# *The $S_N$ Mechanism in Aromatic Compounds. Part XV.**

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[Reprint Order No. 6175.]

The substituent effects of *o*- and *p*-methyl and -trifluoromethyl groups in aromatic nucleophilic substitution have been measured and compared. The methyl group is slightly deactivating; the trifluoromethyl group has an activating power approaching that of methoxycarbonyl and trimethylammonium. The modes of action are discussed.

In Miller's classification (*Rev. Pure Appl. Chem.*, **1951**, **1**, 171) of substituents in $S_N$ reactions in the aromatic series, class (iv) refers to groups attached to the ring by uncharged atoms having no unshared electrons. Subsections (*a*) and (*b*) refer to electron-attracting and electron-repelling groups, which cause activation and deactivation respectively at both *ortho*- and *para*-positions. The present paper confirms the general predictions, and gives a quantitative measure of the effect for methyl and trifluoromethyl groups (Downing, Heppolette, and Miller, *Chem. and Ind.*, 1953, 1260).

The rates of replacement by $OMe^-$ in absolute methanol of the chlorine in (i) 4-chloro-3-nitrotoluene, (ii) 2-chloro-5-nitrotoluene, (iii) 1-chloro-2-nitro-4-trifluoromethylbenzene, and (iv) 1-chloro-4-nitro-2-trifluoromethylbenzene have been measured and by comparison with the rates for *o*- (v) and *p*-chloronitrobenzenes (vi) (Miller, *J.*, 1952, 3550) the substituent rate factors (S.R.F.; Miller, *loc. cit.*) and the steric indices (S.I.; Miller and Williams, *J.*, 1953, 1475) have been calculated. The results are given as Tables 1 and 2.

Table 1.

Rate constant ($10^5k_2$ l. mole$^{-1}$ sec.$^{-1}$)

| Compd. | Subst. | (*a*) At temp. in parentheses | | | | (*b*) At 0° | At 50° | Calc.: At 100° | At 150° |
|---|---|---|---|---|---|---|---|---|---|
| (v) | *p*-H | 3·62<br>(75·3) | 6·82<br>(81·6) | 37·4<br>(100·8) | — | 0·000297 | 0·252 | 35·0 | $151_5$ |
| (vi) | *o*-H | 8·42<br>(71·0) | 23·5<br>(81·6) | 137<br>(100·8) | — | 0·000890 | 0·847 | 128 | 5910 |
| (i) | *p*-Me | 1·42<br>(81·9) | 35·0<br>(114·0) | 158<br>(131·1) | 296<br>(138·4) | — | 0·0299 | 9·18 | 723 |
| (ii) | *o*-Me | 6·07<br>(81·9) | 31·6<br>(99·3) | 193<br>(120·6) | 769<br>(138·4) | — | 0·187 | 33·5 | 1760 |
| (iii) | *p*-$CF_3$ | 49·6<br>(35·4) | 80·0<br>($40·0_5$) | 134<br>(45·6) | 541<br>(60·2) | 0·745 | 205 | 12,500 | — |
| (iv) | *o*-$CF_3$ | 81·7<br>(45·3) | 342<br>(59·9) | 1350<br>(75·3) | 2290<br>(81·6) | 0·367 | 131 | 2690 | — |

Table 2.

| | S.R.F.* | | | | S.I. | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Compd. | 0 | 50 | 100 | 150 | 0 | 50 | 100 | 150 | *E* (cal.) | $\log_{10}$ B |
| (i) | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | $23,6_{50}$ | 10·4 |
| (ii) | 1 | 1 | 1 | 1 | | | | | $24,0_{50}$ | 11·2 |
| (iii) | — | 0·119 | 0·262 | 0·477 | — | 0·538 | 1·00 | 1·60 | 27,400 | 12·0 |
| (iv) | — | 0·221 | 0·262 | 0·298 | | | | | $24,8_{50}$ | 11·1 |
| (v) | 2510 | 813 | 357 | — | 6·08 | 5·25 | 4·72 | — | 19,700 | 10·6 |
| (vi) | 413 | 155 | 75·7 | — | | | | | 20,600 | 11·1 |

* The S.R.F.s for $CO_2Me$ and $NMe_3^+$ at 0° are 7240 and $10,7_{50}$ respectively (Miller, *J. Amer. Chem. Soc.*, 1954, **76**, 448; Bolto and Miller, unpublished work).

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* Part XIV, preceding paper.

*Discussion.*—The methyl group is seen to be slightly deactivating in both the *ortho*- and the *para*-position, the difference being almost negligible but somewhat dependent on the temperature. In $S_E$ reactions in the aromatic series the methyl group is fairly activating, but the $p/o$ ratios of the partial rate factors are always small (close to 1) : thus for nitration of toluene these factors are 58 and 42 for *para*- and *ortho*-positions, giving a $p/o$ ratio of 1·38 (Ingold, " Structure and Mechanism in Organic Chemistry," G. Bell & Sons Ltd., London, 1953, p. 259). This suggests that in $S_N$ reactions in the aromatic series, both the $+I$ and the $+M$ hyperconjugation of the methyl group are small.

The absence of steric hindrance is noteworthy and has already been demonstrated (Miller and Williams, *J.*, **1953**, 1475) even in the more hindered dinitro-series.

Comparison with the $S_E$ reactions suggests that an important part of the activating power of methyl groups in them is due to a hyperconjugative $+E$ effect.

The electron-attracting power of the trifluoromethyl group is seen to be considerable and approaches that for a cationic $-I$ group, *viz.*, $NMe_3^+$ (Bolto and Miller, *loc. cit.*), and is comparable with that for the $-I-T$ methoxycarbonyl group (Miller, *loc. cit.*). With three fluorine atoms attached to one carbon atom, we expect a powerful $-I$ effect; but this alone would lead to a greater S.R.F. for the *o*-trifluoromethyl group, and a steric index less than 1. Mere size would not be expected to lower the S.R.F. of the *ortho*-group to the extent found experimentally. A partial explanation (cf. Miller and Williams, *loc. cit.*) is the repulsion between the electronegative fluorine atoms and the attacking $OMe^-$. More important is probably the hyperconjugative $-E$ effect, acting more effectively from the *para*-position. Such an effect has already been postulated for other reactions, and supporting evidence has been given (de la Mare, Hughes, and Ingold, *J.*, 1948, 17; Roberts, Webb, and McElhill, *J. Amer. Chem. Soc.*, 1950, **72**, 408; Smith and Turton, *J.*, 1951, 1701). The Arrhenius parameters support the hyperconjugative $-E$ effect as paramount, since the values are similar to those for the methoxycarbonyl ($-I-T$) group (Miller, *loc. cit.*; Miller and Williams, *J. Amer. Chem. Soc.*, 1954, **76**, 5482); whereas *ortho*-deceleration due to repulsion between electronegative atoms and $OMe^-$ appears to act by an increase in $E$ not counteracted by an increase in $B$ (Miller and Williams, *loc. cit.*); while the $-I$ cationic group acts by a comparatively small decrease in $E$ augmented by a considerable increase in $B$.

The frequency factors are difficult to classify. For the *p*-H and *p*-$CF_3$ compounds the values are almost identical; however, both $E$ and log $B$ for *p*-methyl are high. This surprising result seems to be definite in view of the large temperature range (56·5°) and good plot of log $k_2$ against reciprocal temperature. The values of the frequency factor are slightly higher for the three *ortho*-compounds than for *p*-H and *p*-$CF_3$, and this may be connected with a more loosely bound transition state caused by small steric factors.

## EXPERIMENTAL

The runs were followed as in Part II (Miller, *loc. cit*), except that graphical plots were used for $k_2$. Runs for each of at least three temperatures were in duplicate. Estimated errors in $E$ are about ±200 cal., the " probable errors " by the method of least squares being less than this.

*Materials.*—4-Chloro-3-nitrotoluene was prepared from 4-amino-3-nitrotoluene by a Sandmeyer reaction. The redistilled product had b. p. 260°/760 mm., 81—82°/0·5 mm. (lit., 260°/745 mm.).

2-Chloro-5-nitrotoluene, prepared from *N*-acetyl-*o*-toluidine by nitration according to Page and Heasman's method (*J.*, 1923, **123**, 3235), hydrolysis, and a Sandmeyer reaction, and recrystallised from aqueous methanol, had m. p. 42·5° (lit., 42·5°).

1-Chloro-2-nitro-4- and 1-chloro-4-nitro-2-trifluoromethylbenzene were commercial products, having the recorded physical constants (m. p. 25—27°, b. p. 94—95°/10 mm.; b. p. 102—103°/5 mm.).

The only new product is *1-methoxy-2-nitro-4-trifluoromethylbenzene*, m. p. 80° (Found : C, 43·5; H, 3·0. $C_8H_6O_3NF_3$ requires C, 43·45; H, 2·7%).

*Typical Kinetic Values.*—A typical run (for 1-chloro-2-nitro-4-trifluoromethylbenzene at 35·4°) is given as Table 3, and the rate constants for the same compound used for calculation of " probable error " by least squares are given as Table 4.

TABLE 3.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Titration value ... | 8·98 | 9·40 | 9·78 | 10·14 | 10·45 | 10·78 | 11·00 | 11·56 | 12·00 |
| log term ............ | 0·1744 | 1824 | 1903 | 1987 | 2065 | 2153 | 2219 | 2400 | 2569 |
| Time (hr.) ............ | 0 | ½ | 1 | 1½ | 2 | 2½ | 3 | 4 | 5 |
| Titration value ... | 12·38 | 12·74 | 13·01 | 13·27 | 13·50 | 13·72 | 13·90 | 16·76 | |
| log term ............ | 2734 | 2911 | 3062 | 3222 | 3383 | 3547 | 3698 | — | |
| Time (hr.) ............ | 6 | 7 | 8 | 9 | 10 | 11 | 12 | ∞ | |

$k_2 = 4{\cdot}92_8 \pm 0{\cdot}011 \times 10^{-4}$ l. mole$^{-1}$ sec.$^{-1}$

TABLE 4.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Temperature ..................... | 35·4° | | 40·0$_5$° | 45·6° | | 60·2° | |
| Rate constants ($10^5k_2$) ......... | 49·3 | 49·9 | 79·9 | 133 | 135 | 538 | 544 |

$E = 196_{70} \pm 130$ cal.

The authors thank Mr. D. T. Downing for the preparation of 4-chloro-3-nitrotoluene.

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[*Received, February 24th,* 1955.]