CLXVII.—*The Nature of the Alternating Effect in Carbon Chains. Part XXVI. The Nitration of ω-Chloro- and ω-Bromo-*p*-xylene.*

By Christopher Kelk Ingold and Eugene Rothstein.

According to Holleman (*Rec. trav. chim.*, 1914, **33**, 1) toluene and its ω-chloro-derivatives yield the following proportions of *m*-derivative on nitration under corresponding conditions: $Ph{\cdot}CH_3$, 4·4%; $Ph{\cdot}CH_2Cl$, 4·2%; $Ph{\cdot}CHCl_2$, 33·8%; $Ph{\cdot}CCl_3$, 64·5%; and from these results it has been inferred that the successive replacement of the ω-hydrogen atoms in toluene by chlorine increases the electron-affinity and *m*-orienting tendency of the side chain. Nevertheless, the figure for benzyl chloride is anomalous from this point of view, and a reinvestigation of the nitration of this substance is being undertaken in these laboratories.* In the meantime, the development (Burton and Ingold, this vol., p. 904) of a hypothesis of orientation for conjugative additions required, for its application to the addition of halogens to hydrocarbons, a qualitative comparison of the orienting effects of $^-CH_3$ on the one hand and $^-CH_2Cl$ and $^-CH_2Br$ on the other; for, in the absence of the necessary *direct* knowledge relating to anionotropy, the hypothesis may be applied by making use of the analogy (*loc. cit.*) between the *op*-orienting power of groups in aromatic substitution, and their action in facilitating anionotropic change. For this reason we have examined the nitration of ω-chloro- and ω-bromo-*p*-xylene, and are able to show that predominating substitution occurs in the position ortho to the methyl group. These experiments complete the evidence on the basis of which Burton and Ingold explained the course pursued by the action of bromine on butadiene and isoprene,

---

* This has since been completed by Miss F. R. Shaw, who finds that 16% of *m*-isomeride is produced.

and predicted the results which should accrue from a re-examination of earlier work on the addition of bromine to βγ-dimethylbutadiene.

EXPERIMENTAL.

ω-Bromo-*p*-xylene (60 g.) was converted into *p*-tolylcarbinyl acetate by heating for 1·5 hours under reflux with acetic acid (20 g.) and potassium acetate (30 g.), and the acetate (46 g.) hydrolysed with boiling 10% alcoholic sodium hydroxide (150 c.c.). The carbinol, after crystallisation from ligroin, was treated with a 20% excess of phosphorus trichloride, and the resulting ω-chloro-*p*-xylene (yield, 87%) purified by careful fractionation.

A solution of ω-chloro-*p*-xylene (16·1 g.) in acetic anhydride (30 c.c.) was added very gradually to a solution of fuming nitric acid (9 g.) in acetic anhydride (20 c.c.) at 10—12°. After 6 hours, ice was added, and, after the decomposition of the excess of acetic anhydride, the product was neutralised with sodium carbonate and extracted with ether. It contained a considerable quantity of un-nitrated ω-chloro-*p*-xylene (which in itself guarantees the absence of dinitro-derivatives), but before this was removed by distillation, 6·3 g. of practically pure ω(1)-chloro-3-nitro-*p*-xylene separated and was collected. The mononitration product had b. p. about 140°/4 mm., and the distillate (8·6 g.) yielded a further 4·6 g. of the same chloronitro-compound. The liquid portion, on treatment with ethyl-alcoholic trimethylamine, precipitation of the quaternary ammonium chlorides with ether, and conversion of these into the picrates (3·0 g.), gave 3-nitro-4-methylbenzyltrimethylammonium picrate (this vol., p. 1217), together with an isomeride which could not be separated (Found, for a mixture having m. p. 125—128° : C, 46·6; H, 4·6. Calc.: C, 46·7; H, 4·3%). The ethereal alcoholic filtrate from the quaternary chlorides on evaporation yielded a halogen-free liquid, b. p. 115—120°/3 mm. (1·7 g.), consisting essentially of 2- and 3-*nitro*-4-*methylbenzyl ethyl ethers* (Found: C, 62·1; H, 7·1. $C_{10}H_{13}O_3N$ requires C, 61·5; H, 6·7%), and containing a considerable proportion of the 3-nitro-ether, as was proved by treatment with hydrogen bromide in acetic acid, ω(1)-bromo-3-nitro-*p*-xylene then being obtained. The proportion of nitration in position 3 is therefore more than 73%. The ω(1)-chloro-3-nitro-*p*-xylene was identified by direct comparison with the product described by Steven, Short, and Gladding (J., 1920, **117**, 525).

The nitration of ω-bromo-*p*-xylene and the separation of ω(1)-bromo-3-nitro-*p*-xylene (this vol., p. 1217) was carried out in a similar way, excepting that, owing to the tendency of the bromonitro-compound to decompose on distillation, the unchanged ω-bromo-*p*-xylene was distilled from a water-bath at 3 mm. after each separation of the crystalline bromonitro-compound. The yield of the latter was 66% of the nitration product, and the remainder contained a further quantity, as was shown by conversion into a mixture of nitro-4-methylbenzyltrimethylammonium picrates, from which the 3-nitro-salt was separated. The small ultimate residues obtained after separation of the quaternary salt consisted as before of nitro-4-methylbenzyl ethyl ethers.

We wish to thank the Chemical Society for a grant in aid of this work.

THE UNIVERSITY, LEEDS. [*Received, April 2nd,* 1928.]