

## Nucleophilic Displacement in Polyhalogenoaromatic Compounds. Part 7.<sup>1</sup> Kinetics of Methoxydefluorination of Polyfluoronitrobenzenes

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Rates and orientations of methoxydefluorination (NaOMe–MeOH) of twelve polyfluoronitrobenzenes have been measured at 298.2 K. The fluorine substituent effects are less well defined in the presence of the nitro-group, and are dependent not only upon the orientation of the fluorine substituent with respect to the reaction site, but also with respect to the nitro-group. The resulting attenuation seems to be electronic rather than steric in origin, and may be described as a mutually weakening interaction of the mesomeric effects of halogen and nitro-group. Two fluorine atoms *ortho* to the nitro-group cause a further diminution of effect consistent with this explanation.

HALOGEN substituents, with the general exception of fluorine in the *para*-position, accelerate aromatic nucleophilic substitution.<sup>2-4</sup> In the methoxydefluorination of polyfluorobenzene derivatives, fluorine and chlorine substituent effects have been found to be almost completely additive regardless of the extent of substitution of the system upon which they act,<sup>2</sup> so that no evidence of saturation of effect<sup>5</sup> or mutual interaction of groups<sup>6</sup> is seen. The nitro-group has been the most popular single activating substituent in such processes,<sup>7</sup> although its effect is subject to steric influences. In *ortho*- and *para*-halogenonitrobenzenes the relative rates of attack appear to depend upon the nature of the nucleophile and the solvent; amines<sup>8</sup> and non-polar media encourage attack *ortho* to the nitro-group,<sup>9</sup> a trend observed in the reactions of 2,4-dinitrofluorobenzene<sup>10</sup> as well as those of pentafluoronitrobenzene;<sup>11</sup> the reactions of 2,4-dichloronitrobenzene show similar behaviour.<sup>9,12</sup>

These observations have been interpreted<sup>9-12</sup> in terms of solvation and/or electronic effects, including secondary steric effects. The present paper describes the extension of such studies to a number of polyfluoronitrobenzenes in the hope of quantifying the effect of the nitro-substituent upon methoxydefluorination in polyfluorobenzenes.

### DISCUSSION

The polyfluoronitrobenzenes whose rates of methoxydefluorination were measured at 298.2 K are listed in

<sup>1</sup> Part 6, R. Bolton and J. P. B. Sandall, preceding paper.

<sup>2</sup> R. Bolton and J. P. B. Sandall, *J.C.S. Perkin II*, 1977, 1541; R. Bolton, S. M. Kazerooni, and J. P. B. Sandall, *J. Fluorine Chem.*, 1976, **8**, 471.

<sup>3</sup> (a) R. D. Chambers, J. S. Waterhouse, and D. L. H. Williams, *J.C.S., Perkin II*, 1977, 585; (b) R. D. Chambers, W. K. R. Musgrave, J. S. Waterhouse, D. L. H. Williams, J. Burdon, W. B. Hollyhead, and J. C. Tatlow, *J.C.S. Chem. Comm.*, 1974, 239; (c) J. Burdon, W. B. Hollyhead, and J. C. Tatlow, *J. Chem. Soc.*, 1965, 6375.

<sup>4</sup> R. L. Heppollette, J. Miller, and V. A. Williams, *J. Amer. Chem. Soc.*, 1956, **78**, 1975; M. Liveris, P. G. Lutz, and J. Miller, *ibid.*, p. 3375; K. C. Ho and J. Miller, *Austral. J. Chem.*, 1966, **19**, 423.

Table 1, together with the derived rate constants for attack at individual sites where more than one fluorine was displaced concurrently. The course of each

TABLE 1

Second-order rate constants for methoxydefluorination of polyfluoronitrobenzenes (NaOMe–MeOH; 298.2 K)

| Nitrobenzene             | $10^3 k_2^a$                           | $10^3 k_{ortho}^a$ | $10^3 k_{para}^a$ |
|--------------------------|--|--------------------|-------------------|
| 2-Fluoro (1)             | $0.18 \pm 0.02$                        | 0.18               |                   |
| 4-Fluoro (2)             | $0.26 \pm 0.02$                        |                    | 0.26              |
| 2,4-Difluoro (3)         | $8.8 \pm 0.5$ ;<br>$8.8 \pm 0.8^{b,c}$ | 5.0                | 3.7               |
| 2,5-Difluoro (4)         | $0.26 \pm 0.01$ ;<br>$0.29 \pm 0.04^b$ | 0.26               |                   |
| 3,4-Difluoro (5)         | $3.1 \pm 0.2^b$                        |                    | 3.1               |
| 2,3,4-Trifluoro (6)      | $174 \pm 5$                            | 110                | 64                |
| 2,3,5-Trifluoro (7)      | $8 \pm 6^d$                            | 8                  |                   |
| 2,4,5-Trifluoro (8)      | $144 \pm 8$ ;<br>$149 \pm 5^b$         | 6                  | 141               |
| 2,4,6-Trifluoro (9)      | $53 \pm 3$ ;<br>$56 \pm 2^b$           | 17                 | 19                |
| 3,4,5-Trifluoro (10)     | $66 \pm 1^d$                           |                    | 66                |
| 2,3,4,5-Tetrafluoro (11) | $1\ 710 \pm 75$                        | 190                | 1\ 520            |
| 2,3,4,6-Tetrafluoro (12) | $640 \pm 45$                           | 300                | 340               |
| Pentafluoro (13)         | $43\ 000 \pm 27\ 000^e$                | 1\ 720             | 40\ 000           |

<sup>a</sup>  $d[F^-]/dt = k[ArF][MeO^-]$ ;  $k$  in  $l\ mol^{-1}\ s^{-1}$ . <sup>b</sup>  $-d[MeO^-]/dt = k[ArF][MeO^-]$ . <sup>c</sup>  $10^3 k_2 = 8.6 \pm 0.3$  (AnalaR methanol);  $8.7 \pm 0.2$  (0.1% water in methanol);  $9.3 \pm 0.4$  (undried methanol);  $9.1 \pm 0.1$  (redistilled methanol); 5.89 (ref. 10). <sup>d</sup> See text for explanation of errors and source of rate constants. <sup>e</sup> Ref. 3 c.

reaction could be followed by measurement of the fluoride ion concentration, and the methoxydefluorination of less

<sup>5</sup> S. Nishida, *J. Org. Chem.*, 1967, **32**, 2695, 2697.

<sup>6</sup> R. Bolton and J. P. B. Sandall, in preparation.

<sup>7</sup> J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, 1951, **49**, 273; J. F. Bunnett, *Quart. Rev.*, 1958, **12**, 1; J. Miller, *Rev. Pure Appl. Chem.*, 1951, **1**, 171; J. Miller, 'Aromatic Nucleophilic Substitution', Elsevier, Amsterdam, 1968.

<sup>8</sup> G. S. Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 334.

<sup>9</sup> J. F. Bunnett and R. Morath, *J. Amer. Chem. Soc.*, 1955, **77**, 5051, 5055.

<sup>10</sup> T. O. Bamkole, J. Hirst, and E. I. Udoessian, *J.C.S. Perkin II*, 1973, 110.

<sup>11</sup> J. G. Allen, J. Burdon, and J. C. Tatlow, *J. Chem. Soc.*, 1965, 1045.

<sup>12</sup> Th. J. de Boer and I. P. Dirckx, 'The Chemistry of the Nitro and Nitroso Groups', ed. H. Feuer, Interscience, New York, 1969, ch. 8.

rapid substrates could also be followed by acid-base titration of the alkoxide ion. Sodium fluoride is only sparingly soluble in methanol ( $[\text{NaF}]$  ca. 0.001 M; 298.2 K) and this is not greatly increased by the presence of 0.1% water ( $[\text{NaF}]$  ca. 0.003 M; 298.2 K), so that the reaction solutions soon become supersaturated at higher initial concentrations, and precipitation of the salt may cause errors. At low concentrations, however, acid-base titrations are unsuitable, particularly when fluoride ion acts as a buffer in the titration of unchanged base. The two analytical methods are complementary, but in some cases (2,4-, 2,5-, and 3,4-difluoronitrobenzenes; 2,4,5- and 2,4,6-trifluoronitrobenzenes) the precipitation of sodium fluoride from reaction mixtures was sufficiently delayed to allow both methods to be used concurrently. In these cases (Table 1) the expected kinetic equivalence  $-d[\text{MeO}^-]/dt = d[\text{F}^-]/dt = k_2[\text{MeO}^-][\text{ArF}]$  prevails.

The orientation of attack was measured by  $^{19}\text{F}$  n.m.r. spectroscopy; the derived rate constants in Table 1 show that orientation of attack is the same to within experimental error for each in the pairs of compounds (3) and (6), (9) and (12), (8) and (11), and (11) and (13). The two components of each pair undergo attack at the same positions, both of which are equally affected within the molecule by the new substituent which causes the difference between the pair. Thus, both 2,4-di- and 2,3,4-tri-fluoronitrobenzenes undergo attack at the 2- and 4-positions, the 3-fluorine substituent having the same influence upon both sites. There is no evidence of a difference in susceptibility to substituent effects for displacement of fluorine at sites *ortho* and *para* to the nitro-group.

The rates of reaction of the polyfluoronitrobenzenes show quite different fluorine substituent effects from those found in the absence of the nitro-substituent. In the latter case, fluorine in the *meta*-position increases the rate of methoxydefluorination by a factor of 180 at 323.2 K; *ortho*-fluorine accelerates by a factor of 42, while *para*-fluorine is somewhat less effective than hydrogen ( $f_p$  0.75).<sup>1,2</sup> The analogous reaction of the polyfluoronitrobenzenes shows (Table 2) that both *meta* ( $f_m$  23  $\pm$  2) and *ortho* ( $f_o$  19  $\pm$  3) fluorine substituents are less strongly activating for the same reaction at 298.2 K, while in the *para*-position ( $f_p$  1.3  $\pm$  0.3) fluorine is weakly activating. Where there are two halogen atoms adjacent to the nitro-group, the apparent *meta*-fluorine substituent effect is even smaller ( $f'_m$  3.7  $\pm$  1.3), which may be understood in terms of a secondary steric effect upon the nitro-substituent.

Methoxydefluorination shows a sensitivity to fluorine substituents apparently dependent upon the presence of a nitro-substituent, for the difference is too great to be accounted for by the difference in the temperatures at which measurements were made.<sup>7</sup> If the transition states in each set of reactions occur at the same position

along the reaction co-ordinate, the only alteration in the system is the inclusion of the nitro-group and it is here that the source of the difference in behaviour must be.

*The Nitro-group Effect.*—Earlier workers have commented<sup>7,13</sup> that in aromatic nucleophilic substitution the measured substituent effect of a nitro-group is affected by the presence of other groups in the substrate. The additivity of substituent effect found in the

TABLE 2  
Derived fluorine substituent constants (methoxydefluorination; 298.2 K)

| Polyfluoronitrobenzenes compared <sup>a</sup> | No. of F groups adjacent to NO <sub>2</sub> | $k/k_H$       |
|---|---|---------------|
| <i>o</i> -F                                   |   |               |
| 2,3,4,5-F <sub>4</sub> /2,4,5-F <sub>3</sub>  | 1   | 30 $\pm$ 10   |
| 2,3,4,5-F <sub>4</sub> /2,4,5-F <sub>3</sub>  | 1   | 11 $\pm$ 1    |
| 2,3,4-F <sub>3</sub> /2,4-F <sub>2</sub>      | 1   | 18 $\pm$ 3    |
| 2,3,4-F <sub>3</sub> /2,4-F <sub>2</sub>      | 1   | 17 $\pm$ 3    |
| 2,4,5-F <sub>3</sub> /2,4-F <sub>2</sub>      | 1   | 38 $\pm$ 7    |
| 3,4,5-F <sub>3</sub> /3,4-F <sub>2</sub>      | 0   | 21 $\pm$ 3    |
| 2,3,5-F <sub>4</sub> /2,5-F <sub>3</sub>      | 1   | 31 $\pm$ 24   |
| 2,3,4,5-F <sub>4</sub> /2,3,4-F <sub>3</sub>  | 1   | 24 $\pm$ 3    |
| 2,3,4,6-F <sub>4</sub> /2,4,6-F <sub>4</sub>  | 2   | 18 $\pm$ 3    |
| 2,3,4,6-F <sub>4</sub> /2,4,6-F <sub>3</sub>  | 2   | 18 $\pm$ 3    |
| 3,4-F <sub>2</sub> /4-F                       | 0   | 12 $\pm$ 3    |
| <i>m</i> -F                                   |   |               |
| 2,3,4,6-F <sub>4</sub> /2,4,5-F <sub>3</sub>  | <i>b</i>                                    | 2.5 $\pm$ 0.4 |
| 2,3,4,6-F <sub>4</sub> /2,3,4-F <sub>3</sub>  | <i>b</i>                                    | 5.3 $\pm$ 0.7 |
| 2,4,6-F <sub>3</sub> /2,4-F <sub>2</sub>      | <i>b</i>                                    | 3.4 $\pm$ 0.7 |
| 2,4,6-F <sub>3</sub> /2,4-F <sub>2</sub>      | <i>b</i>                                    | 5.1 $\pm$ 1.0 |
| 2,4-F <sub>2</sub> /4-F                       | <i>b</i>                                    | 14 $\pm$ 2    |
| 2,4,5-F <sub>3</sub> /2,5-F <sub>2</sub>      | 1   | 22 $\pm$ 11   |
| 2,4,5-F <sub>3</sub> /3,4-F <sub>2</sub>      | <i>b</i>                                    | 45 $\pm$ 7    |
| 2,3,4-F <sub>3</sub> /3,4-F <sub>2</sub>      | <i>b</i>                                    | 21 $\pm$ 2.7  |
| 2,3,4,5-F <sub>4</sub> /2,3,5-F <sub>3</sub>  | 1   | 24 $\pm$ 20   |
| 2,3,4,5-F <sub>4</sub> /3,4,5-F <sub>3</sub>  | <i>b</i>                                    | 23 $\pm$ 2    |
| <i>p</i> -F                                   |   |               |
| 2,3,4,5-F <sub>4</sub> /2,3,4-F <sub>3</sub>  | 1   | 1.7 $\pm$ 0.9 |
| 2,4,5-F <sub>3</sub> /2,4-F <sub>2</sub>      | 1   | 1.2 $\pm$ 0.7 |

<sup>a</sup> Displaced fluorine italicised; figures refer to the orientation of the fluorine atoms with respect to the nitro-group. 2,3,4-F<sub>3</sub> refers therefore to 2,3,4-trifluoronitrobenzene. <sup>b</sup> Removal of the substituent may also alter the secondary steric effect.

sequence fluorobenzene, *m*-fluoronitrobenzene, and 3,5-dinitrofluorobenzene<sup>13,14</sup> is in sharp contrast to the observations found in the methoxydefluorination of the series fluorobenzene, *o*-(*p*-) fluoronitrobenzene, 2,4-dinitrofluorobenzene, 2,4,6-trinitrofluorobenzene<sup>13,15</sup> where saturation of effect appears to take place. Saturation of effect suggests that part of the substituent effect is lost when it is acting upon a system already considerably polarised; that is, part of the electronic effect is reaction dependent.

The nitro-group is well known to be polarisable. The variation of electronic effect in electrophilic and nucleophilic processes is reflected by the attempts<sup>16,17</sup> to find consistent values for the substituent constant ( $\sigma$ ) for the *p*-nitro-group; even the earliest reviews of the Hammett equation pointed the need for two such constants associated with the ionisation of benzoic acid or of phenols

<sup>13</sup> J. Miller, *Austral. J. Chem.*, 1956, **9**, 61.

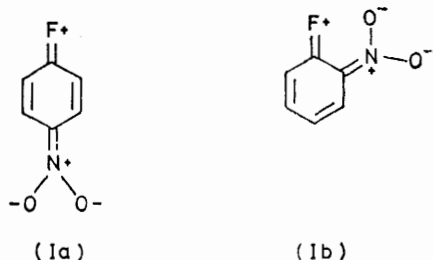
<sup>14</sup> C. W. L. Bevan, J. Hirst, and S. J. Una, *Chem. and Ind.*, 1966, 341.

<sup>15</sup> C. W. L. Bevan and G. C. Bye, *J. Chem. Soc.*, 1954, 3091.

<sup>16</sup> R. W. Taft and I. C. Lewis, *J. Amer. Chem. Soc.*, 1958, **80**, 2436; 1959, **81**, 5343; H. van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. Trav. chim.*, 1959, **78**, 815.

<sup>17</sup> P. R. Wells, *Chem. Rev.*, 1963, **63**, 171.

and amines.<sup>18</sup> The distinction was usually made between structures in which direct conjugation could occur between the reaction site (*e.g.* *p*-nitrophenol, *p*-nitroaniline) and those where it could not (*e.g.* *p*-nitrobenzoic acid) with the implication that such conjugative interactions could affect the stability of the system. In the polynitrofluorobenzene systems<sup>13,15</sup> where the nitro-groups are *ortho* and *para* to the reaction sites, structures such as (Ia and b) may be drawn. These show how the mesomeric effect of halogen and nitro-group may cancel each other; perhaps more specifically they also show that the carbon atom under attack is less electron poor than might be expected, and that the carbon-halogen bond undergoing fission acquires some multiplicity.



Mere cancellation of two opposing effects does not explain the observation, for saturation of effect suggests a greater difficulty in removing electrons from the reaction site. This must be held in mind on considering the series<sup>13,14</sup> in which the nitro-groups are *meta* to each other and to the reaction site, for although the nitro-groups are acting in concert upon the reaction site their effect is presumably relayed inductively from carbon atoms *ortho* to the carbon atom bearing fluorine, a situation in which the polarisability effects are much less prominent.

Some idea of the differences involved can be found from comparing the effects of introducing the nitro-substituent to some polyfluorobenzene systems. Table 3 shows the apparent partial rate factors for the nitro-group both *ortho* and *para* to the displaced fluorine atoms in fluoro-, 1,2,3,4-tetrafluoro-, 1,2,3,5-tetrafluoro-4-nitro-, and pentafluoronitrobenzene. Although the comparison is made between methoxydefluorination at 323.2 (polyfluorobenzenes) and 298.2 K (polyfluoronitrobenzenes) the changes in the ratio of the rates seem significant. Essentially, the more fully fluorinated systems are less activated by the nitro-group.

In our own studies, we have found that the polyfluoronitrobenzene systems are less activated by the fluorine substituent. The apparent contradiction involves the effect of introducing a polarisable substituent to a non-polarisable system, or the effect of introducing a non-polarisable substituent to a polarisable system. In each case, the apparent substituent effect is attributed only to the new group, although it is obviously conditioned by the perturbability of substituent and substrate by each other.

*The Polyfluoronitrobenzenes.*—The relatively small substituent effects seen (Table 2) in the methoxydefluorination of polyfluoronitrobenzenes arises from the repression of the polarisability contribution of the nitro-substituent. Fluorine *meta* to the displaced group is most affected because it must necessarily also be *ortho* or *para* to a nitro-group, and so able to conjugate

TABLE 3

Comparison of rates of methoxydefluorination of polyfluorobenzenes (323.2 K) and their nitro-derivatives (298.2 K)<sup>a</sup>

| Ar                    | $10^{-6}(k_{ArNO_2}/k_{ArH})$ |
|-----------------------|-------------------------------|
| 2,3,4,5,6-Pentafluoro | $0.9 \pm 0.7$                 |
| 2,3,4,5,6-Pentafluoro | $0.39 \pm 0.26$               |
| 2,3,4,6-Tetrafluoro   | $0.13 \pm 0.02$               |
| 2,3,4,6-Tetrafluoro   | $0.14 \pm 0.02$               |
| 2,3,4,5-Tetrafluoro   | $1.9 \pm 0.2$                 |
| 2-Fluoro              | $600 \pm 300$                 |
| 4-Fluoro              | $800 \pm 300$                 |

<sup>a</sup> Displaced halogen is italicised; values taken from refs. 2, 3, 7, and 15. Errors are only notional values, because of the large extrapolations occasionally necessary, but are taken from the published errors associated with the Arrhenius plots.

directly with it by interactions such as (Ia or b). To understand the influences of *ortho*- and *para*-fluorine atoms, which appear to be affected in opposite ways, the contribution which the nitro-group must make has to be considered. An *ortho*-fluorine atom, even in the presence of a nitro-group, evidently removes electron density from the carbon atom undergoing attack. The nitro-group is now attempting to remove electrons from a centre more electron poor than in the absence of the *ortho*-fluorine substituent, and must be less successful. In contrast, a *para*-fluorine substituent has very little effect, for the mesomeric and inductive contributions almost exactly cancel each other; it is not remarkable that the nitro-group may now be able to show the same effect as it does in the absence of the *para*-fluorine group, and in fact it is a little better. Of course the substituents are showing simultaneous effects and not sequential influences, but it is more convenient to adopt the latter approach in considering the number of electronic influences which are involved.

Finally, we may compare the rates of displacement of the fluorine atoms in 2,4-difluoronitrobenzene and in the monofluoronitrobenzenes. Introducing a fluorine group *ortho* to the nitro-group in *p*-fluoronitrobenzene causes two effects; one is the expected activation coming from a *meta*-fluorine substituent, while the other is a deactivation arising from interactions such as (Ib) and any secondary steric effect which occurs. A fluorine group at the 4-position of *o*-fluoronitrobenzene shows the same activation, but a deactivation arising only from interactions such as (Ia). Only if these two deactivations are the same in magnitude will the reactions of 2,4-difluoronitrobenzene and of *o*- and *p*-fluoronitrobenzenes show additivity of effect.

<sup>18</sup> H. H. Jaffe, *Chem. Rev.*, 1953, **53**, 191.

## EXPERIMENTAL

*Polyfluoronitrobenzenes.*—The nitration of the appropriate polyfluorobenzene gave 2,3,4,5-tetrafluoronitro-<sup>19</sup> and 1,3,4,5-tetrafluoro-2-nitro-benzene<sup>20</sup> while ion-exchange<sup>21</sup> gave 2,3,4-trifluoronitrobenzene from 2,4-dichloro-3-fluoronitrobenzene.<sup>22</sup> Other polyfluoronitrobenzenes were commercial samples (Bristol Organics) which showed no evidence of impurity (g.l.c.; n.m.r.) but which were washed with sodium carbonate (0.2M) and water before drying (molecular sieve 5A) and distillation under reduced pressure. Further purification of 2,4,5-trifluoronitrobenzene was suggested by an unexpectedly high second-order rate constant. Vacuum distillation, followed by chromatography upon alumina and a third distillation, failed to improve the physical properties of the compound or to change the rate constant.

*3,4,5-Trifluoronitrobenzene.*—2,3,4,5-Tetrafluoronitrobenzene (9.75 g, 0.05 mol) dissolved in dioxan (50 ml) was treated with hydrazine hydrate (99%; 5 ml, 0.1 mol) at room temperature. The dark red suspension became hot and cleared. On standing (0.5 h) the solution became more viscous and deposited a small amount of solid. The resulting suspension was added slowly to a boiling solution of copper(II) sulphate (50 g) in water (400 ml), distilling the volatile products from this mixture as they were formed. Salting out the distillate provided a yellow oil (7.2 g, 90%) showing the presence of 3,4,5-trifluoronitro- (50%), 2,3,5-trifluoronitro- (20%), and 2,3,4-trifluoro-4-hydroxynitrobenzene (30%) (<sup>19</sup>F n.m.r.). This oil, on washing with sodium hydroxide (0.5M) and distillation of the dried (CaCl<sub>2</sub>) material, gave trifluoronitrobenzene (3.8 g, 45%) containing the 3,4,5- (77%) and 2,3,5-isomer (23%), b.p. 69–70° at 7 mmHg.

*Kinetic Procedure and Analysis.*—Purified methanol<sup>1,2</sup> and solutions of standard sodium methoxide were prepared and checked by reported means. The course of the reaction was followed either by the titration method already described<sup>2</sup> or by discharging samples (5 ml) into sodium acetate-acetic acid buffer (pH 5) containing sodium chloride (1M; 10 ml) and a further quantity of water or of sulphuric acid (0.1M; 5 ml); reactions using higher concentrations of methoxide required at least partial neutralisation to avoid overloading the buffer. These solutions were then checked against standards made up in similar solvent mixtures, using an Orion 94-09A fluoride ion specific electrode. Titration against thorium or lanthanum ion, even<sup>23</sup> using this electrode as an indicator of the change of fluoride ion during titration, were unsuccessful. Good second-order kinetic plots were found for all substrates excepting the trifluoronitrobenzene mixture obtained from 2,3,4,5-tetrafluoronitrobenzene. Analysis of the product mixture showed the 3,4,5-isomer to be the more rapidly attacked; simple kinetic analysis<sup>24</sup> of the rate of formation

<sup>19</sup> L. J. Belf, M. W. Buxton, and J. F. Tilney-Bassett, *Tetrahedron*, 1967, **23**, 4719.

<sup>20</sup> G. C. Finger, F. H. Reed, and R. E. Oesterling, *J. Amer. Chem. Soc.*, 1951, **73**, 152.

<sup>21</sup> G. C. Finger, M. J. Gortotowski, R. H. Shiley, and R. H. White, *J. Amer. Chem. Soc.*, 1959, **81**, 94.

<sup>22</sup> K. H. Klaassens and C. J. Schoot, *Rec. Trav. chim.*, 1956, **75**, 186.

of fluoride ion allowed the rate constant for methoxy-defluorination of this species to be obtained to within 0.5%, certainly within the experimental error of the individual measurements. The rate constant associated with the slower isomer, because it was also present in small amount, could only be found by difference, and was therefore subject to an error of the magnitude of 50%.

*N.m.r. Measurements.*—Measurements were made using

TABLE 4

| Nitrobenzene                 | <sup>19</sup> F N.m.r. chemical shifts used for analysis<br>δ(p.p.m. upfield of CFC1 <sub>3</sub> ) <sup>a</sup> |
|------------------------------|--|
| 2-Fluoro-methoxy-4-          | 121.9 (131.1)  |
| 2-Fluoro-4-methoxy           | 113.4 (114.2)  |
| 4-Fluoro-2-methoxy           | 101.0 (101.0)  |
| 2,3-Difluoro-methoxy-4-      | 2-F, 155.0 (155.6); 3-F, 140.6 (141.2)   |
| 1,2-Difluoro-3-methoxy-4-    | 1-F, 126.8 (125.5); 2-F, 150.1 (155.6)   |
| 3,5-Difluoro-methoxy-2-      | 3-F, 119.7 (112.8); 5-F, 102.0 (97.1)  |
| 1,3-Difluoro-5-methoxy-2-    | 117.0 (117.2)  |
| 2,5-Difluoro-4-methoxy       | 2-F, 136.8 (137.2); 5-F, 117.6 (120.4)   |
| 4,5-Difluoro-2-methoxy       | 4-F, 125.4 (125.5); 5-F, 145.4 (145.1)   |
| 2,4-Difluoro                 | 2-F, 111.9 (111.8); 4-F, 98.2 (96.1)   |
| 3,4-Difluoro                 | 3-F, 135.0 (134.1); 4-F, 128.7 (127.5)   |
| 2,3,4-Trifluoro              | 2-F, 137.5 (136.3); 3-F, 155.9 (155.6); 4-F, 122.8 (120.6)   |
| 2,3,5-Trifluoro              | 2-F, 147.8 (148.7); 3-F, 129.8 (130.6); 5-F, 111.6 (112.1)   |
| 2,4,5-Trifluoro              | 2-F, 117.6 (120.6); 4-F, 121.8 (123.6); 5-F, 138.2 (140.2)   |
| 3,4,5-Trifluoro              | 3-F, 130.3 (130.6); 4-F, 150.1 (152.0)   |
| 1,3,5-Trifluoro-2-           | 1-F, 115.3 (111.1); 5-F, 98.8 (95.4)   |
| 1,2,3-Trifluoro-4-methoxy-5- | 1-F, 139.5 (143.7); 2-F, 141.5 (149.9); 3-F, 158.4 (151.2)   |
| 1,3,4-Trifluoro-2-methoxy-5- | 1-F, 132.5 (135.8); 3-F, 150.3 (151.2); 4-F, 145.7 (147.0)   |
| 1,3,4-Trifluoro-5-methoxy-2- | 1-F, 118.9 (122.5); 3-F, 142.8 (137.3); 4-F, 161.5 (161.7)   |
| 1,2,5-Trifluoro-3-methoxy-4- | 1-F, 128.3 (121.6); 2-F, 157.1 (161.7); 5-F, 126.0 (118.9)   |
| 2,3,4,5-Tetrafluoro          | 2-F, 145.1 (142.5); 3-F, 154.2 (156.1); 4-F, 148.8 (145.1); 5-F, 138.8 (136.8)                                   |
| 1,3,4,5-Tetrafluoro-2-       | 1-F, 123.8 (121.4); 3-F, 141.0 (136.1); 4-F, 163.5 (162.1); 5-F, 125.6 (123.8).                                  |

<sup>a</sup> Calculated shifts in parentheses.

ca. 10% solutions in trichlorofluoromethane with a Perkin-Elmer R12B machine operating at 56.4 MHz. Compounds were identified by their chemical shifts and the splitting patterns of each peak, using the detailed methods already described.<sup>25</sup> (Table 4)

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<sup>23</sup> G. H. Cady, Abstracts of the 8th International Symposium on Fluorine Chemistry, Kyoto, 1976, 1–16.

<sup>24</sup> E. S. Swinbourne, 'Analysis of Kinetic Data', Nelson, London, 1971, p. 88.

<sup>25</sup> R. Bolton, S. M. Kazeroonian, and J. P. B. Sandall, *J. Fluorine Chem.*, in the press; see also refs. 1 and 2.