NOTES.

Activating Influence of para-*Groups on the Lability of Chlorine in Chlorobenzenes.*

By G. M. BADGER, J. W. COOK, and (MISS) WENDY P. VIDAL.

IN another investigation, the activating influence of the azo-group on a *p*-chloro-substituent towards reaction with an anionoid reagent (compare Borsche and Exss, *Ber.*, 1923, **56**, 2353) appeared to be somewhat greater than expected, and the present work was undertaken to obtain a quantitative measure of this effect. For this purpose, the percentage reaction with piperidine of various *p*-substituted chlorobenzenes has been determined, under standard conditions, by the gravimetric estimation of the halide ion in the reaction mixture, a method essentially the same as that used by Sandin and Liskear (*J. Amer. Chem. Soc.*, 1935, **57**, 1304). A preliminary trial of the method of Brewin and Turner (*J.*, 1928, 332), which involves weighing the piperidine salt which separates out on cooling the reaction mixture, gave much lower results than were obtained by the method of Sandin and Liskear. This was, no doubt, due to the uncertainty as to the composition of the precipitated salt (Powell and Dehn, *J. Amer. Chem. Soc.*, 1917, **39**, 1717), and also to the fact that piperidine hydrochloride is not completely insoluble in benzene.

Materials.—As solvent, sodium-dried, thiophen-free benzene, was used. Piperidine was dried over potassium hydroxide and kept over this reagent after being distilled. The *p*-chloronitrobenzene was a commercial sample, recrystallised from alcohol, m. p. 83°. *p*-Chloroaniline was also a commercial sample, recrystallised from benzene, m. p. 70°. *p*-Chloroazobenzene, prepared by the method of Jacobson and Loeb (*Ber.*, 1903, **36**, 4090) and recrystallised from alcohol, had m. p. 89°. *p*-Chlorobenzonitrile was prepared from *p*-chlorobenzamide by dehydration with phosphoric oxide; recrystallised from aqueous alcohol, it had m. p. 91°. Chlorobenzene was redistilled, b. p. 130°.

Method.—The *p*-substituted chlorobenzene (0·024 mol.) was heated under reflux in an all-glass apparatus, with piperidine (0·1 mol.) in anhydrous benzene (50 c.c.) for 8 hours. The aqueous extract, after being washed with a little benzene, was acidified with dilute nitric acid (5 c.c.) and the halide precipitated as silver chloride with 0·1N-silver nitrate. The precipitate was collected in a Gooch crucible and dried at 100°.

Results.—The following percentage reactions were obtained: *p*-chloronitrobenzene, 12·9, 12·9%; *p*-chlorobenzonitrile, 5·0%; *p*-chloroazobenzene, 1·97, 1·96%; chlorobenzene, 1·29, 1·31%; *p*-chloroaniline, 1·23, 1·24%.

The activating influence of the azo-group is, under these conditions, less than that of the cyano-group, and considerably less than that of the nitro-group. The amino-group exerts little effect.

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An Improved Preparation of 1 : 8-*Dinitronaphthalene.*

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WHEREAS 1 : 8-dinitronaphthalene is scarcely attacked by aqueous sulphide even at 90° (Hodgson and Walker *J.*, 1933, 1346; E.P. 392,914), it is rapidly converted in methanol suspension by a mixture of sodium sulphide and sodium hydrogen carbonate into sulphide dyes (Hodgson and Ward, *J.*, 1945, 794). When, however, the mixture of 1 : 5- and 1 : 8-dinitronaphthalene obtained by nitration of α-nitronaphthalene (Hodgson and Walker, *J.*, 1933, 721) is treated by the above sodium sulphide–sodium hydrogen carbonate mixture in methanol, in amount just sufficient to reduce the whole of the 1 : 5-dinitronaphthalene (about one-third, as determined by the complete removal of the 1 : 8-isomeride with sodium sulphite), the 1 : 8-dinitronaphthalene is entirely unattacked and remains behind after extraction with hydrochloric acid of the 5-nitro-1-naphthylamine mixed with it. Only one crystallisation of the residue from toluene is necessary for obtaining practically pure 1 : 8-dinitronaphthalene in almost quantitative amount.

The finely divided mixture (10 g.) of 1 : 5- and 1 : 8-dinitronaphthalene was suspended in boiling methanol (150 c.c.) and treated with the reducing agent (14 c.c.) [prepared by dissolution of crystalline sodium sulphide (24 g.) and sodium hydrogen carbonate (8 g.) in water (40 c.c.)] added in one batch, and the boiling was continued for 5 minutes; ice chips were then added quickly to the reddish-brown mixture before pouring it into water (total volume *ca.* 1 l.). No sulphide was present at the end of the reaction. The solid was filtered off, washed with water, and then extracted 4 times with boiling 8% hydrochloric acid (400 c.c. per time); the yield of extracted 5-nitro-1-naphthylamine was 8% of the original mixture and *ca.* 24% of the 1 : 5-dinitronaphthalene originally present. The acid-extracted residue, after being washed with water, was dried, and extracted twice with boiling toluene (200 c.c.); on concentration, the filtered toluene extract afforded 1 : 8-dinitronaphthalene (6·3 g., *i.e.*, 63% of the original mixture and *ca.* 95—96% of the amount of 1 : 8-dinitronaphthalene present; cf. the crude yield of *ca.* 40% obtained by Hodgson and Walker, *loc. cit.*), m. p. 169—171·5°. Increasing the amount of reducing agent beyond that used above lowered the yield of 1 : 8-dinitronaphthalene and also the purity of the 5-nitro-1-naphthylamine.

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