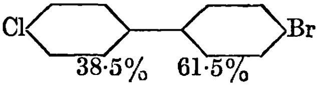
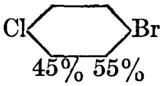
256. *The Quantitative Nitration of* p-*Chloro- and* p-*Bromo-toluene.*

By FLORENCE RUTH SHAW and EUSTACE EBENEZER TURNER.

THE mononitration of 4-chloro-4′-bromodiphenyl proceeds as shown in (I) (Shaw and Turner, this vol., p. 285), and that of *p*-chlorobromobenzene as in (II) (Holleman, *Rec. trav. chim.*, 1915, **34**, 216),



(I.)



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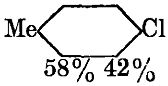


(III.)

and it was concluded (Shaw and Turner, *loc. cit.*) that the figures for the diphenyl compound afford a more satisfactory comparison of the relative directive effects of chlorine and bromine than those for the benzene derivative, since the mutual interference of the two halogen atoms should be less marked in the former instance. The mononitration of 4-chloro(or bromo)-4′-methyldiphenyl should therefore provide valuable information with regard to the relative effects of the methyl group and the halogen atoms. Such information has hitherto been obtainable only from the results of nitrating *p*-chloro- and *p*-bromo-toluene.

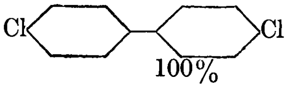
Holleman and van den Arend (*Rec. trav. chim.*, 1909, **28**, 418; compare Holleman, *Proc. K. Akad. Wetensch. Amsterdam*, 1908, **11**, 257) nitrated *p*-chlorotoluene at 0° and obtained the results shown in (III). Their nitration product was, however, distilled in a vacuum, which entailed a loss of about 12% of material. The analytical methods used were based on freezing-point and density determinations. Fry (*J. Amer. Chem. Soc.*, 1916, **38**, 1327), who used Holleman's conditions of nitrating, and of isolating the product, determined the proportion of isomerides by means of sodium methoxide, and obtained figures indicating 36·18% of 3-nitration. Gindraux (*Helv. Chim. Acta*, 1929, **12**, 921) carried out various nitrations in presence of sulphuric acid, and found that 37·5—47% of 3-nitro-compound was produced.

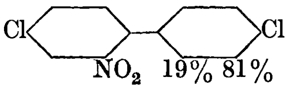
The nitration of *p*-bromotoluene was studied by Holleman (*Rec. trav. chim.*, 1915, **34**, 283), using two methods of analysis. A freezing-point method gave 43·7% of 3- and 56·3% of 2-nitro-compound, but indicated the presence of a third substance: estimation by means of sodium methoxide gave 41·3% of the 3-isomeride. Holleman showed that phenols, and also compounds containing more than one bromine atom, were produced during his nitration, but the temperature was allowed to rise from 0° to 28°, and the product was distilled in a vacuum before analysis.

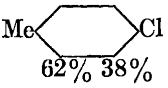
Before proceeding to a quantitative study of the nitration of 4-chloro(or bromo)-4′-methyldiphenyl, we therefore had to make an independent investigation of the nitration of *p*-chloro- and *p*-bromo-toluene. We carried out nitrations under the conditions employed by Holleman, and at −15° and 0°, using excess of nitric acid; the proportion of the 3-isomeride was determined by the piperidine method (Shaw and Turner, *loc. cit.*, Method *A*). The results are in the annexed table, and refer to the composition of actual total mononitration products: the method of analysis was checked by examination of artificial mixtures of the two pure individual components:

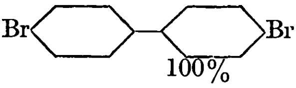
	p-Chlorotoluene. Isomerides, %.		*p*-Bromotoluene. Isomerides, %.	
Temp.	2-.	3-.	2-.	3-.
−15°	64·4 ∓ 0·2	35·6 ± 0·2	63·7 ∓ 0·7	36·3 ± 0·7
0	62·0	38·0	61·9	38·1
0—50	58·8	41·2	60·1	39·9

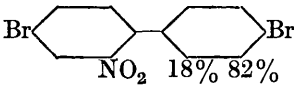
The most striking feature of these results is that, when present in the 4-position in the toluene molecule, chlorine and bromine produce almost exactly the same quantitative effect, and this becomes of greater significance in comparison with the results (Shaw and Turner, *loc. cit.*) of nitrating certain diphenyl derivatives (all nitrations at 0°):

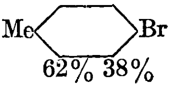








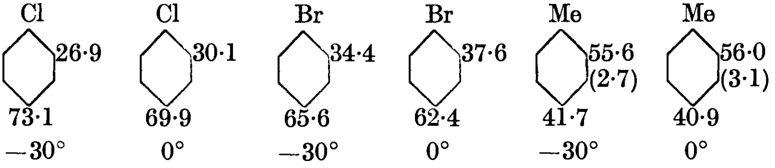




The similarity in behaviour of these three pairs of chlorine and bromine derivatives cannot be attributed to chance, and is of considerable importance in connexion with the general problems of aromatic substitution.

It seems possible that in the *p*-halogenotoluenes the halogen atoms, by their mere presence, allow most of the activation acquired by the *p*-carbon atom in toluene itself to become available at the *m*-positions (in the halogenotoluenes) so that *m*-substitution, detectable in toluene, becomes very pronounced in the halogen compounds.

Comparison of the figures now obtained for the nitration of chloro- and bromo-toluene with those (compare Bradfield and Jones, J., 1928, 1106) for the nitration of chlorobenzene, bromobenzene, and toluene at —30° and 0° brings out further interesting points in connexion with the variation of the proportion of isomerides with temperature of nitration :



From these figures may be calculated the following ortho/para ratios :

	−30°.	0°.
Chlorobenzene	0·37	0·43
Bromobenzene	0·52	0·60
Toluene	1·33	1·37

so that the ratios of ortho : para nitration at 0° to that at −30° are 1·17, 1·15, and 1·03 for chlorobenzene, bromobenzene, and toluene respectively. It would therefore appear that the ratio of 3 : 2 nitration in *p*-chlorotoluene should increase more rapidly with rise of temperature than the corresponding ratio for *p*-bromotoluene. Qualitative confirmation of this statement is afforded by the data given in the first table above.

EXPERIMENTAL.

4-*Chloro*-2-*nitrotoluene*.—This (m. p. 37—38°) was prepared from *o*-nitro-*p*-toluidine by the Gattermann process, steam-distilled from dilute alkali solution, and crystallised from light petroleum (b. p. 40—60°). After 8 hours' heating with piperidine (1 g. in 5 c.c.) in a boiling water-bath, no ionic chlorine was detectable.

4-*Chloro*-3-*nitrotoluene*.—*m*-Nitro-*p*-toluidine was prepared from aceto-*p*-toluidide (Gattermann, *Ber.*, 1885, **18**, 1483), purified by solution in and precipitation from excess of concentrated sulphuric acid and crystallisation from alcohol, and converted by the Gattermann method into 4-chloro-3-nitrotoluene. Distillation of this gave (*a*) a fraction, b. p. 133°/16—17 mm., liquid at 0°, and (*b*) a fraction, b. p. 135°/15 mm., and b. p. 144°/24 mm. or 142°/23·5 mm., m. p. 6°, after redistillation : (*a*) was found to be (*b*) contaminated with a chlorine-free substance. 0·3588 G. of (*b*) gave by the piperidine method 0·2960 AgCl, and 0·3500 g. gave 0·2900 AgCl, whence the percentage of 3-nitro-compound is 98·7 and 99·2 respectively.

4-Chloro-3-nitrotoluene (3 g.) was added to 10 c.c. of nitric acid (*d* 1·5°) at −15° and poured into water after a few minutes. An ethereal extract gave very little coloured material to sodium carbonate solution, showing that little or no phenols had been formed, and that therefore the phenols present in some nitration mixtures (Holleman, *loc. cit.*) are formed prior to mononitration, or as a result of dinitration.

Analysis of an Artificial Mixture of 4-*Chloro*-2- and 4-*Chloro*-3-*nitrotoluene.*—0·2702 G. (35·1%) of the latter, 0·5000 g. (64·9%) of the former, and 5 c.c. of piperidine were heated in a sealed tube for 8 hours at 100°. After removal of organic matter, 0·2256 g. of silver chloride was obtained, corresponding to 35·1% of 3-nitro-compound.

Nitration of p-*Chlorotoluene.*—Chlorotoluene was prepared from *p*-toluidine by the Sandmeyer method; b. p. 161·0—161·4° after two distillations.

(I) *Nitration at* —15°. (*a*) 9·5 G. were added to 30 c.c. of nitric acid (*d* 1·5) at —15° during 1½ hours. The solution was poured into ice-water. The product was at once isolated, washed (sodium carbonate; water), and dried (anhydrous sodium sulphate) in purified ether, recovered, and freed from traces of ether by aeration (yield, 11·5 g.; 89%) (Found: Cl, 20·1. Mononitro-compounds require Cl, 20·7%). Analysis by piperidine: 0·5822 gave 0·1738 AgCl; 0·6686 gave 0·1976 AgCl; whence 3-nitro-isomeride, 35·7, 35·4%.

(*b*) 10 G. of *p*-chlorotoluene similarly gave 12·5 g. (92%) of product (Found: Cl, 20·7%). Analysis by piperidine: 0·6442 gave 0·1914 AgCl, 0·6274 gave 0·1870 AgCl; whence 3-nitro-isomeride, 35·6, 35·7%.

(II) *Nitration at* 0°. 10 G. were added to 25 c.c. of nitric acid (*d* 1·5) at 0°. Yield, 12·5 g., 92% (Found: Cl, 19·9%). Analysis by piperidine: 0·7018 gave 0·2222 AgCl, 0·5614 gave 0·1784 AgCl; whence 3-nitro-isomeride, 37·9, 38·0%.

(III) *Nitration at* 0—54°. 10 G. were added in two half-portions to 20 c.c. of nitric acid (*d* 1·5). The first addition raised the temperature from 0° to 52°, the second from 0° to 54°. The mixture was again cooled to 0°, poured into water, and worked up as before (yield, 12·0 g.; 88%) (Found: Cl, 20·2%). Analysis by piperidine: 0·6888 gave 0·2370 AgCl, 0·5968 gave 0·2052 AgCl; whence 3-nitro-isomeride, 41·2, 41·2%.

4-*Bromo*-2-*nitrotoluene.*—This was prepared, purified (m. p. 46—47°), and tested (no ionic bromine) in the same way as the 4-chloro-analogue.

4-*Bromo*-3-*nitrotoluene.*—This was prepared by the Gattermann method from *m*-nitro-*p*-toluidine, steam-distilled from dilute alkali solution, extracted and dried in carbon tetrachloride, and distilled. The fraction, b. p. 158—165°/25 mm., was cooled in ice; the solid obtained, crystallised from light petroleum (b. p. 40—60°), had m. p. 31—32°; the oily portion would not crystallise, showing that, as in the case of the chloro-compound, an unexpected impurity

(? *m*-nitrotoluene) was present. Piperidine analysis: 0·3530 gave 0·3072 AgBr, corresponding to 100·1% of 3-nitro-compound.

1 G. was added to 5 c.c. of nitric acid (*d* 1·5) at −15° during 10 minutes and then poured into water. An ethereal extract gave a small amount of a phenol to sodium carbonate solution.

Artificial Mixture of 4-*Bromo*-2-*nitro- and* 4-*Bromo*-3-*nitro-toluene.*—When 0·5000 g. of the 2-nitro- and 0·2806 g. (36·0%) of the 3-nitro-compound were heated with piperidine, 0·2454 g. of silver bromide was obtained, corresponding to 36·2% of 3-nitro-compound.

Nitration of p-*Bromotoluene.*—Bromotoluene was prepared from *p*-toluidine by the Gattermann method; b. p. 184·8—185·2°, m. p. 27—28°. It was nitrated under the same conditions as those for *p*-chlorotoluene.

(I) *At* −15°. (*a*) The nitration proceeded more slowly than that of *p*-chlorotoluene and less phenol was formed. 10 G. gave 11·5 g.; 91% (Found: Br, 36·0, 36·1. Mononitro-compounds require Br, 37·0%). Piperidine analysis: 0·6350 gave 0·1984 AgBr, 0·6962 gave 0·2240 AgBr, 0·7423 gave 0·2352 AgBr; whence 3-nitro-isomeride, 35·9, 37·0, and 36·5% respectively.

(*b*) 10 G. gave 11·5 g.; 91% (Found: Br, 35·8%). Piperidine analysis: 0·6786 gave 0·2102 AgBr, 0·5320 gave 0·1664 AgBr; whence 3-nitro-isomeride, 35·6, 36·0%.

(II) *At* 0°. 10 G. gave 11·5 g.; 91% (Found: Br, 35·5%). Analysis by piperidine: 0·7390 g. gave 0·2440 AgBr, 0·6916 gave 0·2294 AgBr; whence 3-nitro-isomeride, 38·0, 38·2%.

(III) *At* 0—50°. First rise, 0° to 50°; second rise, 0° to 38°. 10 G. gave 12 g.; 95% (Found: Br, 36·5%). Piperidine analysis: 0·6254 gave 0·2182 AgBr, 0·6475 gave 0·2240 AgBr; whence 3-nitro-isomeride, 40·0, 39·8%.

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BEDFORD COLLEGE,
UNIVERSITY OF LONDON.

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