Nucleophilic Displacement in Polyhalogenoaromatic Compounds. Part 8.[1] Kinetics of Methoxydefluorination of Some Polyfluoronaphthalenes

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The kinetics of methoxydefluorination of some 2-X-heptafluoronaphthalenes (X = H, F, Cl, OMe, or C_6H_5) and of 1,2,3,4,5,6-hexafluoronaphthalene in methanol at 323.2 K have been measured. The orientation of attack has been confirmed in the naphthalene derivatives as mainly involving displacement at C-6, although some evidence has been found for attack at C-7 in 2-methoxyheptafluoronaphthalene. Similar studies have been made of the orientation of methoxydefluorination of 2,3,4,5,6-penta- and of octa-fluorotoluene, together with a study of the rate of reaction of the latter compound. The rate constants are explained in terms of a transmission of the total substituent effect of the groups across the biannular system.

METHOXYDEFLUORINATION of polyfluorobenzene derivatives is a reaction in which halogen substituents show nearly complete additivity of effect [2,3] but the nitro-substituent [1] is more polarisable, so that its apparent influence depends upon the electron density of the ring and so upon the presence of the substituents already attached. Kinetic studies of nucleophilic displacement of polyfluorinated polyannular benzenoid compounds have been confined to some early reports by Tamborski [4] on the reactions of decafluorobiphenyl. Similarly, the reactions of octafluoronaphthalene have been shown to involve mainly displacement at the β-carbon atom (C-2),[5] and subsequent nucleophilic attack has been reported to occur at C-6, an orientation explained by reference to the transmission of an I_π effect across the naphthalene system.[6] In view of our strictures on this concept,[2,3,7] and following observations of the transmission of total electronic effects across the biphenyl and fluorene systems,[8] we now report the synthesis and the rates of methoxydefluorination of some polyfluorinated derivatives of naphthalene, together with a re-examination of the corresponding reactions of 2,3,4,5,6-pentafluorotoluene and of octafluorotoluene. Detailed ^{19}F n.m.r. spectroscopy allowed the orientation of attack to be determined with certainty, by using the work of Kobrina and her colleagues [9] and by referring to the earlier reports of Thomas *et al.*[10] and of Suschitzky *et al.*[6]

DISCUSSION

Polyfluoronaphthalenes.—Octafluoronaphthalene was the starting material for the preparation of these compounds, the first stage usually being the formation of 2-hydrazinoheptafluoronaphthalene.[5]

Oxidation of this compound with Fehling's solution [5] provided 2*H*-heptafluoronaphthalene; using copper(II) chloride in hydrochloric acid (8M) similarly gave 2-chloroheptafluoronaphthalene. Like 4-hydrazinononafluorobiphenyl [11] and pentafluorophenylhydrazine,[12] 2-hydrazinoheptafluoronaphthalene loses both the hydrazino group and a fluorine atom on treatment with sodium methoxide in methanol (0.5M). The product is 1,2,3,4,5,6-hexafluoronaphthalene, showing that the fluorine atom at C-1, and not that at C-3, is mainly displaced. The orientation of displacement was most simply shown by the ^{19}F n.m.r. spectrum, which showed six discrete fluorine absorptions; both probable alternative structures, 1,2,3,4,5,6,8- and 1,2,4,5,7,8-hexafluoronaphthalene, are expected to show only three absorptions, and of these the 1,2,4,5,7,8-isomer should show no coupling of *peri*-fluorine substituents. Finally, 2-methoxyheptafluoronaphthalene was obtained from the reaction of octafluoronaphthalene and sodium methoxide (1.0 mole per mole); the crude material contained a compound showing absorption foreign to both the starting material and the 2-methoxy derivative; it was therefore thought to be the 1-isomer. The amounts in which it was obtained did not allow the separation of a pure sample, and this assignment must be regarded as tentative.

The orientation of attack by methoxide could be demonstrated most readily in the reaction of 2-methoxyheptafluoronaphthalene, where the ^{19}F n.m.r. spectrum is simplified by the presence of two identical substituents in the naphthalene system. Because the methoxy substituent deactivates the ring towards aromatic nucleophilic substitution [13,14] the second attack is unlikely to occur at C-1, -3, or -4 of the naphthalene system; however the attack at a β-position is likely by analogy with octafluoronaphthalene itself [5] and so the dimethoxy-

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[1] Part 7, R. Bolton and J. P. B. Sandall, *J.C.S. Perkin II*, 1978, 141.

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[3] R. Bolton and J. P. B. Sandall, *J.C.S. Perkin II*, 1978, 137.

[4] R. de Pasquale and C. Tamborski, *J. Org. Chem.*, 1967, **32**, 3163.

[5] B. Gething, C. R. Patrick, and J. C. Tatlow, *J. Chem. Soc.*, 1962, 186.

[6] D. Price, H. Suschitzky, and J. I. Hollies, *J. Chem. Soc. (C)*, 1969, 1967.

[7] R. Bolton and G. H. Williams, *Adv. Fluorine Chem.*, 1974, **5**, 1.

[8] R. Bolton and R. E. Burley, *J.C.S. Perkin II*, 1977, 428.

[9] L. S. Kobrina, V. D. Shteingarts, and L. N. Shchgoleva, *Izvest. sibirsk. Otdel. Akad. Nauk S.S.S.R., Ser. khim.*, 1974, **1**, 68.

[10] R. A. Fletton, R. D. Lapper, and L. F. Thomas, *Chem. Comm.*, 1969, 1049.

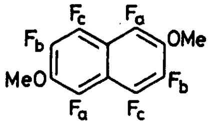
[11] D. G. Holland, G. J. Moore, and C. Tamborski, *J. Org. Chem.*, 1964, **29**, 1562, 3042; D. G. Holland and C. Tamborski, *ibid.*, 1966, **31**, 280.

[12] Imperial Smelting Corporation, Neth. Appl. 6 410 365 (*Chem. Abs.*, 1965, **63**, 8256dP).

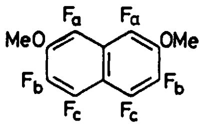
[13] J. Miller, 'Aromatic Nucleophilic Substitution,' Elsevier, Amsterdam, 1968.

[14] J. Burdon, W. B. Hollyhead, and J. C. Tatlow, *J. Chem. Soc.*, 1965, 6375; K. C. Ho and J. Miller, *Austral. J. Chem.*, 1966, **19**, 423; J. Burdon, *Tetrahedron*, 1965, **21**, 3373; R. D. Chambers, 'Fluorine in Organic Chemistry,' Wiley, New York, 1973.

hexafluoronaphthalene obtained from the further reaction of 2-methoxyheptafluoronaphthalene is most likely to be the 2,6- or 2,7-isomer. In his analysis of the orientation of similar reactions of 2-substituted heptafluoronaphthalenes, Suschitzky[6] deduced the 2,6-orientation by a consideration of the effects of spin–spin decoupling upon the ^{19}F n.m.r. spectrum, by using the unusually high *peri*-fluorine interactions (J_{F-F} *ca.* 60 Hz) to identify fluorine in the α-position. The distinction between 2,6-dimethoxyhexafluoronaphthalene (I) and the 2,7-isomer (II) is most easily made by considering the number of such *peri*-fluorine interactions, for (II) cannot show such effects (as C-4 and -5 are equivalent, and so are C-1 and -8) whereas (I) shows a definite *peri*-interaction because C-1 and -8 are different environments, although C-4 and -5 constitute a pair identical with C-1 and -8. The chemical shifts of each fluorine atom in (I) and (II) are expected to be indistinguishable because each has a counterpart in the other molecule which is in an almost identical environment.



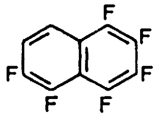
(I)



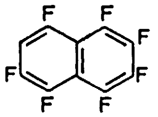
(II)

On this basis we find the major product of dimethoxydefluorination is the 2,6-isomer (I); the crude product shows contributions to the downfield component of each pair of peaks from the *peri*-fluorine atoms in the n.m.r. spectrum which are assigned to (II) because of their chemical shifts. Up to 25% of the crude product may be (II) on this basis.

The products of substitution of 1,2,3,4,5,6-hexafluoronaphthalene (III) and of 2*H*-heptafluoronaphthalene (IV) may both be identified by ^{19}F n.m.r. spectroscopy. Attack on (III) produced an oil whose spectrum showed not only the expected chemical shifts associated with 3-methoxy-1,2,4,5,6-pentafluoronaphthalene, but also a specific broadening of the absorptions from the fluorine atoms at C-2 and -4 which is consistent with the presence of an adjacent methoxy group at C-3. Similar arguments were applied to the product of reaction of (IV), which was 3-methoxy-1,2,4,5,6,8-hexafluoronaphthalene. The prior assignment of the *peri*-fluorine atoms allowed the chemical shifts arising from fluorine atoms at C-2 and -6 to be obtained. The consistency between this spectrum and those of 2-methoxyheptafluoronaphthalene and of 3-methoxy-1,2,4,5,6-pentafluoronaphthalene gave further confirmation of our analysis. In addition, our assignments for 2*H*- and 2-methoxyheptafluoronaphthalenes are in complete agreement with those of Kobrina *et al.*[9]



(III)



(IV)

Kinetics of Methoxydefluorination.—The second-order rate constants obtained for methoxy-defluorination in methanol at 323.2 K are in Table 1. The simplest benzenoid structure analogous with the naphthalene system is *o*-xylene; in the absence of a ready source of either tetra- or deca-fluoro-*o*-xylene we have measured the rates of attack on 2,3,4,5,6-pentafluorotoluene and on octafluorotoluene, and have determined the orientation of substitution in both compounds. Pentafluorotoluene underwent displacement mainly at the *para*-position (97%), as did octafluorotoluene (96%). The minor products are interesting, however, for while octafluorotoluene showed a second component (4%) whose chemical shifts in the ^{19}F n.m.r. spectrum were consistent with attack at the position *ortho* to the CF_3 group, pentafluorotoluene showed minor attack entirely (3%) at the position *meta* to the CH_3 group. While there was insufficient material for the isolation of this minor component, the derived coupling constants and the chemical shifts of the four non-equivalent fluorine atoms make this assignment most probable.

TABLE 1

Second-order rate constants for methoxydefluorination (NaOMe–MeOH; 323.2 K)

Arene	10^2k_2(exp.) [a]	10^2k_2(calc.) [a]
2,3,4,5,6-Pentafluorotoluene	0.0061 ± 0.0003	
Octafluorotoluene	135 ± 3	
Octafluoronaphthalene	4.3 ± 0.1	3.4
2*H*-Heptafluoronaphthalene	0.92 ± 0.02	0.78
1,2,3,4,5,6-Hexafluoronaphthalene	0.045 ± 0.001	0.042
2-Chloroheptafluoronaphthalene	4.8 ± 0.1	4.0 [b]
2-Phenylheptafluoronaphthalene	1.18 ± 0.05	1.00
2-Methoxyheptafluoronaphthalene	0.28 ± 0.01	0.32 [c]
2,3,4,5,6-Pentafluorobiphenyl	0.0123 ± 0.0007	

[a] Rate constants quoted in l mol^{-1} s^{-1}; see text for details of calculation. [b] 10^2k_2, 1.6 for attack at C-3. [c] Combined attack at C-6 and -7; see text.

The substituent rate factors which we have derived were obtained in two ways. Intrinsically, a substituent rate factor measures the effect of a substituent upon a site within the system compared with the effect of hydrogen upon the same position. Thus, the effect of the *p*-CH_3 group is derived directly by comparing the rate constant for attack on the relevant site ($0.97 \times 6.1 \times 10^{-5}$ l mol^{-1} s^{-1} at 323.2 K) with that found for the attack of the same site in pentafluorobenzene ($0.96 \times 1.01 \times 10^{-4}$ l mol^{-1} s^{-1} at 323.2 K). The ratio of these terms, 0.6, is the resulting substituent rate factor for the *p*-methyl substituent. However, this method is not available if the amount of isomer formed by attack at the particular site is small, or not easy to measure accurately. Thus, the derivation of the rate constant for attack at the site *meta* to CH_3 in pentafluorotoluene is possible ($0.015 \times 6.1 \times 10^{-5} = 9 \times 10^{-7}$ l mol^{-1} s^{-1} per site) but the comparison with pentafluorobenzene is not possible because no *meta*-attack has been reported in this reaction.

We have shown[2,3] that additivity prevails with halogen substituents, especially fluorine, through the entire range from fluorobenzene to hexafluorobenzene, to within quite small limits. Hexafluorobenzene may therefore be used as an intermediate in these calculations, because the effect of the fluorine substituent does not appreciably change. We can isolate the substituent rate factor for a *meta*-fluorine group ($f_{m\text{-F}}$ 180) [2,3] and the rate constant associated with displacement of fluorine from one specific position of hexafluorobenzene is 76×10^{-6} l mol^{-1} s^{-1}. It can therefore be deduced that the *meta*-position of pentafluorobenzene (*i.e. meta* to hydrogen) has a rate constant of $(76/180) \times 10^{-6} = 4.2 \times 10^{-7}$ l mol^{-1} s^{-1} at 323.2 K for methoxydefluorination. This figure is consistent with the absence of detectable attack at this site in pentafluorobenzene, for it corresponds to a total amount of 0.8% of 2-methoxy-1,3,4,5-tetrafluorobenzene in the reaction product. It also allows now the estimation of $f_{m\text{-Me}}$ (9/4.2 = 2.1—2.2).

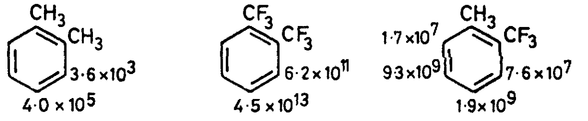
This second method, using hexafluorobenzene as a secondary standard or intermediate, does not have general use throughout aromatic nucleophilic substitution unless an intermediate compound is used which does not show an effect dependent upon the demands of the reaction. We have shown that the fluorine substituent effect in the present reaction is unusually rigid and uninfluenced by such interference, in contrast with that of the nitro-group,[1] and so the substituent rate factors derived by this less direct method are still tenable.

The apparently odd orientation of attack on pentafluorotoluene falls in a regular sequence of reactivity and orientation. Highly activating groups (towards nucleophilic displacement) generally cause the sites *ortho* and *para* to them to be attacked; in the case of weak ' substituents ' such as hydrogen, this orientation results from the directing effects of the four fluorine substituents. Deactivating groups, which are usually characterised by predominantly *meta*-attack, show that these fluorine substituents are the prime directors in determining orientation. The mildly deactivating methyl group now falls into a regular sequence in which *ortho*- and *para*-attack becomes less favoured while *meta*-substitution is relatively less affected.

These substituent rate constants, together with those found for the fluorine substituent,[2] may be used to obtain rate constants and orientations of methoxydefluorination of 3,4,5,6-tetra- and deca-fluoro-*o*-xylene, themselves analogues of 1,2,3,4-tetrafluoronaphthalene and of octafluoronaphthalene, respectively. Thus, the composite substituent rate factor for attack at C-3 of 3,4,5,6-tetrafluoro-*o*-xylene may be derived from equation (1) by using the substituent rate factors $f_{o\text{-Me}}$ 0.3

$$f_{\text{C-3}} = f_{o\text{-Me}} f_{m\text{-Me}} f_{o\text{-F}} f_{m\text{-F}} f_{p\text{-F}} = 0.3 \times 2.1 \times 42 \times 180 \times 0.75 = 3.6 \times 10^3 \quad (1)$$

(a maximum value), $f_{m\text{-Me}}$ 2.1, and $f_{p\text{-Me}}$ 0.6 arising from our rate and product measurements. The other composite factors may be similarly derived, and are shown in (V)—(VII). In each case, nucleophilic substitution occurs predominantly at the site *para* to the methyl or trifluoromethyl groups, the latter being favoured in (VII). Whether or not the second ring in octafluoronaphthalene resembles a cyclic alkyl or perfluoroalkyl system, this approximation suggests that nucleophilic substitution in both octafluoronaphthalene and 1,2,3,4-tetrafluoronaphthalene should occur mainly at C-2 and that this tendency should be seen even in the reactions of 1,2,3,4,5,6-hexafluoronaphthalene [(III); *cf.* (VII)], in agreement with experiment.[5,15]



(V) (VI) (VII)

(Aromatic fluorine substituents not shown)

Table 1 shows that a fluorine substituent at C-2 activates nucleophilic attack at C-6 by a factor of *ca.* 1.1, judging from the rates of methoxydefluorination of octafluoronaphthalene and 2*H*-heptafluoronaphthalene. Comparison of the results for 2*H*-heptafluoronaphthalene and 1,2,3,4,5,6-hexafluoronaphthalene similarly shows that fluorine at C-1 activates nucleophilic attack at C-6 by a factor of 20. The effects of other substituents at C-2 upon methoxydefluorination at C-6 may be similarly derived from Table 1, and are compared in Table 2 with the similar ratios found in the reactions of the analogous pentafluorobenzene derivatives.

TABLE 2

Substituent effects in methoxydefluorination of 2-X-heptafluoronaphthalenes and C_6F_5X (NaOMe–MeOH; 323.2 K)

X	k_X/k_H (2-X-$C_{10}F_7$) [a]	k_X/k_H (C_6F_5X) [b]
H	1.0	1.0
F	1.1	0.75
Cl	5.2	26
Ph	1.2	1.6
OMe	0.3	0.08

[a] Attack at C-6. [b] Attack at C-4.

The substituent effects in both systems parallel each other, regardless of whether the group accelerates or decelerates the reaction. If k is the second-order rate constant for attack of the 2-substituted heptafluoronaphthalene, and k' that of 1,2,3,4-tetrafluoronaphthalene, the product of the appropriate substituent rate factors (f_A) derived from the corresponding reactions of the substituted pentafluorobenzenes, suitably attenuated, reflects the total effect of substituents in the second ring of 1,2,3,4-tetrafluoronaphthalene [equation (2)]. The

$$\log_{10}k = \log_{10}k' + a\log_{10}f_A \quad (2)$$

attenuation parameter a has the empirical value of 0.52 for methoxydefluorination in methanol at 323.2 K, and k' has the value of 4×10^{-6} l mol^{-1} s^{-1} under these conditions. Thus, for the attack on 2-methoxyheptafluoronaphthalene at C-6 the effects of three fluorine substituents at C-1, -3, and -4, and one methoxy group at

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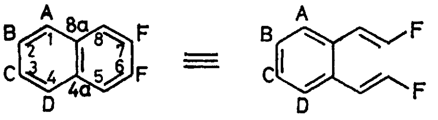
[15] P. L. Coe, G. M. Pearl, and J. C. Tatlow, *J. Chem. Soc.* (*C*), 1971, 604.

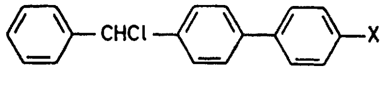
C-2, must be considered. Which orientation is appropriate for each substituent rate factor (*i.e.* f_o, f_m, or f_p) is determined by considering the naphthalene as a benzene unit with extended conjugation (VIII).



(VIII)

The perturbations within the benzene ring are then transmitted selectively along each vinylic system so that the change of electron density at C-8a is seen, diminished, at C-7 while that at C-4a is similarly observed at C-6. Such specific transmission of the total electronic effect is demanded by the parallelism between the results in the benzene and the naphthalene systems. In the methoxydefluorination of 2-methoxyheptafluoronaphthalene we must therefore consider the substituent effects upon C-4a and -8a, and so the total electronic effect of the four substituents acting as in a benzene system. The electron density at C-8a is governed by the composite ($f_{o\text{-F}}f_{m\text{-F}}f_{p\text{-F}}f_{m\text{-OMe}}$), whereas that at C-4a is dependent upon the term ($f_{o\text{-F}}f^2_{m\text{-F}}f_{p\text{-OMe}}$). The numerical values of these products are 3.12×10^4 and 1.09×10^5. The term $a\log_{10}f_A$ therefore becomes 2.34 and 2.62 respectively and the derived rate constants for attack at C-6 and -7 are 2.09×10^{-3} and 1.10×10^{-3} respectively. This compares with the experimental figure (Table 1) of 2.8×10^{-3} l mol^{-1} s^{-1} for the total methoxydefluorination of 2-methoxyheptafluoronaphthalene. The calculated rates in Table 1 are derived on such a basis. The relative rates for attack of 2-methoxyheptafluoronaphthalene also suggest *ca.* 30% reaction at C-7, in agreement with the experimental result.

This parallelism between substituent effects in benzene and in naphthalene is not unique. Similar behaviour is seen in the transmission of substituent effects across the biphenyl or fluorene systems in the solvolysis of derivatives of secondary halides such as (IX) [8,16] and seems to arise from a similar relay of the *total* electronic effect of the substituent across the conjugated system.



(IX)

EXPERIMENTAL

2,3,4,5,6-Pentafluorotoluene, b.p. 117°, and octafluorotoluene, b.p. 103°, were samples generously given by Imperial Smelting Corporation, Avonmouth. Octafluoronaphthalene, m.p. 86—87° (Bristol Organics), gave 2-hydrazinoheptafluoronaphthalene from which 2*H*-heptafluoronaphthalene, m.p. 64.5—65.5° (lit.,[5] 63—64.5°), 2-phenylheptafluoronaphthalene, m.p. 169—170° (lit.,[17] 169.5—170°), and 2-chloroheptafluoronaphthalene, m.p. 74.5—75.5°, *m/e* 288 and 290 (3 : 1), were obtained by standard oxidation processes using Fehling's solution,[5] bleaching powder in benzene,[19] or copper(II) chloride in

TABLE 3

^{19}F N.m.r. chemical shifts used for analysis

Arene	δ (p.p.m. upfield of $CFCl_3$) [a]
2,3,4,5,6-Pentafluorotoluene	2-F, 144.0 (lit.,[18] 144.0); 3-F, 164.3 (lit.,[18] 164.3); 4-F, 159.3 (lit.,[18] 159.3)
3-Methoxy-2,4,5,6-tetrafluorotoluene	2-F, 137.8 [b] (140.0); 4-F, 155.0 [c] (155.8); 5-F, 166.0 [d] (166.5); 6-F, 145.8(?) (148.0)
4-Methoxy-2,3,5,6-tetrafluorotoluene	2-F, 145.8 [e] (146.0); 3-F, 159.5 (160.5)
Octafluorotoluene	2-F, 140.0 (lit.,[18] 140.0); 3-F, 160.3 (lit.,[18] 160.6); 4-F, 147.6 (lit.,[18] 147.9)
2-Methoxyheptafluorotoluene	3-, 4-, 6-F obscured; 5-F, 162.0 [f] (164.6)
4-Methoxyheptafluorotoluene	2-F, 142.4 (142.0); 3-F, 157.0 (157.6)
1,2,3,4,5,6-Hexafluoronaphthalene	1-F, 148.5 (144.9); 2-F, 158.0 (156.7); 3-F, 155.8 (153.7); 4-F, 146.8 (146.2); 5-F, 144.3 (143.9); 6-F, 137.2 (137.8) [g]
3-Methoxy-1,2,4,5,6-fluoronaphthalene	1-F, 151.0 (150.4); 2-F, 153.2 (153.0); 4-F, 141.4 (141.8); 5-F, 145.4 (144.3); 6-F, 139.0 (137.2) [g]
2*H*-Heptafluoronaphthalene	1-F, 116.4 (lit.,[9] 116.8); 3-F, 133.9 (lit.,[9] 134.6); 4-F, 149.9 (lit.,[9] 150.0); 5-F, 146.2 (lit.,[9] 146.5); 6-F, 153.7 (lit.,[9] 153.8); 7-F, 156.7 (lit.,[9] 156.8); 8-F, 144.9 (lit.,[9] 144.9)
3-Methoxy-1,2,4,5,6,8-hexafluoronaphthalene	1-F, 147.3 (146.6); 2-F, 151.2 (149.0); 4-F, 141.0 (139.5); 5-F, 151.2 (149.9); 6-F, 135.8 (133.9); 8-F, 117.5 (116.4) [h]
Octafluoronaphthalene	1-F, 145.5 (lit.,[9] 145.9); 2-F, 154.5 (lit.,[9] 154.6)
2-Methoxyheptafluoronaphthalene	1-F, 139.5 (lit.,[9] 139.8); 3-F, 149.0 (lit.,[9] 148.7); 4-, 5-F, 146.6 (lit.,[9] 146.6); 6-F, 158.2 (lit.,[9] 158.2); 7-F, 156.3 (lit.,[9] 156.3); 8-F, 145.9 (lit.,[9] 145.9)
2,6-Dimethoxyhexafluoronaphthalene	1-F, 141.2 (139.5); 3-F, 151.0 (149.0; lit.,[6] 150.7); 4-F, 148.0 (146.6; lit.,[6] 146.4) [i]
2,7-Dimethoxyhexafluoronaphthalene	1-F, 140.5 (139.5); 3-F, 151.0 (149.0); 4-F, 148.8 (146.6)

[a] Calculated chemical shifts in parentheses. [b] Broad doublet ($J_{2.5}$ 8.5 Hz). [c] Broad doublet ($J_{4.5}$ 19.6 Hz). [d] 1 : 1 : 2 : 2 : 1 : 1 sextet ($J_{4.5}$ 19.6, $J_{5.6}$ 19.6, $J_{2,5}$ 8.5 Hz). [e] ($J_{2,3}$ 20, $J_{2.5}$ 9, $J_{2,6}$ 1 Hz). [f] Other fluorine absorptions obscured by parent compound or by 4-isomer; 1 : 2 : 1 triplet ($J_{4.5} = J_{5.6} = 22$ Hz). [g] For 1,2,3,4,5,6-hexafluoronaphthalene ($J_{1.2}$ 17, $J_{1.3}$ 3, $J_{1.4}$ 16, $J_{2.3}$ 17, $J_{2.4}$ 3.5, $J_{3.4}$ 17, $J_{4.5}$ 53, $J_{1.8}$ 17 Hz). Chemical shifts of this compound used to calculate those of the methoxy derivative ($J_{1.2}$ 17, $J_{3.4}$ 17, $J_{4,5}$ 56, $J_{5,6}$ 16, $J_{1.8}$ 17 Hz). [h] $J_{1,8}$ 65, $J_{4,5}$ 63.7 Hz (*cf.* ref. 10). [i] $J_{1,8}$ 68 Hz.

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hydrochloric acid (8M). After steam distillation these products were shaken with sodium hydroxide (0.5M) and with water, and then dissolved in light petroleum (b.p. 40—60°) and passed down a column of alumina before recrystallisation from aqueous ethanol.

1,2,3,4,5,6-Hexafluoronaphthalene was obtained as an oil by treating 2-hydrazinoheptafluoronaphthalene (1.8 g) with sodium methoxide (0.5M, 50 cm^3)[11,12] and adding water to the solution after the evolution of gas had ceased. It was identified by ^{19}F n.m.r. spectroscopy, which showed it to be *ca.* 95% pure. All other substrates were pure by this criterion. 2,3,4,5,6-Pentafluorobiphenyl, m.p. 110—111° (lit.,[20] 111–112.5°), was obtained from pentafluoroaniline by conventional methods. Methanol (AnalaR) was dried over magnesium before distillation, rejecting the first and last 20%. The resulting solvent contained $<0.05\%$ water, but showed the same rate constant for methoxydefluorination of octafluoronaphthalene as the commercial solvent. Cleaned sodium metal was dissolved in methanol to give concentrated solutions of sodium methoxide which were regularly standardised by conventional acid–base titration with standard solutions of mineral acids.

The course of each methoxydefluorination was followed by measuring the fluoride ion concentration produced. Samples (5 cm^3) were added by pipette to a mixture of a buffer solution (sodium acetate–acetic acid; pH 5; 1M-sodium chloride; 10 cm^3) and water or, with higher initial concentrations of base, standard acid (0.1M, 5 cm^3). The fluoride ion concentration was measured using an Orion 94-09 specific ion electrode and an EIL 7050 Laboratory pH meter, calibrated by standard solutions of sodium fluoride (AnalaR; dried under vacuum at 100°), over the range $10^{-5}\text{M} < [\text{F}^-] < 10^{-2}\text{M}$. The solubility of sodium fluoride in methanol[7] precludes the need of measurements above these levels. This method allowed more samples to be taken, and greater accuracy of measurement, than the alternative of titrating the unchanged base with acid because of the complications of carbon dioxide uptake and the buffering which fluoride ion provides.

The organic products of methoxydefluorination were isolated after treatment of the polyfluoroarenes with a deficiency of sodium methoxide in methanol at 323.2 K, and were identified by the number, chemical shifts, and coupling constants of the fluorine nuclei showing ^{19}F n.m.r. activity (Perkin-Elmer R12B; 56.4 MHz; CFCl$_3$ solvent–standard). This method of analysis allowed relatively small amounts of products to be characterised without the need of independent synthesis (Table 3).

TABLE 4

Orientation of methoxydefluorination of substituted polyfluoroarenes (323.2 K; NaOMe–MeOH) (yield in parentheses)

Substrate	Product
2,3,4,5,6-Pentafluorotoluene	3-Methoxytetrafluorotoluene (3%) 4-Methoxytetrafluorotoluene (97%)
Octafluorotoluene	2-Methoxyheptafluorotoluene (4%) 4-Methoxyheptafluorotoluene (96%)
Octafluoronaphthalene	1-Methoxyheptafluoronaphthalene (≯20%) 2-Methoxyheptafluoronaphthalene (>80%)
2*H*-Hptaafluoronaphthalene	3-Methoxy-1,2,4,5,6,8-hexafluoronaphthalene (>95%)
2-Chloroheptafluoronaphthalene	2-Chloro-3-methoxyhexafluoronaphthalene (22%); 2-chloro-6-methoxyhexafluoronaphthalene (66%); 2-chloro-7-methoxyhexafluoronaphthalene (12%) [a]
2-Methoxyheptafluoronaphthalene	2,6-Dimethoxyhexafluoronaphthalene (>75%); 2,7-dimethoxyhexafluoronaphthalene (≯25%)
1,2,3,4,5,6-Hexafluoronaphthalene	3-Methoxy-1,2,4,5,6-pentafluoronaphthalene (>95%)

[a] ^{1}H N.m.r. spectrum showed absorptions at δ 4.15 (3-MeO), 4.08 (6-MeO), and 3.91 (7-MeO).

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