277. *The Influence of Substituents on the Coupling of Phenols with Diazonium Salts.*

By Donald H. Richardson.

A convenient method of measuring the relative polar effects of the halogens in the benzene ring is afforded by coupling *p*-nitrobenzenediazonium sulphate with the equivalent quantity of phenol in competition with the equivalent quantity of halogenophenol. Coupling velocity ratios relative to phenol may be calculated from the composition of the mixed dyes determined by estimation of halogen. By coupling competitions between other substituted phenols and *o*-bromophenol the polar effects of other groups meta or ortho to the coupling position may be compared with those of bromine, and hence with hydrogen in unsubstituted phenol. The results obtained confirm the current view that chlorine in aromatic combination exerts a more powerful deactivating (inductive) effect than bromine, and further show that the ratio of the effects of the two halogens is very nearly the same whether they are meta or ortho to the coupling position. Iodine activates the coupling position, but not very much more when ortho than when meta to it, and this result suggests that activating effects, presumably mesomeric or electromeric, may be transmitted to a meta position more powerfully than has been suggested. Competitive coupling between guaiacol and *o*-bromophenol shows that the methoxyl group exerts a very powerful activating effect upon the coupling position meta to it, and this is compared with the much weaker activating inductive effect due to methyl by competition between *o*-cresol and *o*-bromophenol.

Preliminary experiments showed that the halogenophenols (with the exception of *p*-bromo- and -iodo-phenols), when coupled with the equivalent quantity of *p*-nitrobenzenediazonium sulphate in dilute solution, give good yields of azo-compounds which, without any purification, contain not less than 96% of the theoretical amount of halogen for the pure dye. Thus the composition of mixed dyes obtained by coupling the diazonium salt with the equivalent quantity each of phenol and a halogeno-phenol could be determined with fair accuracy by estimation of halogen. Analyses were made of mixed dyes prepared from phenol and *o*- and *m*-chloro-, -bromo-, and -iodo-phenols, and the results were checked by competition couplings between *o*-chloro- and -bromo-phenols, and *o*-bromo- and -iodo-phenols. Mixed halogen analyses of the products gave coupling ratios closely agreeing with those calculated from the competitions with phenol. The effect of two halogen atoms on the coupling reaction was investigated by competition between 2 : 6-dichloro- and 2 : 6-dibromo-phenol, and the coupling ratios were unchanged when benzenediazonium sulphate was substituted for *p*-nitrobenzenediazonium sulphate.

The coupling reaction having been proved to be bimolecular (Conant and Peterson, *J. Amer. Chem. Soc.*, 1930, **52**, 1220), the coupling velocity of each halogenophenol relative to that of phenol can be calculated from the molecular composition of the mixed dye by means of the equation developed by Ingold and Shaw (J., 1927, 2922), *viz.*,

$$\frac{k_y}{k_x} = \log\left\{1 - \frac{z_0}{y_0}\left(\frac{R}{1+R}\right)\right\} \Big/ \log\left\{1 - \frac{z_0}{x_0}\left(\frac{1}{1+R}\right)\right\}$$

where R is the molar ratio in which phenol and halogenophenol couple, and x_0, y_0, and z_0 are the initial concentrations of phenol, halogenophenol, and diazonium salt respectively. *o*-Chloro- (0·51), *m*-chloro- (0·36), *o*-bromo- (0·84), and *m*-bromo- (0·63) phenols couple more slowly, and *o*-iodo- (1·13) and *m*-iodo- (1·24) phenols more rapidly than phenol to the extent indicated in parentheses. These results confirm the current view that the halogens exert a deactivating inductive effect decreasing from chlorine to bromine, and afford clear evidence of an activating effect in the case of iodine. If this effect is mesomeric or electromeric in nature, its transmission by iodine meta, as well as ortho, to the coupling position would indicate that these effects reach the *m*-position with greater force than has been suggested (*e.g.*, Jones, J., 1935, 1838).

To test this point, competitive couplings were made between *o*-bromophenol and guaiacol, and *o*-bromophenol and *o*-cresol. Determination of bromine in the mixed dyes obtained gave coupling ratios relative to *o*-bromophenol, and from the coupling velocity of the latter relative to phenol it is calculated that guaiacol couples 28·4 and *o*-cresol 6·6 times as fast as phenol. The meta (coupling) position is thus much more powerfully activated by the mesomeric and electromeric effects of the methoxyl group than by the inductive effect of the methyl group. It may be noted that the deactivating effect of chlorine is greater than that of bromine in very nearly the same ratio (1·7 : 1) whether the halogen is meta or ortho to the coupling position, and that the deactivating effect of two *m*-chlorine atoms does not exceed that of two *m*-bromine atoms by much more than this amount. The latter result suggests that the process by which the deactivating effect reaches the coupling position cannot operate on both sides of the benzene ring simultaneously.

EXPERIMENTAL.

o-Chloro and *o*-bromo-phenols (purchased as pure) were redistilled, and *o*-iodophenol was prepared from *o*-chloromercuriphenol (" Organic Syntheses," Vol. IV, 13). 2 : 6-Dichloro- and -dibromo-phenols were prepared by chlorinating or brominating *p*-hydroxybenzoic acid in cold glacial acetic acid (Zincke and Walbaum, *Annalen*, 1891, **261**, 208) and heating the product with quinoline as described by Blicke, Smith, and Powers (*J. Amer. Chem. Soc.*, 1932, **54**, 1468), except that a lower temperature (160°) was found advantageous. The author is indebted to Mr. C. Hinkley for the first two preparations, Mr. B. A. Bleiweis for the third, and Messrs. J. C. Morpeth and W. Reis for the preparation of the *m*-halogenophenols from *m*-nitroaniline.

To prepare the azo-dyes, 6·9 g. of *p*-nitroaniline (0·05 mol.) in 82·5 c.c. of glacial acetic acid were diazotised with 3·8 g. of sodium nitrite in 26·5 c.c. of concentrated sulphuric acid (Hodgson, J., 1933, 1620), and one half of the solution poured into an *N*/100-solution of the halogenophenol (0·025 mol.) and phenol (0·025 mol.) in 2500 c.c. of ice-cold *N*/2-sodium hydroxide, the other half being coupled with the halogenophenol alone under similar conditions. After standing for several hours, the clear solutions were acidified, and the precipitated dyes collected, washed, and dried. With one exception the yields of azo-dye were not less than 80% of the theoretical calculated on the assumption that the *p*-nitroaniline was quantitatively diazotised.

$NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}SO_4H$ coupled with	Yield, %.	Purity of azo-dye, %.	Mol. coupling ratio. Phenol = 1.	Coupling velocity ratio. Phenol = 1.
o-Chlorophenol	81	96·0	—	—
,, + PhOH	81	—	0·63	0·51
o-Bromophenol	88	98·1	—	—
,, + PhOH	—	—	0·89	0·84
o-Iodophenol	97	96·8	—	—
,, + PhOH	88	—	1·09	1·13
m-Chlorophenol	92	97·4	—	—
,, + PhOH	88	—	0·50	0·36
m-Bromophenol	74	100	—	—
,, + PhOH	82	—	0·73	0·63
m-Iodophenol	80	97·8	—	—
,, + PhOH	—	—	1·16	1·24
			o-Bromophenol = 1.	*o*-Bromophenol = 0·84.
o-Chloro- + *o*-bromo-phenol	86	—	0·70	0·50
o-Iodo- + *o*-bromo-phenol	93	—	1·19	1·09
2 : 6-Dichlorophenol	97	98·1	—	—
2 : 6-Dibromophenol	93	98·4	—	—
			2 : 6-Dibromo-phenol = 1.	2 : 6-Dibromo-phenol = 1.
2 : 6-Dichlorophenol + 2 : 6-dibromophenol	85	—	0·65	0·54
Do. coupled with $C_6H_5{\cdot}N_2{\cdot}SO_4H$ ...	—	—	0·65	0·54
			o-Bromophenol = 1.	*o*-Bromophenol = 0·84.
o-Cresol	84	—	—	—
,, + *o*-bromophenol	88	—	4·23	6·6
Guaiacol	84	—	—	—
,, + *o*-bromophenol	91	—	12·45	28·4

The halogen in both pure and mixed dyes was determined by heating 0·5 g. dissolved in 100 c.c. of *N*/10-potassium hydroxide with 10 g. of potassium permanganate on the steam-bath for 5 hours, the halogen being eliminated from the phenolic ring on account of the complete oxidation of the latter. Addition of excess sulphurous acid gave a perfectly clear solution in which the halogen was estimated gravimetrically. Mixed halogens were determined from the weight of mixed silver halide precipitated by a weighed amount of silver nitrate, the excess of which was estimated as silver bromide.

The results are tabulated on page 1364.

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