CCCXLVII.—*Studies in the Reactivity of Aromatic Hydroxyl Groups. Part II.*

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In continuation of the work previously reported (J., 1930, 1313), the rates of reaction of certain halogenated phenols with acetyl bromide have now been determined, and as the experiments were carried out under exactly the same conditions as before, the figures obtained in the two series are strictly comparable.

The compounds dealt with in the present paper are the monohalogenated phenols, *s*-trichlorophenol, and *o*-bromo-*p*-cresol. All these reacted normally with the exception of the *o*- and *p*-iodophenols. The half-periods of the reactions, in minutes, were as follows. The reciprocals of these values, against phenol as unity, are given in parentheses, and to facilitate discussion the results already recorded for phenol and the cresols are included.

p-Cresol	6·17 (2·35)	*m*-Iodophenol	87 (0·167)
m-Cresol	8·5 (1·71)	*m*-Bromophenol	95 (0·153)
Phenol	14·5 (1·0)	*o*-Bromo-*p*-cresol	136 (0·107)
o-Cresol	25·25 (0·574)	*o*-Chlorophenol	142 (0·102)
p-Chlorophenol	41 (0·354)	*o*-Bromophenol	210 (0·069)
p-Bromophenol	43 (0·337)	*s*-Trichlorophenol	very slow
m-Chlorophenol	57 (0·254)		

In general this series indicates that (so far as may be judged from the ionisation constants recorded for phenols) the rate of reaction of acetyl bromide with a phenol in a non-ionising solvent increases with the acidity of the phenol. The notable exception is that the *o*-substituted phenols are abnormally slow in reaction, and this may be ascribed to steric hindrance. With *s*-trichlorophenol there was very little reaction even after several days at room temperature. It is of particular interest that a *p*-methyl group activates *o*-bromophenol to nearly the same extent as it activates phenol. Steric hindrance effects are undoubtedly due to a combination of spatial and chemical factors and it can scarcely be supposed that the spatial factor can be affected by the presence of a *p*-methyl group, so this result opens up the possibility of separating the effects of these two factors: experiments are in progress on these lines. Since it has been suggested by various workers (compare Olivier, *Rec. trav. chim.*, 1929, **48**, 227) that the first stage in the reaction of an acid halide with a hydroxy-compound is addition, it is a reaction in which the spatial factor might be expected to have a substantial effect.

In each case the *p*-substituted phenol reacts more rapidly than its *m*-isomeride. The groups concerned are *op*-directing and work at present in progress indicates that in monosubstituted phenols in which the substituent is *m*-directing the *m*-compound reacts more rapidly than the *p*-isomeride.

Finally, it may be of significance that, if the substituting groups are arranged in order of diminishing *op*-directing influence ($Br > I > Cl > CH_3$), the ratio para-rate/meta-rate also diminishes in the same order. It is true that owing to the abnormal reaction of *p*-iodophenol the ratio for the iodophenols cannot be obtained directly, but it is indicated by the fact that *m*-iodophenol reacts more rapidly than *m*-bromophenol, and this accords with the anomalous position of iodine in the series.

EXPERIMENTAL.

As in the previous examples (*loc. cit.*), the experiments were carried out by dissolving in ethyl acetate a quantity of the phenol equivalent to 1 c.c. of acetyl bromide, and making up the solution to 8 c.c. To this 1 c.c. of acetyl bromide was added, the whole being maintained at 0°. The reaction was followed by withdrawing quantities of 1 c.c. at suitable intervals, quenching with water, and titrating with standard alkali.

Probably owing to the ready hydrolysis of the acetates, the end-points were a little difficult to obtain, especially in the slower reactions. In the case of the *o*- and *p*-iodophenols bromine slowly separated during the reaction, especially with the *o*-compound. On addition of water and starch, the yellow colour due to the bromine changed to blue after a few minutes, showing the development of free iodine.

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