Homolytic Reactions of Polyfluoroaromatic Compounds. Part 16.[1] Competitive Phenylation of Polyfluorobenzenes

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Pairs of polyfluorobenzenes were allowed to compete for phenyl radicals generated by the thermolysis of benzoyl peroxide at 80°. From the relative yields of biaryl, and the yields of each biaryl formed upon arylation of each arene individually, the relative rates of attack of each site in each arene were deduced. Neither iron(III) benzoate nor trichloroacetic acid uniformly improved yields of biaryl, although in some cases the isomer distribution altered, when decomposition of benzoyl peroxide was carried out in the presence of such additives, to favour products of aryldehydrogenation or of aryldefluorination, respectively. Competition did not usually affect the distribution of attack of a particular arene, except when hexafluorobenzene was used, in which case greater selectivity of attack of the second arene occurred. This suggested the formation of a 'stabilised' phenyl radical, and supported an earlier suggestion of species such as $[C_6F_6,Ph^{\cdot}]$; other evidence also supported the postulate.

Homolytic aromatic arylation of polyfluorobenzenes involves the displacement of hydrogen and in most cases, of fluorine.[1] The effects of substituents (X) upon the rate of displacement of hydrogen from arenes (PhX) by phenyl radicals generated by the thermolysis of benzoyl peroxide shows that additivity prevails in the mono- and di-substituted benzenes.[2,3] In contrast the corresponding reactions of derivatives of pentafluorobenzene (C_6F_5X, where X = H, F, Br, or CF_3)[4] gave little evidence of such additivity, especially when there are considerable differences in the π-electron density of the radical source and the substrate. This led to the proposal[4,5] that specific interactions between radicals and substrates constituted a second selection process whose discrimination between substrates is different from that shown by the radical itself.

The orientation of some aryldefluorination[4] and aryldehydrogenation[2] reactions did not, however, change in competition reactions, suggesting that this complication arose only in intermolecular and not in intramolecular selection processes. Moreover, our previous studies have indicated that this complication is serious only with the more fully fluorinated arenes penta- and hexa-fluorobenzene[1] since it appears likely that with polyfluorobenzenes ($C_6H_{6-x}F_x$) where $x \leqslant 4$ the orientation of attack was successfully predicted by the substituted rate factors (s.r.f.s) found for the aryldehydrogenation of fluorobenzene assuming additivity.

We now report a more detailed study conducted in order to test the above tentative conclusions.

Discussion

The couse of each experiment now described, whether involving a single substrate or a competition reaction, was followed by measuring the amount of each biaryl produced. Table 1 shows the yields and relative proportions of biaryls obtained from the phenylation of each polyfluorobenzene in the absence of additives and in the presence of iron(III) benzoate or of trichloroacetic acid, which have previously been found to improve the yields of products of aryldehydrogenation[3] and aryldefluorination,[6] respectively. Although some small effects are discernible, no great increases in biaryl yields occurred, however, in the reactions now described, and competition reactions were therefore conducted without additives.

Our assumption that most of the decomposition of benzoyl peroxide produces phenyl radicals is justified by the relatively small extent to which aroyloxydehydrogenation products arise in the decomposition of benzoyl peroxide in simple arenes[7,8] and in our reacting systems (Table 2). Trichloroacetic acid, however, substantially increases the yields of products of benzoyloxylation.

Aroic acids have also been shown to encourage aryldefluorination of hexafluorobenzene.[6,9,10] Since benzoic acid is a product of phenyldehydrogenation it was possible, in principle, that aryldefluorination of a polyfluorobenzene could depend upon aryldehydrogenation to provide the necessary aroic acid. Aryldefluorination would then lag behind, and be consequent upon, aryldehydrogenation and so the isomer distribution might change perceptibly throughout the course of arylation. Table 3 shows this not to be the case with pentafluorobenzene, at least past the first half-life.

The results might also be influenced by the possible instability of the higher boiling polynuclear products, which are known, in the case of hexafluorobenzene, to be capable of pyrolysis at 80°[11] and at higher temperatures[12] to give additional pentafluorobiphenyl. We therefore checked the stability of our reaction mixtures towards further formation of biaryls by prolonged heating and found no improvement in yield over 200 h at 80° (*e.g.* Table 3). We concluded that this instability, at least at 80°, is confined to the benzoyl peroxide–hexafluorobenzene system.

Wherever possible, every pair of polyfluorinated benzenes was studied in competition. The limits were set by the inability of n.m.r. spectroscopy or of g.l.c. to differentiate the individual biaryls formed, or by the coincidence of two forms of reaction giving the same product. For example, aryldefluorination of 1,2,3,5-tetrafluorobenzene and aryldehydrogenation of 1,3,5-trifluorobenzene both give 2,4,6-trifluorobiphenyl. Although the relative proportions of the other products allow the relative contributions of each mode of reaction to be calculated, this assumes that the isomer distribution was unchanged, and we wished to avoid this unnecessary assumption. Competition reactions were performed at two relative amounts of substrates, corresponding to 2 : 3 and 3 : 2 by volume. The relative yields of products quoted in Table 4 refer to these two sets of reaction conditions, the first figure corresponding to the mixture containing 40 vol % of component A. In each case, the observed yields of biaryl have been multiplied by two factors. The first, by incorporating the percentage yield of biaryl formed by the thermolysis of benzoyl peroxide in the

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Table 1. Yields from phenylation of polyfluorobenzenes (Bz_2O_2; 80 °C; 72 h)

Arene	Polyfluorobiphenyl	Yield [a]	Yield [b] (FeBz)	Yield [c] (acid)
C_6F_5H (1)	2,3,4,5-Tetrafluoro- (11)	5.8 (9)	5.1 (11)	6.0 (10)
	2,3,4,6-Tetrafluoro- (12)	30.1 (50)	24.5 (45)	31.2 (53)
	2,3,5,6-Tetrafluoro- (13)	13.3 (21)	7.6 (14)	10.2 (18)
	2,3,4,5,6-Pentafluoro- (14)	12.8 (20)	16.6 (30)	10.8 (19)
1,2,3,4-$C_6F_4H_2$ (2)	2,3,4-Trifluoro- (15)	7.4 (18)	8.9 (15)	5.0 (13)
	2,3,6-Trifluoro- (17)	19.8 (49)	18.8 (36)	17.7 (49)
	2,3,4,5-Tetrafluoro- (11)	12.1 (33)	25.6 (49)	13.9 (38)
1,2,3,5-$C_6F_4H_2$ (3)	2,3,5-Trifluoro- (16)	4.7 (9)	2.7 (7)	5.8 (11)
	2,4,6-Trifluoro- (18)	15.8 (29)	10.8 (28)	15.6 (30)
	3,4,5-Trifluoro- (20)	1.6 (3)	1.2 (3)	1.6 (3)
	2,3,4,6-Tetrafluoro- (12)	32.4 (59)	23.7 (62)	29.7 (56)
1,2,4,5-$C_6F_4H_2$ (4)	2,4,5-Trifluoro- (19)	16.5 (26)	11.9 (22)	20.2 (35)
	2,3,5,6-Tetrafluoro- (13)	47.1 (74)	43.3 (78)	37.5 (65)
1,3,5-$C_6H_3F_3$ (5)	3,5-Difluoro- (26)	4.1 (8)	3.8 (5)	3.9 (7)
	2,4,6-Trifluoro- (18)	50.8 (92)	75.8 (95)	52.7 (93)
1,2,4-$C_6H_3F_3$ (6)	2,4-Difluoro- (22)	3.3 (6)	2.9 (5)	3.5 (7)
	2,5-Difluoro- (24)	3.6 (7)	2.9 (5)	4.5 (9)
	3,4-Difluoro- (25)	<1.0 (<1)	2.2 (4)	1.8 (4)
	2,3,5-Trifluoro- (16)	15.9 (30)	16.5 (27)	12.5 (26)
	2,3,6-Trifluoro- (17)	19.5 (37)	22.9 (38)	15.9 (33)
	2,4,5-Trifluoro- (19)	10.1 (19)	12.9 (21)	10.4 (21)
1,2-$C_6H_4F_2$ (7)	2-Fluoro- (27)	7.4 (11)	7.0 (9)	6.3 (13)
	2,3-Difluoro- (21)	39.1 (59)	41.9 (57)	28.1 (56)
	3,4-Difluoro- (25)	19.8 (30)	25.2 (34)	15.5 (31)
1,3-$C_6H_4F_2$ (8)	3-Fluoro- (28)	0	0	0
	2,4-Difluoro- (22)	21.8 (39)	22.4 (41)	20.5 (41)
	2,6-Difluoro- (24)	21.8 (39)	23.1 (42)	19.2 (39)
	3,5-Difluoro- (26)	12.2 (22)	9.8 (17)	9.8 (20)
1,4-$C_6H_4F_2$ (9)	4-Fluoro- (29)	<1.0 (<2)	<1.0 (<2)	<1.0 (<2)
	2,5-Difluoro- (23)	70.4 (>98)	65.6 (>98)	40.2 (>98)

[a] Mol per mol of peroxide decomposed × 100; relative ratios given in parentheses. [b] Added iron(III) benzoate. [c] Added trichloroacetic acid.

appropriate single substrate, allows for the diversion of the intermediate radicals away from forming biaryl. The second factor normalises the biaryl yield ratio to equimolar amounts of the two competing substrate. The agreement between the two values in Table 4 is some indication of the correctness of the assumption used in these calculations.

Within each substrate, the best available s.r.f.s found by the competition of fluorobenzene and benzene [13] ($f_{o\text{-F}}$, 2.0; $f_{m\text{-F}}$, 1.1; $f_{p\text{-F}}$, 1.1) successfully predicted the orientation of phenylation when used in conjunction with an empirical parameter, 0.30, to represent the relative ease of displacement of fluorine and hydrogen under the reaction conditions. Since the values now obtained differ only slightly from those reported earlier,[1] in which older and probably less reliable f values for fluorobenzene were used for calculation, the detailed results are not reproduced here. As before, however, the match between observed and calculated orientations is very good for di- and tri-fluorobenzenes and for 1,2,3,4-tetrafluorobenzene, but somewhat less so for the other tetrafluorobenzenes and for pentafluorobenzene.

However, no such consistent set of factors may be found to apply to the results of competition studies. Thus (Table 4) the competition of *o*- (7) and *p*-difluorobenzene (9) provides 2,5-difluorobiphenyl (23) and 2,3-difluorobiphenyl (21) in the relative amounts of 1.5—1.6 to 1. There are two sites in (7), and four sites in (9), which undergo aryldehydrogenation to give (21) and (23), respectively, and each of the six sites formally is influenced by two fluorine substituents, one *meta* and one *ortho* to the site of attack. The expected ratio of (23) to (21) is therefore 2.0, and the discrepancy is outside the experimental error.

Fluorine substituents generally show a deactivating effect (Table 4) regardless of their orientation towards the reaction site. The distribution of attack does not, however, change markedly under competition conditions (Table 5) although hexafluorobenzene (10) seems to have a particular influence on the orientation of attack on less fully fluorinated arenes (Table 6). In a number of cases the biaryl yields alter so as to promote the formation of those products already in largest amount. Such increased selectivity implies stabilisation of the attacking radical, and is consistent with complex formation between Ph· and (10).[2] Although not all fluorinated arenes show this effect [*cf.* 1,2,4-trifluorobenzene (6)], and changes in the orientation of attack on some arenes [notably 1,2,3,4-tetrafluorobenzene (2)] may be discerned in the absence of (10), the behaviour is well marked only in reactions in which (10) is present.

Aryldefluorination occurs in the phenylation of a number

Table 2. Yields of aryl benzoates arising from aroyloxylation of polyfluoroarenes (Bz_2O_2; 80 °C; 72—100 h)

Arene	Substituents in Ar·O·CO·Ph	Yield [a]	Yield [b] (acid)	^{19}F N.m.r. shifts (p.p.m. upfield of $CFCl_3$)
1,2,3,4-$C_6F_4H_2$	2,3,4-Trifluoro-	4.3	7.4	F-2 146.4; F-3 158.0; F-4 137.0 [c]
1,2,3,5-$C_6F_4H_2$	2,4,6-Trifluoro-	<1	5.6	F-2 122.8; F-4 110.3 [d]
	3,4,5-Trifluoro-	<1	2.8	F-3 132.1; F-4 166.6 [e]
1,2,4,5-$C_6F_4H_2$	2,4,5-Trifluoro-	7.0	21.0	F-2 129.7; F-4 136.7; F-5 140.6 [f]
1,3,5-$C_6F_3H_3$	3,5-Difluoro-	0	2.9	F-3 113.1
1,2,4-$C_6F_3H_3$	2,4-Difluoro-	5.8	16.6	F-2 124.2; F-4 113.3 [g]
	2,5-Difluoro-	<1	4.2	F-2 134.3; F-5 117.3 [h]
	3,4-Difluoro-	1.8	9.0	F-3 135.8; F-4 141.7 [i]
1,2-$C_6H_4F_2$	2-Fluoro-	2.3	12.2	F-2 128.9 [j]
1,3-$C_6H_4F_2$	3-Fluoro-	0	4.2	F-3 111.5 [k]
1,4-$C_6H_4F_2$	4-Fluoro-	6.0	34.0	F-4 117.6 [l]

[a] Mol per mol of peroxide consumed × 100. [b] In the presence of trichloroacetic acid. [c] Calculated, assuming additivity of substituent effects ($\Delta\delta_{o-F}$, 24.5; $\Delta\delta_{m-F}$, -3.9; $\Delta\delta_{p-F}$, 6.1 p.p.m.) upon the chemical shifts of the monofluorophenyl benzoates, as F-2, 149.5; F-3, 160.5 F-4, 138.2 p.p.m. [d] Calc.: F-2, 121.1; F-4, 109.8 p.p.m. [e] Calc.: F-3, 132.1; F-4, 166.6 p.p.m. [f] Calc.: F-2, 131.1; F-4, 138.2; F-5, 142.1 p.p.m. Found (authentic material): F-2, 129.7; F-4, 136.7; F-5, 140.6 p.p.m. [g] Calc.: F-2, 125.0; F-4, 113.7 p.p.m. [h] Calc.: F-2, 135.0; F-5, 117.6 p.p.m. [i] Calc.: F-3, 136.0; F-4, 142.1 p.p.m. [j] Found (authentic material): F-2, 128.9 p.p.m. [k] Found (authentic material): F-3, 111.5 p.p.m. [l] Found (authentic material): F-4, 117.6 p.p.m.

Table 3. Isomer distribution in the phenylation of pentafluorobenzene (1) (Bz_2O_2; 80 °C)

	Isomer distribution (%)			
t/h	2,3,4,5-F_4 biphenyl	2,3,4,6-F_4 biphenyl	2,3,5,6-F_4 biphenyl	2,3,4,5,6-F_5 biphenyl
18	9	48	21	22
24	9	49	21	21
48	10	48	21	21
90	9	48	22	21

of substrates, and Table 7 shows the results of attempts to determine s.r.f.s for this process from the competition reactions studied. The first contrast with aryldehydrogenation (Table 4) is the accelerating effect of fluorine substituents in aryldefluorination. The second is that reasonably self-consistent s.r.f.s can be found. The empirically selected values for this process (f_o, 3.0; f_m, 0.8; f_p, 1.2) reflect the effect of fluorine substituents tolerably well over the range of substrates and suggest that phenylation at carbon atoms bearing fluorine has electrophilic properties (Table 7). When these parameters are applied to the results of competitions involving hexafluorobenzene (10) as one of the substrates they are less successful. A somewhat better description comes from using the values f_o, 3.5; f_m, 1.0; and f_p, 0.9 for the required s.r.f.s. This difference, if significant, reflects the greater selectivity which a radical such as Ph· would be expected to show upon complexing.

To summarise, therefore, our results establish (a) that associations of phenyl radicals with polyfluoroarenes give species which are more selective than free phenyl radicals in phenylation, (b) that it is inter- rather than intra-molecular selection which is mainly affected, and (c) that the effect is more noticeable with the more fluorinated substrates, while not entirely confined to them.

Experimental

The polyfluorobenzenes were commercial samples (Bristol Organics) which were dried ($CaCl_2$) and purified by fractional distillation. Although their physical constants and densities agreed well with the literature[14] ^{19}F n.m.r. spectroscopy was the preferred measure of purity.

Commerical benzoyl peroxide (B.D.H.) was purified by reported[2] methods. 4-Fluorobiphenyl (Aldrich; 99%) and trichloroacetic acid (May and Baker; >98%) were used without further treatment after their purity had been checked (g.l.c.). Polyfluorophenols which were not commercially available could, in some cases, be prepared by heating a polyfluorobenzene (3.8 g), potassium hydroxide (4 g, excess), and dimethyl sulphoxide (15 cm^3) under reflux with stirring for 4 h. Non-acidic materials were removed by steam distillation, after which further distillation in steam of the acidified aqueous solution provided the phenol. In this way 2,3,5-trifluorophenol, δ_F (p.p.m. upfield of $CFCl_3$) 169.3 (F-2, 168.7), 134.8 (F-3, 133.6), and 115.4 (F-5, 115.2) was prepared from (3), 2,3,6-trifluorophenol, δ_F 157.5 (F-2, 158.7), 142.0 (F-3, 143.0), and 140.6 p.p.m. (F-6, 140.3), from (2a), and 2,4,5-trifluorophenol, δ_F 142.0 (F-2, 143.4), 146.2 (F-4, 145.2), and 142.0 p.p.m. (F-5, 143.0) from (4). The calculated chemical shifts, given in parentheses, were found by assuming an additive effect of an *o*-fluorine ($\Delta\delta$ 24.5 p.p.m.), an *m*-fluorine ($\Delta\delta$ -3.9 p.p.m.), and a *p*-fluorine ($\Delta\delta$ 6.1 p.p.m.) substituent upon the chemical shifts of fluorine in the monofluorophenols (δ *o*-fluorophenol, 141.2; *m*-fluorophenol, 112.4; and *p*-fluorophenol, 124.6 p.p.m.).

In the same way, the identity of the phenyl benzoate derivatives formed by Schotten–Baumann acylation of these phenols (*o*-fluoro, m.p. 65°; *m*-fluoro, m.p. 41°; *p*-fluoro, m.p. 55°; 2,6-difluoro, m.p. 64°; 2,3,5-trifluoro, m.p. 33°; 2,3,6-trifluoro, m.p. 39°; and 2,4,5-trifluoro, m.p. 41°) was confirmed by ^{19}F n.m.r. spectroscopy (Table 2).

^{19}F N.m.r. spectra were measured using a JEOL FX-90Q multinuclear Fourier transform instrument with $CDCl_3$ as solvent and $CFCl_3$ as reference. G.l.c. was carried out using a Pye-Unicam 204 instrument 15% OV-1 on Chromosorb W 80—100 as stationary phase and a nitrogen flow rate of 40 cm^3 min^{-1}. Mass spectrometry, used to identify compounds and to confirm identification, generally required a VG-

Micromass 12B machine at 2—4 kV accelerating voltage and 20—70 eV ionisation potential; higher resolution was obtained on the VG-Micromass 70-70 instrument at University College, London and we are grateful to Professor J. H. Ridd for extending this facility to us.

The general procedure for studying reactions involved dissolving accurately weighed amounts of benzoyl peroxide (*ca.* 1 mmol), the reference compound (usually 4-fluorobiphenyl; *ca.* 0.1 g) and the catalyst (where appropriate; 10—20 mg) in the purified solvent or mixture of solvents (5.0 cm^3). Competition was studied using mixtures of two solvents, *A* and *B*, in the ratios 2 : 3 and 3 : 2 v/v. The results in Tables 4 and 7 show values from each set of reaction conditions, expressed for equimolar amounts of *A* and *B*. One or two small lumps of carbon dioxide were added to displace atmospheric oxygen, and the reaction mixture was then heated under reflux in a thermostat at 80° until all the peroxide was consumed (72—100 h). The excess of fluorocarbon was carefully removed by distillation (water-bath) and was checked (g.l.c.) for the absence of biaryls. The distillation residue was then distilled in steam, and the steam-volatile materials were taken up in chloroform, when the dried ($MgSO_4$) organic layer was then evaporated to dryness and the residue was dissolved in $CDCl_3$–$CFCl_3$ before analysis.

Polyfluorobiphenyls were identified by ^{19}F n.m.r. spectroscopy on the following considerations: (a) that the number, relative intensities, chemical shifts, and splitting patterns of

Table 4. Competition between arenes; relative yields of phenylation products

Arene A	Arene B	Yield ratios [a]
(2)	(7)	(11)/(21), 0.67, 0.75; (11)/(25), 0.95, 0.70
(3)	(7)	(12)/(21), 0.48, 0.42; (12)/(25), 0.69, 0.62
(4)	(7)	(13)/(21), 0.91, 0.91; (13)/(25), 1.20, 1.05
(5)	(7)	(18)/(21), 0.46, 0.51; (18)/(25), 0.76, 0.82
(8)	(7)	(22)/(21), 0.37, 0.40; (24)/(21), 0.42, 0.45; (26)/(21), 0.13, 0.16; (22)/(25), 0.65, 0.76; (24)/(25), 0.73, 0.78; (26)/(25), 0.26, 0.31
(9)	(7)	(23)/(21), 1.60, 1.50; (23)/(25), 2.68, 2.33
(2)	(9)	(11)/(23), 0.20, 0.22
(3)	(9)	(12)/(23), 0.27, 0.26
(4)	(9)	(13)/(23), 0.35, 0.45
(5)	(9)	(18)/(23), 0.18, 0.21
(8)	(9)	(22)/(23), 0.34, 0.36; (24)/(23), 0.33, 0.39; (26)/(23), 0.17, 0.17
(5)	(2)	(11)/(21), 0.62, 0.77
(8)	(2)	(11)/(22), 0.70, 0.53; (11)/(24), 0.48, 0.58; (11)/(26), 1.20, 1.48
(3)	(4)	(13)/(12), 1.34, 1.44
(5)	(4)	(13)/(18), 1.26, 1.39
(8)	(4)	(13)/(22), 1.43, 1.17; (13)/(24), 1.36, 1.26; (13)/(26), 3.4, 2.2

[a] The experimental yields of each biaryl have been multiplied by two factors before taking their ratio. The first factor (1/biaryl yield in Table 1) allows for diversion of the radical intermediate to give other products; the second factor expresses the results from two ratios of competing substrates in terms of a competition between equimolar amounts of each substrate. Arenes A and B, and the polyfluorobiphenyls are identified in Table 1.

Table 5. Competition between arenes; isomer distributions

Arene A	Arene B	Isomer distribution [a]
(2)	(7)	(11) 42, (15) 18, (17) 40; (21) 50, (25) 36, (27) 12
(3)	(7)	(12) 54, (16) 13, (18) 27, (19) 6; (21) 53, (25) 37, (27) 10
(4)	(7)	(13) 73, (19) 27; (21) 53, (25) 37, (27) 10
(5)	(7)	(18) 92, (26) 8; (21) 54, (25) 35, (27) 11
(8)	(7)	(22) 40, (24) 45, (26) 15; (21) 60, (25) 32, (27) 8
(9)	(7)	(23) >98; (21) 53, (25) 32, (27) 13
(2)	(9)	(11) 35, (15) 17, (17) 48; (23) >98
(3)	(9)	(12) 52, (16) 15, (18) 27, (20) 6; (23) >98
(4)	(9)	(13) 71, (19) 29; (23) >98
(5)	(9)	(18) 83, (26) 7; (23) >98
(8)	(9)	(22) 40, (24) 42, (26) 18; (23) >98
(5)	(2)	(18) 92, (26) 8; (13) 78, (19) 22
(8)	(2)	(22) 37, (24) 45, (26) 18; (11) 35, (15) 16, (17) 49
(3)	(4)	(12) 66, (16) 10, (18) 24; (13) 77, (19) 23
(5)	(4)	(18) 92, (26) 8; (13) 78, (19) 23
(8)	(4)	(13) 74, (19) 26; (22) 40, (24) 43, (26) 17

[a] See Table 1 for the numbering of biaryls; percentage isomer distribution for the attack of *each* arene is given after the compound number.

Table 6. Effect of hexafluorobenzene upon the orientation of phenylation

	Isomer distribution of biaryls	
Arene	Absence of C_6F_6	Presence of C_6F_6
(2)	(15) (18%), (17) (49%), (11) (33%)	(15) (9%), (17) (36%), (11) (55%)
(3)	(16) (9%), (18) (29%), (20) (3%), (12) (59%)	(16) (7%), (18) (20%), (20) (<1%) (12) (73%)
(4)	(19) (26%), (13) (74%)	(19) (13%), (13) (87%)
(5)	(18) (92%), (26) (8%)	(18) (93%), (26) (7%)
(6)	(22) (6%), (23) (7%), (25) (<1%), (16) (30%), (17) (37%), (19) (19%)	(22) (3%), (23) (4%), (25) (2%) (16) (32%), (17) (39%), (19) (20%)
(7)	(27) (11%), (21) (59%), (25) (30%)	(27) (6%), (21) (67%), (25) (27%)
(8)	(22) (39%), (24) (39%), (26) (22%)	(22) (36%), (24) (49%) (26) (15%)

Table 7. Substituent rate factors in aryldefluorination

Arene A	Arene B	Yield ratio [a]	Calculated s.r.f. [b]
(2)	(7)	(15)/(27), 1.24, 1.69	$f_m \cdot f_p$, 1.0
		(17)/(27), 2.70, 2.18	$f_o \cdot f_m$, 2.4
(3)	(7)	(16)/(27), 0.52, 0.54	f_m^2, 0.64
		(18)/(27), 2.12, 2.08	$f_o \cdot f_p$, 3.6
(5)	(7)	(26)/(27), 0.14, 0.12	$f_m^2 \cdot f_o$, 0.2
(4)	(3)	(19)/(16), 1.52, 1.73	f_p/f_m, 1.5
		(19)/(18), 0.31, 0.27	f_m/f_o, 0.27
(2)	(5)	(15)/(26), 3.7, 4.2	$f_o \cdot f_p/f_m$, 4.5
		(17)/(26), 10.2, 12.2	f_o^2/f_m, 11.3
(4)	(5)	(19)/(26), 4.2, 4.3	$f_o \cdot f_p/f_m$, 4.5
(10)	(2)	(14)/(15), 3.6, 3.3	$f_o \cdot f_m$, 2.4 (4.0)
		(14)/(17), 1.04, 1.29	$f_m \cdot f_p$, 1.0 (1.0)
(10)	(3)	(14)/(16), 7.6, 7.9	$f_o \cdot f_p$, 3.6 (3.2)
		(14)/(18), 1.26, 1.16	f_m^2, 0.64 (1.2)
(10)	(4)	(14)/(19), 3.8, 3.6	$f_o \cdot f_m$, 2.4 (4.0)
(10)	(5)	(14)/(26), 12.0, 11.4	$f_o^2 \cdot f_p$, 10.8 (11.0)

[a] Yield calculated from the relative yields of biaryls and the ratio of biaryl formed to peroxide decomposed in phenylation of the single substrates, as in Table 4. [b] Using f_o, 3.0; f_m, 0.8; f_p, 1.2 as s.r.f.s for fluorine substituents; values in parentheses are calculated using f_o, 3.5; f_m, 1.1; f_p, 0.9.

the absorptions agreed with prediction and with reported[1] values, (b) that, where the same compound results from the attack of two different substrates, the ^{19}F n.m.r. detailed spectra agreed in both cases, and (c) that the spectrum agreed in all details with that of authentic materials where these were available. The absorbances used analytically have already[1] been reported.

Yields were measured by comparison of the integrated ^{19}F n.m.r. absorbances of the biaryls with that of the standard (2- or 4-fluorobiphenyl). Better reproducibility was obtained when the standard was added before the decomposition of the peroxide, and so this technique was followed. Both yields and isomer distributions were reproducible to ±2%.

The benzoates which were formed by benzoyloxylation were isolated with the biaryls by steam distillation and were identified by comparison of their g.l.c. and ^{19}F n.m.r. properties with those of authentic samples, or by analysis of their n.m.r. chemical shifts and the coupling constants associated with each absorption, or by the similarity between calculated and experimentally found chemical shifts. Ester hydrolysis (NaOH–MeOH) rapidly removed them from the reaction products and confirmed their identity.

The non-steam volatile residues from the thermolysis of benzoyl peroxide in 1,3,5-trifluorobenzene (5) and in 1,2,3,4-tetrafluorobenzene (2) were separately dissolved in benzene (20 cm^3) and heated (80°; 300 h) under reflux. Exhaustive steam distillation, after the solvent had been removed, gave only small amounts of tri- and tetra-fluoroterphenyls, benzoic acid, and biphenylcarboxylic acids (m.s.).

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