d, *J* 8.5), 7.15 (2 H, d, *J* 8.8) and 8.05 (1 H, w); δ_F($CDCl_3$) 64.8 (2 F, d), 81.8 (1 F, t) and 88.5 (2 F, t); *m/z* 261 (M^+ + 1, 20%), 260 (M^+, 100%), 241 (8%), 231 (6%), 45 (29%) and 44 (36%).

4-Methyl-2-pentafluorophenylphenol **14ba** and *4-methyl-3-pentafluorophenylphenol* **14bb**. **14ba** (47%), m.p. 58 °C. (Found: C, 56.3; H, 2.5; F, 35.0. Calc. for $C_{13}H_7F_5O$: C, 56.62; H, 2.60; F, 34.90%); ν_{max}/cm^{-1} 3350, 2840, 1605, 1530, 1490, 1400, 1320, 1240, 1125, 1060, 985 and 885; δ_H($CDCl_3$) 2.75 (3 H, s), 6.25–6.62 (3 H, m) and 8.65 (1 H, w); δ_F($CDCl_3$) 64.4 (2 F, d), 81.8 (1 F, t) and 88.5 (2 F, t; *m/z* 275 (M^+ + 1, 15%), 274 (M^+, 100%), 255 (10%) and 198 (13%); **14bb** (30%), m.p. 86 °C

(Found: C, 56.2; H, 2.3; F, 35.0. Calc. for $C_{13}H_7F_5O$: C, 56.62; H, 2.60; F, 34.90%); ν_{max}/cm^{-1} 3350, 1660, 1610, 1580, 1510, 1490, 1270, 1230, 1160, 1120, 1055 and 995; $\delta_H(CDCl_3)$ 2.73 (3 H, s), 6.23–6.53 (3 H, m) and 8.19 (1 H, w); $\delta_F(CDCl_3)$ 65.4 (2 F, d), 81.3 (1 F, t) and 87.5 (2 F, t); *m/z* 275 (M^+ + 1, 24%), 276 (M^+, 100%), 255 (23%) and 107 (13%).

4-*Chloro-2-pentafluorophenylphenol* **14ca** *and* 4-*Chloro-3-pentafluorophenol* **14cb**. **14ca** (48%) oil (Found: C, 48.8; H, 1.0; Cl, 11.8; F, 32.0. Calc. for $C_{12}H_4ClF_5O$: C, 48.92; H, 1.37; Cl, 12.03; F, 32.25%); ν_{max}/cm^{-1} 3400, 1515, 1495, 1300, 1260, 1220, 1185, 1100, 1065, 990, 945 and 875; $\delta_H(CDCl_3)$ 6.25–6.75 (3 H, m) and 9.13 (1 H, w); δ_F 64.0 (2 F, d), 80.5 (1 F; t) and 87.9 (2 F, t); *m/z* 297 (M^+ + 1, 5%), 296 (M^+, 23%), 294 (M^+, 100%), 261 (13%), 260 (16%), 231 (21%), 200 (12%) and 193 (11%); **14cb** (12%) m.p., 89 °C (Found: C, 48.7; H, 1.2; Cl, 12.0; F, 32.0. Calc. for $C_{12}H_4ClF_5O$: C, 48.92; H, 1.37; Cl, 12.03; F, 32.25%); ν_{max}/cm^{-1} 3450, 1605, 1545, 1500, 1280, 1145, 1025, 985 and 820; $\delta_H(CDCl_3)$ 6.30 and 6.82 (3 H, m) and 8.75 (1 H, w); $\delta_F(CDCl_3)$ 64.8 (2 F, d), 80.7 (1 F, t) and 87.8 (2 F, t); *m/z* 297 (M^+ + 1, 5%), 296 (M^+, 11%), 295 (M^+ + 1, 24%), 294 (M^+,70%), 262 (33%), 260 (100%) and 43 (43%).

4-*Nitro-2-pentafluorophenylphenol* **14d**. (62%) m.p. 100–102 °C. The structure of **14d** was assumed to be as shown because it was the only product detected, and because in the other *p*-X-phenol reactions, the position *ortho* to the OH was always attacked to a greater extent from the position *meta* (Found: C, 47.0; H, 1.4; F, 30.95; N, 4.55. Calc. for $C_{12}H_4F_5NO_3$: C, 47.21; H, 1.36; F, 31.12; N, 4.59%); F, 30.95; N, 4.55; ν_{max}/cm^{-1} 3300, 1605, 1585, 1490, 1340, 1280, 1200, 1160, 1105, 985, 860 and 720; $\delta_H(CDCl_3)$ 4.5 (1 H, w), 6.23 (1 H, dd, 9.5 Hz, 3.0 and 7.39 (2 H, m); $\delta_F(CDCl_3)$ 64.2 (2 F, d), 79.6 (1 F, t) and 87.4 (2 F, t); *m/z* 305 (M^+, 22%), 231 (10%), 211 (14%), 183 (13%), 140 (16%), 139 (Ar^+ + 1, 100%), 123 (10%), 109 (54%), 93 (25%) and 65 (83.95).

Photoinduced reaction of hydroquinone **15** and pentafluoroiodobenzene **1** was carried out similarly to give 2,3,4,5,6-pentafluoro-1′,4′-dihydroxybiphenyl **16** (10%), m.p., 178–180 °C (Found: C, 52.0; H, 1.4; F, 34.1. Calc. for $C_{12}H_5F_5O_2$: C, 52.19; H, 1.83; F, 34.40%); $\delta_H([^2H_6]acetone)$ 6.40–7.02 (3 H, m), 7.40 (1 H, s) and 8.00 (1 H, s); $\delta_F([^2H_6]acetone)$ 65.0 (2 F, d), 80.1 (1 F, t) and 87.2 (2 F, t).

Reaction of Pentafluoroiodobenzene **1** *and Sodium Phenoxides* **18**.—Typical procedure. Under a N_2 atmosphere, NaH (0.15 g, 5 mmol) was slowly added to a DMF (5 cm^3) solution of phenol (0.47 g, 5 mmol). The mixture was stirred for 20 min, and then **1** (1.47 g, 5 mmol) was added. After 30 min, ^{19}F NMR spectroscopy indicated that **1** had been completely converted. The mixture was then poured into water (30 cm^3) and extracted with ether (3 × 15 cm^3). The organic layer was washed with water (3 × 10 cm^3), dried ($MgSO_4$) and concentrated. The residue was subjected to column chromatography on silica gel using light petroleum–ether (20:1) as eluent to give 2,3,5,6-tetrafluoro-4-iododiphenyl ether **19aa** (1.80 g, 98%) containing ^{19}F NMR) 2% of 3,4,5,6-tetrafluoro-2-iododiphenyl ether **19ab**. **19aa**, m.p., 68–70 °C (Found: C, 38.9; H, 1.15; F, 20.4; I, 34.2. Calc. for $C_{12}H_5IOF_4$: C, 39.16, H, 1.37; F, 20.64; I, 34.48%); ν_{max}/cm^{-1} 1620, 1590, 1480, 1200, 1155, 1075, 975, 825, 760 and 720; $\delta_H(CDCl_3)$ 7.25 (m); $\delta_F(CDCl_3)$ 42.5 (2 F, d) and 74.2 (2 F, d); *m/z* 369 (M^+ + 1, 23%), 368 (M^+, 64%), 348 (18%), 341 (30%), 340 (27%), 318 (13%), 263 (13%), 241 (39%), 222 (36%), 213 (57%), 155 (52%) and 77 (100%).

2,3,5,6-*Tetrafluoro-4-iodo-4-methyldiphenyl ether* **19ba**. M.p., 48–50 °C (Found: C, 41.1; H, 1.7; F, 19.7; I, 33.0. Calc. for $C_{13}H_7IOF_4$: C, 40.86; H, 1.85; F, 19.89; I, 33.01%) ν_{max}/cm^{-1} 1600, 1480, 1450, 1270, 1195, 1165, 1100, 970, 840, 815 and 720 $\delta(CDCl_3)$: 2.32 (3 H, s), 6.92 (2 H, d, 8.0) and 7.18 (2 H, d, 8.0) ppm; $\delta_F(CDCl_3)$ 42.9 (2 F, d) and 72.4 (2 F, d); *m/z* 383 (M^+ + 1, 91%), 382 (M^+, 11%), 256 (16%), 92 (100%), 89 (16%) and 65 (48%).

4-*Chloro-2′,3′,5′,6′-tetrafluoro-4′-iododiphenyl ether* **19ca**. M.p. 72–74 °C (Found: C, 35.7; H, 0.9; F, 18; I, 31.2. Calc. for $C_{12}H_4ClF_4O$: C, 35.81; H, 1.00; F, 18.88; I, 31.53%); $\delta_H(CDCl_3)$ 7.03 (2 H, d, *J* 9.0) and 7.30 (2 H, d, *J* 9.0) $\delta_F(CDCl_3)$ 41.6 (2 F, d) and 74.0 (2 F, d); *m/z* 404 (M^+, 34%), 402 (M^+, 100%), 275 (16%) and 127 (34%).

2,3,5,6-*Tetrafluoro-4-iodo-4′-nitrodiphenyl ether* **19da**. M.p. 76–78 °C. Calc. for $C_{12}H_4F_4INO_3$: C, 34.89; H, 0.98; N, 3.39; F, 18.40; I, 30.72. (Found: C, 34.8; H, 1.0; F, 18.3; I, 30.6; N, 3.2); ν_{max}/cm^{-1} 1590, 1480, 1340, 1270, 1220, 1160, 1105, 1065, 1000, 975, 860, 845, 800 and 795; $\delta_H(CDCl_3)$ 7.19 (2 H, d, *J* 9.0) and 8.13 (2 H, d, *J* 9.0); $\delta_F(CDCl_3)$ 40.7 (2 F, d) and 73.8 (2 F, d); *m/z* 414 (M^+ + 1, 52%), 413 (M +, 100%), 383 (19%), 339 (13%) and 240 (10%).

The reaction of chloropentafluorobenzene **17** and sodium phenoxide **18a** was similar to that of **1** and **18** and gave, after work-up, 4-chloro-2,3,5,6-tetrafluorodiphenyl ether **20a** (88%), m.p. 44–46 °C (Found: C, 52.0; H, 1.5; Cl, 12.6; F, 27.7. Calc. for $C_{12}H_5ClF_4O$: C, 52.10; H, 1.83; Cl, 12.82; F, 27.47%); ν_{max}/cm^{-3} 1590, 1485, 1285, 1195, 1160, 1085, 980, 805 and 750; $\delta_H(CDCl_3)$ 7.20; $\delta_F(CDCl_3)$ 63.5 (2 F, d) and 75.7 (2 F, d); *m/z* 278 (M^+, 29%), 276 (M^+, 100%), 248 (32%), 213 (14%), 193 (8%) and 154 (9%).

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