

Nucleophilic Displacement in Polyhalogenoaromatic Compounds. Part 9.¹ Kinetics of Azidodefluorination and Methoxydefluorination of Some Polyfluorobenzonitriles

By Roger Bolton * and John P. B. Sandall, Chemistry Department, Bedford College, London NW1 4NS

Pentafluorobenzonitrile and 4-chlorotetrafluorobenzonitrile do not show good second-order kinetic behaviour in their reactions with sodium methoxide in methanol. The reaction rate falls rapidly until a position of apparent equilibrium is reached, after which methoxydefluorination proceeds slowly to completion. This behaviour appears to arise from competition between methoxydefluorination and a reversible addition of methoxide ion to the carbon-nitrogen triple bond. The reaction of azide ion with polyfluorobenzonitriles does not show this competition. The sensitivity of azidodefluorination in methanol at 323.2 K to *para*-substituent effects in C_6F_5X , as shown by the Hammett reaction constant (ρ 6.2 \pm 0.3), is slightly greater than that shown by methoxydefluorination under the same conditions, which is consistent with a less reactive and more selective reagent. The azidodefluorination of 4-substituted tetrafluorobenzonitriles, although involving attack at positions *ortho* to the cyano-group and *meta* to X, shows the same sensitivity to substituent effects (ρ 6.0 \pm 0.5); this, in turn, suggests that the electronic effect of the cyano-group is less perturbed by the electron density of the ring upon which it acts than is the electronic effect of the nitro-group.

NUCLEOPHILIC displacement in aromatic systems is assisted by the presence of cyano-substituents;² for example, pentafluorobenzonitrile reacts with methanolic sodium methoxide at a rate 460 000 times that for pentafluorobenzene.³ Such displacement reactions of polycyanopolyhalogenobenzenes may also be used preparatively,^{4,5} as in the fluorodechlorination of pentachlorobenzonitrile.⁶ In the methoxydefluorination of polyfluorobenzene derivatives we have found that the very commonly used nitro-substituent shows an activating power which apparently depends upon the electron density of the aromatic system upon which it acts.⁷ The significant differences in the Hammett reaction constant for methoxydechlorination of 1-chloro-2-nitro-4-X-benzenes (ρ 4.59) and of 1-chloro-2,6-dinitro-4-X-benzenes (ρ 3.80)⁸ and the lack of additivity of the nitro-group effect upon further substitution in *o*- or *p*-chloronitrobenzene are consistent with such a dependence although other explanations are not excluded. If this mutual interaction and weakening of effect between nitro-groups and the aromatic system is a general property of these compounds, then the apparent substituent effect of a group attached to the aromatic system depends upon a variable amount of back-donation to the nitro-group and is not an accurate measure of the effect for this reason.

Halogen substituents show substantially complete additivity of effect in the methoxydefluorination of polyfluorobenzenes in methanol at 323.2 K, and we sought to study the effects of cyano-groups upon the rate of this reaction. Previous work has included a study of the reaction of bromobenzene derivatives with piperidine in ethylbenzene,⁹ which showed that the

activating effect of the *p*-cyano-substituent is less affected by flanking methyl substituents than is that of the nitro-group, although a detailed kinetic study was not made. Miller and his co-workers^{10,11} observed a second process in addition to the expected methoxydechlorination of cyano-derivatives of *o*- and *p*-chloronitrobenzene. This process, first deduced from the unexpectedly low reaction rates found for the substitution, involved the nucleophilic addition of methoxide ion to the carbon-nitrogen triple bond and was assisted by the electron-withdrawing groups present in the aromatic ring. This complication was not reported³ in the methoxydefluorination of pentafluorobenzonitrile, and we therefore began a study of substituent effects in this reaction.

DISCUSSION

Methoxydefluorination of Polyfluorobenzonitriles.—Nucleophilic displacement in pentafluorobenzonitrile involves over 90% attack at the *para*-position to give high yields of the substitution products.⁴ In our kinetic studies of the methoxydefluorination of this substrate, the observed rate constant decreased after the first 20% reaction and soon fell sharply to become nearly zero at an apparent position of equilibrium. This was not the result of the presence of impurities in the reagent or substrate, and did not seem to be caused by the limited solubility of sodium fluoride in methanol.⁷ 4-Chlorotetrafluorobenzonitrile also showed this behaviour, but 4-methoxytetrafluorobenzonitrile gave good kinetic plots to 95% completion.

The proposed reactions (1) and (2) are consistent with such observations. At the initial stages of the reaction, $d[F^-]/dt = k_1[C_6F_5CN][MeO^-]$ and $-d[MeO^-]/dt = (k_1 + k_2)[C_6F_5CN][MeO^-]$, in which the apparent con-

¹ Part 8, R. Bolton and J. P. B. Sandall, *J.C.S. Perkin II*, 1978, 746.

² J. Miller, 'Aromatic Nucleophilic Substitution,' Elsevier, Amsterdam, 1968.

³ K. C. Ho and J. Miller, *Austral J. Chem.*, 1966, **19**, 423.

⁴ J. M. Birchall, R. N. Haszeldine, and M. E. Jones, *J. Chem. Soc. (C)*, 1971, 1343.

⁵ J. M. Birchall, R. N. Haszeldine, and J. O. Morley, *J. Chem. Soc. (C)*, 1970, 456.

⁶ J. M. Birchall, R. N. Haszeldine, and M. E. Jones, *J. Chem. Soc. (C)*, 1971, 1341.

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

⁸ R. L. Heppollette and J. Miller, *J. Chem. Soc.*, 1956, 2329; unpublished work; J. Miller, *Austral. J. Chem.*, 1956, **9**, 61; ref. 2, p. 79.

⁹ W. C. Spitzer and G. W. Wheland, *J. Amer. Chem. Soc.*, 1940, **62**, 2995.

¹⁰ J. Miller, *J. Amer. Chem. Soc.*, 1954, **76**, 448; R. L. Heppollette, J. Miller, and V. A. Williams, *ibid.*, 1956, **78**, 1975.

¹¹ N. S. Bayliss, R. L. Heppollette, L. H. Little, and J. Miller, *J. Amer. Chem. Soc.* 1956, **78**, 1978.

centrations of the two reagents approximate to the true values. Subsequently the establishment of equilibrium

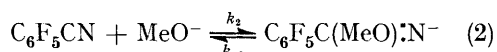
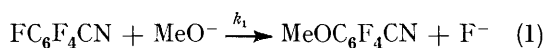
TABLE 1

Experimental observations in the methoxydefluorination of some derivatives of tetrafluorobenzonitrile (MeOH; 323.2 K)

Substrate	10^2 [ArF] _o / M	10^2 [OMe ⁻] _o / M	Apparent equilibrium position (%) *	k_2 */ $1 \text{ mol}^{-1} \text{ s}^{-1}$ $\times 10^{-2}$
Pentafluorobenzonitrile	0.032	0.031	75–80	29.5 ± 1.0
	0.017	0.017	71	30.9 ± 1.1
	0.017	0.017	73	31.1 ± 1.8
4-Chlorotetrafluoro- benzonitrile	0.280	0.280	65	3.46 ± 0.13
	0.290	0.290	65	3.45 ± 0.24
4-Methoxytetrafluoro- benzonitrile	0.300	2.90	>96	9.19 ± 0.32

* The apparent equilibrium position was measured as the point at which methoxydefluorination had slowed to very small rates, and using the criterion that the half-life found using this equilibrium position as an apparent 'infinity' value was at least one-tenth of the time needed to reach the equilibrium position, *i.e.* that equilibrium occurred after ten half-lives for methoxydefluorination. Because of drifting in the apparent equilibrium position, rate constants were taken over the first 50% reaction, corresponding to between nine and fourteen measurements.

(2) removes all but a small amount of methoxide ion, for which reactions (1) and (2) compete. At the start



of the kinetic study, therefore, the value of k_1 can be obtained by following the rate of formation of fluoride ion; the second-order rate constant for pentafluorobenzonitrile under three different sets of initial concentrations of reactants was the same [k_1 30 ± 1 $1 \text{ mol}^{-1} \text{ s}^{-1}$ (323.2 K)] and close to that previously reported (39.5).³ The corresponding value for 4-chlorotetrafluorobenzonitrile [k_1 3.5 $1 \text{ mol}^{-1} \text{ s}^{-1}$ (323.2 K)] suggests that, for attack at the carbon atoms *ortho* to the cyano-group, *m*-chloro-substituents are slightly better activating groups than *m*-fluoro (k_1 1.5 $1 \text{ mol}^{-1} \text{ s}^{-1}$). In the same position, the methoxy-group has a much weaker effect (k_1 0.092 $1 \text{ mol}^{-1} \text{ s}^{-1}$ at 323.2 K, 4-methoxytetrafluorobenzonitrile). The good kinetic behaviour of the last compound presumably reflects the powerfully deactivating electronic effect of the methoxy-substituent *para* to the cyano-group which strongly inhibits the nucleophilic addition reaction, although the *m*-methoxy-group is expected to assist slightly methoxydefluorination at the 2-position of 4-methoxytetrafluorobenzonitrile.

Measurements of rate constants from the initial slope of a kinetic plot are often inaccurate, and the alternative treatment of the kinetic results as though the methoxydefluorination were indeed an equilibrium process was not completely successful because of the gradual development of fluoride ion after the position of apparent equilibrium had been reached. The high reaction rate of

¹² A. V. Kashin, Yu. L. Bakhmutov, and N. N. Marchenko, *Zhur. Vsesoyuz. Khim. obshch. im D. I. Mendeleeva*, 1970, **15**, 591 (*Chem. Abs.*, 1971, **74**, 12729k).

¹³ A. J. Parker and J. Miller, *J. Amer. Chem. Soc.*, 1961, **83**, 117.

methoxydefluorination of these cyano benzene derivatives precluded a detailed study of the initial stages of the reactions, and so we selected a less reactive nucleophile which would not show these kinetic complications.

Azidodefluorination.—The azidodefluorination of pentafluorobenzonitrile occurs readily in acetone;⁴ the corresponding displacements in less activated systems are reported to occur in *NN*-dimethylformamide¹² and the kinetics of reaction of a number of derivatives of fluoronitrobenzene in a number of solvents have been well documented.¹³ In our systems, methoxydefluorination takes place at *ca.* 10^3 times the rate of azidodefluorination. Table 2 shows the second-order rate constants for azidodefluorination of some simple derivatives of pentafluorobenzene in methanol at 323.2 K. The very slow reactions of the substrate ($k < 10^{-6}$ $1 \text{ mol}^{-1} \text{ s}^{-1}$) could not be followed over a substantial extent of reaction, and the associated rate constants may be too high; however, the scatter in the individual points was often no worse than with much more rapid processes and the main source of error appears to be the possible presence of minor impurities.

TABLE 2

Second-order rate constants for azidodefluorination of $\text{C}_6\text{F}_5\text{X}$ (NaN_3 -MeOH; 323.2 K; $k_2/1 \text{ mol}^{-1} \text{ s}^{-1}$)

X	H	F ^a	Br
$10^4 k_2$	3×10^{-5}	5.5×10^{-4}	2.1×10^{-3}
CF_3	CN	NO_2	NO
2.1 ³	550	2.9×10^3	2.8×10^5

^a All positions.

The products of reaction of pentafluoronitrosobenzene, tetrafluorophthalonitrile, nitropentafluorobenzene, pentafluorobenzonitrile, and octafluorotoluene with sodium azide in methanol at 323.2 K were all substantially (>95%) those arising from attack at the carbon atom *para* to the group X in $\text{C}_6\text{F}_5\text{X}$. This behaviour was therefore in keeping (i) with the orientation of attack found with other nucleophiles¹⁴ and (ii) with considerations of the electronic effects of the groups. We therefore assumed that azidodefluorination of pentafluorobenzene and of its bromo-derivative also proceeded substantially with the same orientation, and applied the results to a Hammett plot. The resulting slope (ρ 6.2 ± 0.3) suggested that the reaction is somewhat more sensitive to substituent effects than is methoxydefluorination of polyfluorobenzenes¹⁵ or methoxydechlorination of polynitrochlorobenzenes.² Use of the less appropriate substituent constants σ and not σ^- , found by Miller² to be more apt measures of the interaction between *para*-substituents and nucleophilic reaction sites, gave a much greater scatter of points around a steeper line (ρ 9 ± 1). Azidodefluorination is evidently more sensitive to substituent effects, this greater selectivity being paralleled by the slower rates of reaction.

A second series of compounds was studied in which the

¹⁴ J. Burdon, *Tetrahedron*, 1965, **21**, 3373; R. D. Chambers, 'Fluorine in Organic Chemistry,' Wiley, New York, 1973.

¹⁵ R. Bolton and J. P. B. Sandall, *J.C.S. Perkin II*, 1976, 1541.

4-position of 2,3,5,6-tetrafluorobenzonitrile contained both electron-withdrawing and -attracting substituents. The resulting rates of displacement of fluorine from carbon atoms *ortho* to the cyano-group are shown in Table 3. The *m*-chloro substituent is again slightly more activating than is *m*-fluoro, as observed in the methoxydefluorination of the substituted polyfluorobenzonitriles; in both cases, however, the comparison is dependent upon the measurement of a small amount (*ca.* 5%) of *ortho*-attack in the pentafluorobenzonitrile reactions, and may not be very accurate. A cyano-group itself in this second series (tetrafluoroterephthalonitrile) seems to show the predicted activating effect when it is *meta* to the reaction site. This behaviour can also be deduced from the rates of reaction of tetrafluorophthalonitrile and pentafluorobenzonitrile, when the cyano-group effect at sites *meta* and *para* to the carbon atom attacked is substantially that predicted by the Hammett substituent constants.

The Hammett reaction constant (ρ 6.0 \pm 0.5) for this series of compounds is the same as that found earlier (Table 2).

This agreement suggests that the effect of the cyano-group in the substituted polyfluorobenzonitriles in Table 3 is unaltered by the multiple electronic effects of

TABLE 3

Second-order rate constants for azidodefluorination of $\text{XYC}_6\text{F}_3\text{CN}$ ($\text{NaN}_3\text{-MeOH}$; 323.2 K; $k_2/\text{l mol}^{-1} \text{s}^{-1}$)

X	F	F	F ^a	F	<i>m</i> -H	<i>o</i> -CN ^b	F	<i>o</i> -CN ^b
Y	<i>p</i> -H	<i>p</i> -OMe	F	<i>p</i> -Cl	<i>p</i> -CN	<i>p</i> -H	<i>p</i> -CN	F
$10^3 k_2$	0.0041	0.005	(0.17)	0.22	6.7	8.1	33	227

^a Attack *ortho* to CN in pentafluorobenzonitrile. ^b Attack *para* to CN.

the other aromatic substituents. Although this may be so to within the quoted errors of the two Hammett plots, more sensitive kinetic criteria perhaps indicate some degree of polarisability of the cyano-group. The comparison of apparent substituent effects shown by fluorine in the polyfluoronitrobenzenes was the most direct method by which the variable electronic effect of the nitro-group could be deduced in methoxydefluorination.⁷ The higher sensitivity and slower rates of azidodefluorination of the polyfluorobenzonitriles made this approach more difficult, for the comparison between fluorine- and hydrogen-containing systems meant the measurement of very slow rates of azidodefluorination in order to determine fluorine substituent effects over a range of extent of halogen substitution in the benzonitrile system. Direct measurement may be made by comparing pentafluoro- and 2,3,5,6-tetrafluoro-benzonitriles (giving the effect of a *m*-fluoro-substituent), and tetrafluorophthalonitrile and 3,4-dicyano-1,2,5-trifluorobenzene (*o*-fluoro); the similar comparison between tri- and tetra-fluoroterephthalonitrile gave the *p*-fluoro-

¹⁶ L. J. Belf, M. W. Buxton, and G. Fuller, *J. Chem. Soc.*, 1965, 3372.

¹⁷ F. D. Evans and P. F. Tiley, *J. Chem. Soc. (B)*, 1966, 134.

¹⁸ W. J. Feast and W. K. R. Musgrave, in 'Rodd's Chemistry of Carbon Compounds,' Elsevier, Amsterdam, 1971, vol IIIa, p. 261.

substituent effect. The resulting substituent rate factors (s.r.f.) (s.r.f._{*o*} 14; s.r.f._{*m*} 42; s.r.f._{*p*} 1.3) are much less than those found for methoxydefluorination in the absence of nitro-groups (42, 180, and 0.75 at 323.2 K) and are more in keeping with the values found in the presence of such groups (*ca.* 20, *ca.* 20, and 1.5 at 323.2K). Such values are not consistent with a *more* sensitive substitution process.

This analysis by detailed comparison of individual rate constants involves, in two instances, polycyano benzenes where any polarisability of the cyano-group may be exacerbated. This is especially relevant because such systems have been used to obtain s.r.f.s. for fluorine substituents in positions *ortho* or *para* to the reaction site, but not *meta*. However, the very necessity of considering the number of the cyano-substituents implies some degree of perturbability, and while the Hammett plots for azidodefluorination gave no evidence of such polarisability by the substituents as in the methoxydefluorination of polyfluoronitrobenzenes, which is appreciably less sensitive (ρ 4.6) than methoxydefluorination of polyfluorobenzenes without the nitro-group (ρ 5.0), some degree of polarisability of the cyano-group seems probable from our results.

EXPERIMENTAL

Pentafluorobenzonitrile, b.p. 161—162° at 757 mmHg (lit.,⁶ 160—161°), tetrafluorophthalonitrile, m.p. 86—87° (lit.,⁵ 86°), tetrafluoroterephthalonitrile, m.p. 197—198° (lit.,¹⁶ 196—198°), pentafluorobenzene, b.p. 84.5—84.7° at 754 mmHg (lit.,¹⁷ 84.6°; n_D^{25} 1.388 4; lit.,¹⁸ 1.3881), hexafluorobenzene, b.p. 80.0—80.1° at 761 mmHg (lit.,¹⁷ 80.1°; n_D^{25} 1.376 2; lit.,¹⁸ 1.376 1; m.p. 5.7—5.8°), chloropentafluorobenzene, b.p. 117.0° at 762 mmHg (lit.,¹⁷ 117.0°), bromopentafluorobenzene, b.p. 136.9° at 762 mmHg (lit.,¹⁷ 136.8°), octafluorotoluene, b.p. 103.8—104.0° at 754 mmHg (lit.,¹⁹ 104°; n_D^{20} 1.368 2; lit.,¹⁹ 1.368 7),

TABLE 4

Isomer distribution for azidodefluorination of some polyfluoroarenes ($\text{NaN}_3\text{-MeOH}$; 323.2 K)

Substrate	Product (%)
Pentafluorobenzonitrile	2-Azidotetrafluorobenzonitrile (5.8) 4-Azidotetrafluorobenzonitrile (94.2)
Tetrafluorophthalonitrile	6-Azido-3,4-dicyano-1,2,5-trifluorobenzene (100)
Tetrafluoroterephthalonitrile	2-Azido-1,4-dicyanotrifluorobenzene (100)
4-Azido-3,5,6-trifluorophthalonitrile	4,5-Diazido-3,6-difluorophthalonitrile (100)
Nitropentafluorobenzene	4-Azidotetrafluoronitrobenzene (> 97%)
Nitrosopentafluorobenzene	4-Azidotetrafluoronitrosobenzene (> 95%)
4-Azidotetrafluoronitrosobenzene	2,4-Diazidotrifluoronitrosobenzene (> 95%)

nitropentafluorobenzene (b.p. 160—161° at 754 mmHg (lit.,²⁰ 158—161°), and nitrosopentafluorobenzene, m.p. 44—45° (lit.,²¹ 42.4°), were commercial samples which were

¹⁹ G. Fuller, *J. Chem. Soc.*, 1965, 6264.

²⁰ G. M. Brooke, J. Burdon, and J. C. Tatlow, *J. Chem. Soc.*, 1961, 802.

²¹ J. A. Castellano, J. Green, and J. M. Kauffman, *J. Org. Chem.*, 1966, 31, 821.

purified by distillation where appropriate, and which showed single peaks upon g.l.c.

By a similar preparation of the appropriately substituted arylhydrazine, and its subsequent oxidation with copper(II)

TABLE 5

¹⁹F N.m.r. chemical shifts used for analysis

Compound	δ (p.p.m. upfield of CFC1 ₃) ^a
Pentafluorobenzonitrile	131.9 (2-F), 163.5 (3-F), 143.4 (4-F)
2-Azidotetrafluorobenzonitrile	155.0 (3-F; 149.6), 145.6 (4-F; 145.0), 155.0 (5-F; 149.6), 134.0 (6-F; 133.5)
4-Azidotetrafluorobenzonitrile	133.6 (2-F; 133.5), 149.6 (3-F; 149.6)
Tetrafluoro-2-methoxybenzonitrile	156.2 (3-F; 156.2), 146.4 (4-F; 145.0), 162.8 (5-F; 160.0), 134.0 (6-F; 134.0) ^b
Tetrafluoro-4-methoxybenzonitrile	135.4 (2-F), 156.2 (3-F)
Tetrafluorophthalonitrile	126.3 (3-F; 131.5), 141.6 (4-F; 143.0)
3,4-Dicyano-1,2,5-trifluorobenzene	122.7 (1-F; 119.0), 134.6 (2-F; 128.0), 106.4 (5-F; 107.6) ^c
6-Azido-3,4-dicyano-1,2,5-trifluorobenzene	133.2 (1-F; 127.7), 128.7 (2-F; 127.9), 116.6 (5-F; 112.9) ^d
2,3,5-Trifluoroterephthalonitrile	129.8 (2-F; 132.9), 118.0 (3-F; 124.0), 102.7 (5-F; 105.3) ^e
Tetrafluoroterephthalonitrile	129.2 (2-F; 131.7)
4,5-Diazido-3,6-difluorophthalonitrile	118.4 (3-F; 118.2)
Nitropentafluorobenzene	146.4 (2-F), 158.6 (3-F), 147.6 (4-F)
4-Azidotetrafluoronitrobenzene	149.6 (2-F; 148.0); 147.0 (3-F; 144.7)
Nitrosopentafluorobenzene	160.2 (2-F), 161.0 (3-F), 143.3 (4-F)
4-Azidotetrafluoronitrosobenzene	161.1 (2-F; 161.8), 152.4 (3-F; 147.0)
2,4-Diazidotrifluoronitrosobenzene	139.9 (3-F; 138.5), 138.4 (5-F; 138.5), 149.5 (6-F; 147.2) ^f

^a Assigned fluorine atoms and calculated shifts in parentheses. ^b $J_{3,4}$ 18, $J_{3,5}$ 1, $J_{3,6}$ 8.7, $J_{4,5}$ 19.7, $J_{4,6}$ 4.8, $J_{5,6}$ 20.3 Hz. ^c $J_{3,5}$ 10, $J_{3,F,H}$ 9, $J_{3,6}$ 13.3, $J_{5,6}$ 21.7, $J_{5,F,H}$ 10, $J_{6,F,H}$ 6.8 Hz. ^d $J_{3,5}$ 11.3, $J_{3,6}$ 11.0, $J_{5,6}$ 18.8 Hz. ^e $J_{2,3}$ 20.0, $J_{2,5}$ 12.9, $J_{3,5}$ 9.3, $J_{2,F,H}$ 6.5, $J_{3,F,H}$ 9.3, $J_{5,F,H}$ 8.3 Hz. ^f $J_{3,5}$ 2.6, $J_{3,6}$ 9.8, $J_{5,6}$ 24.0 Hz.

TABLE 6

Experimental second-order rate constants for the azidodefluorination of some polyfluoroarenes in methanol at 323.2 K

Substrate	10^2 [ArF]/M	10^2 [N ₃]/M	$k_2/l \text{ mol}^{-1} \text{ s}^{-1}$	Range (%)
Hexafluorobenzene	25.8	10.2 ^a	$5.1 \pm 0.2 \times 10^{-8}$	0—0.3
Pentafluorobenzene	20.5	10.0 ^b	$3 \pm 1 \times 10^{-9}$	0—0.1
Bromopentafluorobenzene	10.0	10.2 ^a	$2.1 \pm 0.2 \times 10^{-7}$	0—0.7
Octafluorotoluene	15.5	10.2 ^a	$2.3 \pm 0.4 \times 10^{-4}$	0—12
	2.79	10.2 ^a	$1.99 \pm 0.09 \times 0.09$	0—50
	2.65	10.2 ^a	$2.10 \pm 0.10 \times 10^{-4}$	0—13
	2.37	10.2 ^a	$2.10 \pm 0.10 \times 10^{-4}$	0—50
	9.80	10.0 ^b	$1.57 \pm 0.02 \times 10^{-4}$	0—88
Pentafluorobenzonitrile	1.91	2.03 ^a	$6.10 \pm 0.18 \times 10^{-2}$	0—58
	3.84	2.03 ^a	$5.84 \pm 0.17 \times 10^{-2}$	0—74
	1.30	2.00 ^b	$5.68 \pm 0.33 \times 10^{-2}$	0—85
2,3,4,6-Tetrafluorobenzonitrile	0.56	2.00 ^b	$2.31 \pm 0.14 \times 10^{-3}$	0—57
	1.10	2.00 ^b	$2.21 \pm 0.12 \times 10^{-3}$	0—71
2,3,5,6-Tetrafluorobenzonitrile	1.57	10.2 ^a	$4.11 \pm 0.11 \times 10^{-5}$	0—5
	3.54	10.0 ^b	$2.81 \pm 0.22 \times 10^{-5}$	0—33
Tetrafluorophthalonitrile	0.102	0.102 ^a	2.27 ± 0.05	0—61
	0.051	0.203 ^a	^c	
	0.220	0.102 ^a	2.19 ± 0.09	0—64
3,4,6-Trifluorophthalonitrile	2.02	1.00 ^b	$8.1 \pm 0.3 \times 10^{-2}$	0—70
Tetrafluoroterephthalonitrile	0.104	0.102 ^a	$3.29 \pm 0.12 \times 10^{-1}$	0—43
	0.170	0.102 ^a	$3.39 \pm 0.10 \times 10^{-1}$	0—45
Trifluoroterephthalonitrile	0.403	0.500 ^a	$6.66 \pm 0.17 \times 10^{-2}$	0—81
	0.420	0.400 ^a	$6.70 \pm 0.21 \times 10^{-2}$	0—80
4-Chlorotetrafluorobenzonitrile	0.340	2.00 ^a	$2.20 \pm 0.18 \times 10^{-3}$	0—44
	0.720	2.00 ^a	$2.11 \pm 0.21 \times 10^{-3}$	0—88
Tetrafluoro-4-methoxybenzonitrile	1.65	2.03 ^a	$5.7 \pm 0.3 \times 10^{-5}$	0—2
Pentafluoronitrobenzene	1.61	2.04 ^a	$2.92 \pm 0.06 \times 10^{-1}$	0—75
	0.80	2.04 ^a	$2.98 \pm 0.08 \times 10^{-1}$	0—70
Pentafluoronitrosobenzene	0.0247	0.010 ^a	$2.76 \pm 0.20 \times 10^1$	0—99
	0.0252	0.025 ^a	$2.62 \pm 0.16 \times 10^1$	0—93

^a Sodium azide. ^b Potassium azide; reactions with this gegenion showed rate constants which were 0.8 ± 0.1 those found with sodium azide. ^c k_{initial} 2.2 (six points); followed over 156% reaction, giving k_2 0.89 l mol⁻¹ s⁻¹ for the azidodefluorination of 4-azido-1,2-dicyano-3,5,6-trifluorobenzene (4-azidotrifluorophthalonitrile)

From pentafluorobenzonitrile were obtained 4-chloro-tetrafluorobenzonitrile, m.p. 69.2—70.0° (lit.,⁴ 66—67°), 4-methoxytetrafluorobenzonitrile, m.p. 55.5—56.5° (lit.,⁴ 53—54°), and 4-hydrazinotetrafluorobenzonitrile, m.p. 143—145° (lit.,²² 145—146°) by literature methods.^{4,22} Oxidation of the hydrazino-compound gave²² 3-cyano-1,2,4,5-tetrafluorobenzene, m.p. 38—40 (lit.,²² 40—41°).

sulphate, tetrafluorophthalonitrile and tetrafluoroterephthalonitrile were reduced to 3,4-dicyano-1,2,5-trifluorobenzene, b.p. ca. 140° at 10 mmHg, and 1,4-dicyano-2,3,5-trifluorobenzene; both compounds were obtained in small quantity. They were identified, and their purity was checked, by ¹⁹F n.m.r. spectroscopy.

²² C. Tamborski and E. J. Soloski, *J. Org. Chem.*, 1966, **31**, 746.

Sodium azide was purified by recrystallisation from water. Potassium azide was prepared from hydrazine, potassium hydroxide, and pentyl nitrite by an adaptation of the reported method²³ and was purified by recrystallisation from aqueous acetone. Both salts were then dried under vacuum for 5 h at room temperature. The purification of methanol has been already described;⁷ solutions of sodium or potassium azide in purified methanol was made by dissolving weighed amounts of the salt in standard flasks. Such solutions were shown to be >99% pure by argentimetric titration.

The courses of each reaction were followed by measurement of the fluoride ion formed, quenching the samples of the reaction mixture in a buffer of sodium acetate and acetic acid containing sodium chloride, and measuring fluoride ion directly using a specific ion electrode.⁷ The stoichiometry of the reaction of azide ion with pentafluorobenzonitrile was checked by measurement of both the azide ion consumed and the fluoride ion produced; the organic products of each displacement reaction were identified, and their

²³ M. W. Miller and L. F. Audrieth, *Inorg. Synth.*, 1946, **2**, 139.

amounts measured, by ¹⁹F n.m.r. spectroscopy (Table 4). The chemical shifts of the peaks used for analytical purposes were measured using a Perkin-Elmer R12B instrument, with fluorotrichloromethane as solvent and internal standard (Table 5).

The second-order rate constants for azidodefluorination of a number of polyfluoroarenes in methanol at 323.2 K are given in Table 6, together with the initial concentrations of the reactants, the range of the reaction followed (%), and the standard deviation associated with each rate constant.

The very slowly attacked substrates were followed to only a few percent reaction. With the exception of pentafluorobenzene, even these substrates showed fair limits of error in the second-order rate constants which were calculated (Table 6) although the method is obviously liable to error from the presence of impurities at low concentrations. The physical constants and the kinetic plots both suggest a high degree of purity, arguing against such error, but the absolute accuracy of rate constants measured under such conditions ($10^6 k_2 < 1$) cannot be assured.

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