716. *Substituent Effects in Fluorene Derivatives. Part I. The Reaction of Substituted 9-Bromofluorenes with Potassium Iodide in Acetone.*

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The rates of reaction of some substituted 9-bromofluorenes with potassium iodide in acetone have been measured. Except possibly for the methoxy-group, 2-substituents exert influences consistent with their being regarded as analogous to *meta*-substituents in reactions of benzyl halides.

EFFECTS of nuclear substituents on reactions at the 9-position of fluorene are of special interest because polar influences may be transmitted to this position both directly through the substituted ring and indirectly through the other ring. For example, a group in the 2-position can most simply be regarded as equivalent to a *meta*-substituent in benzyl compounds, but transmission of tautomeric effects through the second ring, as in (I), could give the group some of the characteristics of a *para*-substituent also. (The coplanarity of the nuclei[1] favours conjugation between the rings.) Such conjugation, involving the $+T$ effect of the 2-methoxy-group, appears to operate in the rearrangement of 9-fluorenyl azides to give phenanthridines[2] (an electrophilic reaction in which the high electron demand will call forth the $+E$ effect very strongly, as in acid-catalysed decomposition of 1,1-diphenylethyl azides[3,4]), and it is likely that transmission of a $-T$ effect of the 2-nitro-group to the 7-position is responsible for the formation of 2,5-dinitrofluorene along with the 2,7-compound in nitration of 2-nitrofluorene.[5] As a first step in a progressive study of substituent effects in the fluorene system we have measured the rates of reaction of some substituted 9-bromofluorenes with potassium iodide in acetone, a reaction of the S_N2 type.

Sampey and King[6] examined the reaction of 9-bromofluorene with potassium iodide in acetone and found that formation of iodine prevented use of the usual " iodine cyanide " method for determination of iodide ion in presence of bromide ion. They attributed the iodine formation to reaction (1) (R = 9-fluorenyl).

$$2RI \longrightarrow 2RR + I_2 \qquad (1)$$

We have found that iodine is not formed in a solution of 9-iodofluorene in acetone in the dark unless iodide ion is present. The iodine formation presumably involves abstraction of positive iodine from the 9-iodofluorene, as in reaction (2). [An analogous reaction occurs between tri-(*p*-nitrophenyl)methyl bromide and iodide ion [7].]

$$RI + I^- \longrightarrow R^- + I_2 \qquad (2)$$

The fluorenyl anion, which may never be completely free, could disappear by several reactions, one of which might be that shown in reaction (3).

$$R^- + RI \longrightarrow RR + I^- \qquad (3)$$

A reaction of type (2) would not be expected to occur readily with 9-bromofluorene, and this halide with iodide ion does not give iodine except after such a time that significant amounts of iodofluorene must be present. It seems safe to assume that the reactions

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[1] Brown and Bortner, *Acta Cryst.*, 1954, **7**, 139.
[2] Arcus and Coombs, *J.*, 1954, 4139.
[3] Ege and Sherk, *J. Amer. Chem. Soc.*, 1953, **75**, 354.
[4] Okamoto and Brown, *J. Org. Chem.*, 1957, **22**, 485; Brown and Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.
[5] Anantakrishnan and Hughes, *J.*, 1935, 1607.
[6] Sampey and King, *Bull. Furman Univ., Furman Studies*, 1949, **31**, No. 5, p. 22.
[7] Hawthorne, *J. Amer. Chem. Soc.*, 1955, **77**, 5739; Kosower, *ibid.*, 1958, **80**, 3267.

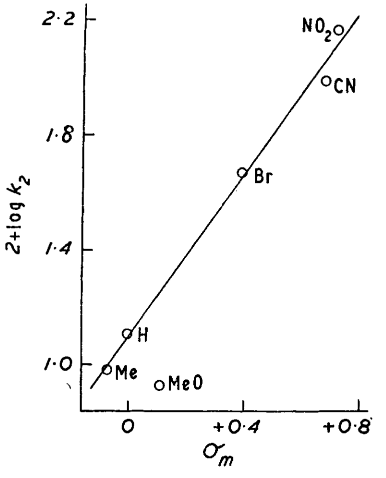
giving rise to iodine do not interfere directly with the interaction of 9-bromofluorene and iodide ion.

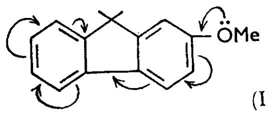
Iodine formation does not interfere with the analysis provided a low concentration of 9-bromofluorene is taken, for at low concentrations iodine is taken up by acetone,[8] and the

$$RI + I^- + COMe_2 \longrightarrow I{\cdot}CH_2{\cdot}COMe + R^- + H^+ + I^- \quad . \; . \; . \; . \; . \quad (4)$$

overall result is as in reaction (4), the iodide-ion concentration being unchanged by the sequence of reactions. The possibility of disturbance of the kinetics by interactions of the fluorenyl anion or other intermediates with the 9-bromofluorene is ruled out by the fact that good second-rate constants are obtained during the first 60% of reaction provided excess of 9-bromofluorene is taken to force the exchange towards completion.

Plot of log k_2 *for 2-substituted 9-bromofluorenes against* σ_m.





(I)

The observed rate constants, k_2, are shown in the Table along with the apparent activation energies, E. Since only two temperatures, 10° apart, were used, values of E are subject to a large error, and we cannot even be certain that the opposition of the trends in rates and activation energies is real.

Reaction of 9-*bromofluorenes*, $X{\cdot}C_9H_8Br$, *with potassium iodide in acetone.*

X	2-NO_2	2-CN	2-Br	3-Me	2-H	2-Me	2-MeO
$10k_2$ (at −0·04°) [a]	14·9	9·8	4·56	1·20	1·27	0·98	0·85
$10k_2$ (at −10·25°) [a]	3·68	2·18	1·17	0·332	0·320	0·311	0·271
E (kcal./mole)	19·6	21·1	19·0	18·0	19·3	16·1	16·0

[a] Min.$^{-1}$ mole^{-1} l.

The reaction is facilitated by strongly electron-withdrawing substituents. When log k_2 (at —0·04°) for the 2-substituted compounds is plotted against the substituent constants, σ_m,[9] applicable to the corresponding *meta*-substituents in benzene derivatives (see Figure), the points fall satisfactorily on a straight line except that for the 2-methoxy-group, which lies off the line in the direction expected if it supplied electrons by the mechanism shown in (I).* Unfortunately, in the absence of experimental evidence we cannot be

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[8] Dawson and Leslie, *J.*, 1909, **95**, 1860.

[9] Jaffé, *Chem. Rev.*, 1953, **53**, 191.

* It would not be surprising to find only the 2-methoxy-group showing such effects. If a 2-substituent is regarded as partly *para* in character, this will make little difference, with, for example, the nitro-group, which in spite of its strong $-T$ effect has similar values of σ_m and σ_p (0·710 and 0·778, respectively).[9] For the methoxy-group, $\sigma_m = +0{\cdot}115$, and $\sigma_p = -0{\cdot}268$.

sure that the *m*-methoxy-group has a " normal " effect in the corresponding reactions of benzyl halides. For the reaction between benzyl chlorides and iodide ion in acetone at 0·1,[10] we find that the log k_2-σ plot approximates to a straight line for the *m*-Cl, *m*-Br, *m*-I, and *m*-NO_2 substituents but the point for the *m*-F and all the points for *para*-groups are well away from the line. Further, the effects of substituents in the benzyl chloride reaction are complex, because, while the electron-withdrawing halogen and nitro-groups facilitate reaction,[10] so also does the *p*-Me group,[11] and this an example of the type of reaction previously discussed,[12] in which use of simple σ-constants is unsatisfactory. It is interesting that a 3-Me substituent in the fluorene series appears to activate at −10·25° (at −0·04° the rate is not significantly different from that of the unsubstituted compound), which is consistent with regarding it as analogous to a *para*-substituent in benzyl halides.

We must conclude that the data in the Table do not conflict with the simplest assumption that in this reaction 2-substituents are analogous to *meta*-substituents in benzyl compounds.

EXPERIMENTAL

The preparation and properties of the 9-bromofluorenes have been described.[13]

Potassium iodide was dried at 100° for 2 hr. Acetone was boiled with potassium permanganate, fractionated, dried under reflux with anhydrous calcium sulphate, and fractionated from fresh calcium sulphate. One stock, protected from atmospheric moisture, was used throughout.

Equal volumes of acetone solutions of potassium iodide (0·01M) and bromofluorene (0·04M) were mixed at the thermostat temperature (−0·04° or −10·25°, both ±0·05°). Aliquot parts (10 ml.) were withdrawn at suitable times, and added to ice-water. The iodide-ion concentration was determined by Dostrovsky and Hughes's modification of the Lang cyanide method,[14] titrations being carried out under standard illumination from a 100 w daylight lamp. With 8—10 samples withdrawn during the first 60% of reaction, the mean deviation of the individual rate constants from their average was <5% (usually <3%). Average rate constants could be duplicated to within 3%.

The following typical run refers to 9-bromo-3-methylfluorene (initially 0·0178M), with potassium iodide (initially 0·00504M) at −0·04°.

Time (min.)	0	87·3	140·5	203·6	260·3	292·3	332·5	361·6	411·3	492·3
Titre (ml.)	25·2	21·2	18·8	17·2	15·2	13·9	12·5	12·4	11·5	9·3
10^3k_2	—	114	122	111	117	123	129	120	118	128

No iodine was formed in a solution of 9-iodofluorene (1 g.) in acetone (100 ml.) during 3 days at room temperature (protected from light and air) or during 50 hours' refluxing (protected from light). With exposure to sunlight, 9% of possible iodine was liberated in 10 hours' refluxing. In the dark, similar solutions containing also 1 g. of sodium iodide gave 65% of possible iodine in 30 hr. at room temperature and 84% in 4 hours' refluxing.

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[10] Bennett and Jones, *J.*, 1935, 1815.

[11] Charlton and Hughes, *J.*, 1956, 855.

[12] Swain and Langsdorff, *J. Amer. Chem. Soc.*, 1951, **72**, 2813; Bartlett in Gilman's " Organic Chemistry," Wiley and Sons, New York, Vol. III, 1953, pp. 33—35; Dickinson and Eaborn, *J.*, 1959, 3036.

[13] Dickinson and Eaborn, *J.*, 1959, 2337.

[14] Dostrovsky and Hughes, *J.*, 1946, 161.