LXVII.—*The Influence of Substituents on the Reimer–Tiemann Reaction.*

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IN the usual recipes for the production of hydroxybenzaldehydes from phenol, the ratio of *o*- to *p*-hydroxybenzaldehyde actually isolable is given as 4—5 : 1, but since the authors' experience with *m*-halogenophenols (J., 1927, 1740, 3041) was that this ratio was nearer unity, it appeared of interest to widen the scope of the inquiry. Accordingly, a standardised reaction has been conducted with a number of phenols, the resulting aldehydes being estimated by two methods depending upon isolation of their *p*-nitrophenylhydrazones (compare Hodgson and Beard, *J. Soc. Chem. Ind.*, 1926, **45**, 56T). The results were as follows :

Initial phenol.	Ortho/para ratio. Method (*a*).	Ortho/para ratio. Method (*b*).	Initial phenol.	Ortho/para ratio. Method (*a*).	Ortho/para ratio. Method (*b*).
Phenol	0·72	0·6	*m*-Chlorophenol	0·79	0·71
o-Cresol	0·56	0·48	*m*-Bromophenol	0·94	0·72
m-Cresol	0·52	0·46	*m*-Iodophenol ...	0·94	0·78
o-Chlorophenol	2·1	1·6			

Although these ratios can only be regarded as approximate, consideration of those given by method (*b*), which are regarded as the more accurate, leads to the following conclusions :

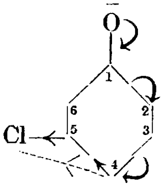
(1) Under Reimer–Tiemann conditions, the para-position in phenol itself is found to be more reactive than the ortho ($o/p = 0·6$). Since activity is due to the charged phenoxide ion, the observed result appears to be in accordance with current electronic theory, alternating (tautomeric) effects reaching the para- more easily than the ortho-positions (Ingold, *Ann. Reports*, 1926, **23**, 141).

(2) The influence of chlorine in the 5-position may be explained from two points of view : (i) If it exerted its usual $p>o$ directing effect, superposed on the $p>o$ directing effect of the phenoxide ion, the o/p ratio (0·71) would tend towards unity. (ii) If it exerted its combined general (direct) and inductive effects (see Allan, Oxford, Robinson, and Smith, J., 1926, 401 ; Baker and Ingold, J., 1927, 832 ; Cooper and Ingold, *ibid.*, p. 836) [see (I)], the 4-position would be deactivated more than the 2-position, with the resultant increase of the o/p ratio (0·6 to 0·71).

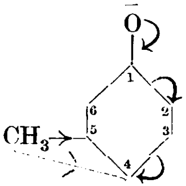
(3) That the second view is probably the more correct would appear to follow from the results with *m*-cresol (II), where the o/p ratio (0·46) has been still further diminished (from 0·6) by the direct and inductive effects (*loc. cit.*) of the methyl group.

(4) The unusual reactivity of the 2- compared with the 4-position

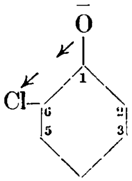
in 6-chlorophenol ($o/p = 1{\cdot}6$) appears to be best explained on the assumption that the positive field (general effect) of the chlorine



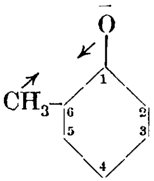
(I.)



(II.)



(III.)



(IV.)

atom attracts the negative field of the oxygen atom sufficiently to relieve the 2-position of a considerable amount of the steric hindrance due to the oxygen atom (III), whilst with *o*-cresol (IV) the exact opposite occurs, *i.e.*, the repulsion produced on the oxygen field by the negative methyl group field increases the steric hindrance effect on 2-position ($o/p = 0{\cdot}48$). This view would appear to be supported by the established abnormal behaviour of *o*-chlorophenol in other respects (compare Sidgwick and Turner, J., 1922, **121**, 2260).

(5) The results with *m*-bromo- and *m*-iodo-phenol agree, even though slightly, with the accepted deactivation order Cl>Br>I.

EXPERIMENTAL.

Method.—The particular phenol (0·05 mol.) was dissolved in a solution of sodium hydroxide (10 g.) in water (40 c.c.) and treated with chloroform (20 g.) at one addition, the mixture being gently refluxed for 2 hours. The reaction product was worked up in two ways :

(*a*) After addition of hydrochloric acid until just acid, the unchanged phenol, chloroform, and *o*-hydroxy-aldehyde were removed by steam distillation, 600—900 c.c. of distillate being necessary according to the phenol used. The oil was separated, dissolved in glacial acetic acid, and treated at 70° with an excess of *p*-nitrophenylhydrazine hydrochloride in the same solvent, this mixture being subsequently added to the aqueous portion of the distillate. The resulting *p*-nitrophenylhydrazone was dried at 80—90° and weighed. After removal of excess of *p*-nitrophenylhydrazine by means of acetone, the unused phenol was estimated by precipitation as bromo-compound. The liquor containing the non-volatile *p*-hydroxy-aldehyde was filtered, the tar extracted six times with boiling water (50 c.c.), and the combined liquor treated with excess of an aqueous solution of *p*-nitrophenylhydrazine hydrochloride, the hydrazine being estimated as above.

(*b*) The entire reaction mixture was dissolved in glacial acetic acid, a little water being added subsequently to keep sodium acetate in solution. The filtered solution was then divided into two equal portions, one of which was steam distilled and estimated as under (*a*), the other having its total aldehyde content determined as a mixture of *p*-nitrophenylhydrazones. The data given above represent the mean values of six determinations for each phenol. In all cases examined, the unchanged phenol was approximately half the amount initially taken, only small quantities of resinous matter and condensation products being formed, which do not appreciably affect the *o*/*p* ratio. Variations up to 5 hours in the time of conducting the Reimer–Tiemann reaction had a negligible effect on the yields of substituted aldehydes and on their ratio, but acidification of the alkaline reaction product by mineral acid appeared to reduce the measurable yield of *p*-hydroxyaldehyde in all cases investigated. The actual loss of *p*-hydroxybenzaldehyde in practice would appear to be consequent on the method of isolation adopted.

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