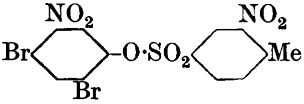
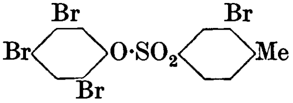
CXIV.—*The Scission of Diaryl Ethers and Related Compounds by Means of Piperidine. Part III. The Nitration of 2 : 4-Dibromo-2′ : 4′-dinitrodiphenyl Ether and of 2 : 4-Dibromophenyl* p-*Toluenesulphonate and Benzoate. The Chlorination and Bromination of* m-*Nitrophenol.*

By Rosalind Venetia Henley and Eustace Ebenezer Turner.

In continuation of previous work (Part II, J., 1929, 512), the nitration of 2 : 4-*dibromophenyl* p-*toluenesulphonate* has been investigated. The sole product of dinitration was 2 : 4-*dibromo*-

5-*nitrophenyl* o-*nitro*-p-*toluenesulphonate* (I), the constitution of which was established by its conversion successively into 2 : 4-*di-*


(I.)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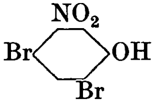

(III.)

bromo-5-*aminophenyl* o-*amino*-p-*toluenesulphonate* and 2 : 4 : 5-*tribromophenyl* o-*bromo*-p-*toluenesulphonate* (II). The latter substance was converted by piperidine at 100° into 2 : 4 : 5-tribromophenol, identical with the product obtained by the replacement of the amino-group by hydroxyl in 2 : 4 : 5-tribromoaniline.

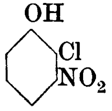
When 2 : 4-dibromo-5-nitrophenyl *o*-nitro-*p*-toluenesulphonate was heated with piperidine, there were formed 1-*o*-nitro-*p*-toluenesulphonylpiperidine and 2 : 4-*dibromo*-5-*nitrophenol* (III), the constitution of which is determined by that of the above tribromophenol. After crystallisation from light petroleum, with subsequent normal drying, the dibromonitrophenol melted at 77—78°, and an identical product was obtained by nitrating 2 : 4-dibromophenyl benzoate, followed by hydrolysis. It seemed probable that the compound obtained by Garzino (*Atti R. Accad. Sci. Torino*, 1889, **25**, 250) by nitrating 2 : 4-dibromophenyl propionate should also be 2 : 4-dibromo-5-nitrophenol, but he gave the m. p. as 90—91°. Crystallisation of our compound from dilute acetone gave a *monohydrate*, m. p. 92—94°, which is probably the product obtained by Garzino.

Another dibromonitrophenol, m. p. 91°, was described by Lindner (*Ber.*, 1885, **18**, 612) as resulting from the dibromination of *m*-nitrophenol, and in Beilstein's " Handbuch " (4th Edn., Vol. VI, 246, 248) it is suggested that this compound is possibly identical with Garzino's dibromonitrophenol. In view of the fact (Part II) that *m*-nitrophenol is dichlorinated in the 2- and 4-positions, it at first seemed unlikely that the dibromination would proceed so differently, and we have accordingly investigated the bromination of *m*-nitrophenol afresh.

Attempts to prepare the dibromo-compound according to Lindner's directions did not yield any chemically pure substance. When, however, bromine, diluted with carbon dioxide, was passed through *m*-nitrophenol at 120—140°, until the latter acquired the correct increase in weight, and the product was worked up exactly in accordance with Lindner's instructions, material was obtained which behaved as regards crystallisation as an individual, melted at 82—98°, and appeared to be a mixture of 4-bromo- and 2 : 4 : 6-tribromo-3-nitrophenol.

When an attempt was made to dibrominate *m*-nitrophenol in glacial acetic acid in presence of anhydrous sodium acetate, the tribromo-compound, m. p. 89—90°, was alone isolated. This substance, m. p. 85°, was obtained by Lindner (*loc. cit.*) by brominating *m*-nitrophenol, and by Daccomo (*Ber.*, 1885, **18**, 1167) by nitrating 2 : 4 : 6-tribromophenyl benzoate. Its constitution has now been definitely proved by converting it in stages into 2 : 3 : 4 : 6-tetrabromophenol. Monobromination of 4-bromo-3-nitrophenol also failed to give a dibromo-3-nitrophenol.

In preparing the monobromo-derivatives of *m*-nitrophenol, we again encountered conflicting results. Pfaff (*Ber.*, 1883, **17**, 612) treated *m*-nitrophenol with bromine in the cold, and described his monobromo-compound as bright yellow needles melting at 110°. Lindner (*loc. cit.*) and Schlieper (*Ber.*, 1892, **25**, 552), using similar methods, obtained what they took to be Pfaff's substance, but they gave the m. p. as 147—148°. Schlieper (*Ber.*, 1893, **26**, 2469) regarded this substance as 2-bromo-3-nitrophenol, since he had obtained the following evidence that the analogous chloro-compound was 2-chloro-3-nitrophenol (IV) : the chloro-compound was methylated, and the ether reduced and then deaminated. The product obtained was thought by Schlieper to be *o*-chloroanisole for two reasons : (1) it had the correct b. p., and (2) nitration gave a chloronitroanisole, m. p. 93—94°, which he took to be (V), because a substance having this constitution and this m. p. had been described by Fischli (*Ber.*, 1878, **11**, 1463). It seemed possible, however, that Schlieper's chloronitrophenol was the 4-compound, in which case his chloronitroanisole would be (VI), which melts at 97·5° (Reverdin, *Ber.*, 1893, **26**, 1689).



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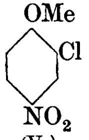

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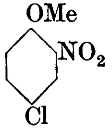

(VI.)

We have found that the monobromination of *m*-nitrophenol at 120—140° (the lowest temperature at which bromination is practicable) gives a mixture of products, at least 50% of which is 4-bromo-3-nitrophenol, m. p. 146·5—147·5°, the constitution of which has been established by its synthesis from *ON*-diacetyl-3-nitro-*p*-aminophenol. Schlieper's supposed 2-bromo-compound is therefore 4-bromo-3-nitrophenol, which substance has indeed already been prepared (Heller and Kammann, *Ber.*, 1909, **42**, 2179) from 3-nitro-*p*-aminophenol.

Monobromination of *m*-nitrophenol in glacial acetic acid in presence of sodium acetate gave indefinite results, but in absence of sodium acetate the product was a monobromo-compound, m. p. 118·5—121°. This we at first thought to be 2-bromo-3-nitrophenol, and in order to prove its constitution, we converted it into the p-*toluenesulphonyl* derivative, reduced the latter, and replaced the amino-group by bromine. During the last stage, the *p*-toluenesulphonyl group was removed by hydrolysis and a dibromophenol, m. p. 73—74°, was formed. At the same time we performed an analogous synthesis, starting from 3-bromo-2-nitrophenol. The dibromophenol obtained in the second synthesis melted at 68—69°, was different from the first, and was clearly the hitherto unknown 2 : 3-*dibromophenol*. It therefore seemed certain that the isomeric compound was 2 : 5-*dibromophenol*. Raiford and Bren (*J. Amer. Chem. Soc.*, 1929, **51**, 2539) recently attempted the preparation of this substance from 2 : 5-dibromoaniline. It has now been obtained in excellent yield by applying the method of Noelting and Kopp (*Ber.*, 1905, **38**, 3506) to this base, and was found to be identical with the product from the bromo-3-nitrophenol, which is therefore the 6-derivative (2-bromo-5-nitrophenol) already described by Heller and Kammann (*loc. cit.*), who obtained it from 5-nitro-2-aminophenol.

Although it has already been shown (Part II) that *m*-nitrophenol is readily converted into 2 : 4-dichloro-3-nitrophenol, the above results made it desirable to investigate the monochlorination. Schlieper (*Ber.*, 1893, **26**, 2466), by direct chlorination of *m*-nitrophenol, obtained a compound, m. p. 120°, which, as is shown above, may be either the 2- or the 4-chloro-compound. Meldola and Eyre (J., 1902, **81**, 996) agreed with Schlieper's conclusion that this was the 2-chloro-compound; they obtained 4-chloro-3-nitrophenol, m. p. 126—127°, by synthesis from 3-nitro-*p*-aminophenol. We find that monochlorination of *m*-nitrophenol at 120—140° gives approximately equal amounts of 4-chloro-3-nitrophenol (A), m. p. 127—128°, and 2-chloro-3-nitrophenol (B), m. p. 120°. A was identical with a specimen prepared from *ON*-diacetyl-3-nitro-*p*-aminophenol, and the constitution of B follows from two facts: (1) dichlorination of *m*-nitrophenol under similar conditions gives the 2 : 4-dichloro-compound in good yield, and (2) reduction of B, followed by replacement of the amino-group by chlorine, gives 2 : 3-dichlorophenol. Although the first of these appears to be sufficient proof, it was desired to prove beyond doubt that B was not 6-chloro-3-nitrophenol (m. p. 118—119°; prepared synthetically by Meldola, Woolcott, and Wray, J., 1896, **69**, 1322).

It is therefore possible that, in this case, Schlieper actually had a 2-chloro-compound, but it is difficult to believe this, since the

4-chloro-compound, which was presumably present, is so readily isolated.

We have not investigated the iodination of *m*-nitrophenol, as the statements in the literature seem to be accurate. Schlieper (1893, *loc. cit.*) described the monoiodo-compound as the 2-iodo-derivative, m. p. 134°, and Datta and Prosad (*J. Amer. Chem. Soc.*, 1917, **39**, 441) state that iodination in the 2-position proceeds quantitatively. There seems little doubt that this substance is different from the 4- and the 6-iodo-derivative, m. p. 156° and 146—147° respectively (Hähle, *J. pr. Chem.*, 1891, **43**, 72; Meldola and Eyre, P., 1901, 238).

In endeavouring to prepare 4-bromo-3-nitrophenol by a different method, we nitrated N-p-*bromophenylphthalimide* in presence of excess of concentrated sulphuric acid, expecting to obtain a considerable proportion of the *m*-nitro-derivative (compare Brady, Quick, and Welling, J., 1925, **127**, 2264). The main product, however, was the *o*-nitro-derivative. This result is interesting, since nitration of *p*-bromoaniline in presence of excess of sulphuric acid gives almost entirely the *m*-nitro-compound (Noelting and Collin, *Ber.*, 1884, **17**, 261) (see Experimental).

The nitration of 2 : 4-dibromo-2′ : 4′-dinitrodiphenyl ether proceeds similarly to that of the analogous dichloro-compound and gives 2 : 4-*dibromo*-5 : 2′ : 4′-*trinitrodiphenyl ether*. This ether readily undergoes scission by piperidine into 2 : 4-dibromo-5-nitrophenol and *N*-2′ : 4′-dinitrophenylpiperidine.

EXPERIMENTAL.

2 : 4-*Dibromophenyl* p-*toluenesulphonate*, readily obtained by the usual type of process, crystallised from glacial acetic acid in colourless plates, m. p. 120° (Found : Br, 39·8. $C_{13}H_{10}O_3Br_2S$ requires Br, 39·4%).

Dinitration of 2 : 4-*Dibromophenyl* p-*Toluenesulphonate*.—The compound was added to 10 parts of nitric acid (*d* 1·5), the resulting solution being left for an hour and then poured into a large bulk of water. Filtration, followed by crystallisation from glacial acetic acid, gave 2 : 4-*dibromo*-5-*nitrophenyl* o-*nitro*-p-*toluenesulphonate* in pale greenish-yellow leaflets, m. p. 122—123° (Found : Br, 32·6. $C_{13}H_8O_7N_2Br_2S$ requires Br, 32·3%).

2 : 4-*Dibromo*-5-*nitrophenol*.—The last-mentioned compound was heated for 1 hour at 100° with 2 parts of piperidine. No piperidine hydrobromide separated. Excess of dilute alkali was added, and the solution shaken with benzene; this extracted the 1-*o*-nitro-*p*-toluenesulphonylpiperidine, but, contrary to expectation, it also extracted the piperidine salt of the phenol. It was therefore shaken

with dilute hydrochloric acid and then with alkali. Acidification of the alkaline solution precipitated 2 : 4-*dibromo*-5-*nitrophenol*. This crystallised from light petroleum (b. p. 80—100°) in long yellow needles, m. p. (after being dried over-night in a vacuum over concentrated sulphuric acid) 77—78° (Found : Br, 53·5. $C_6H_3O_3NBr_2$ requires Br, 53·9%), and from very dilute acetone as the *hydrate*, $C_6H_3O_3NBr_2,H_2O$, in long yellow needles, m. p. 92—94° (with previous softening), the m. p. depending on the rate of heating (0·5236 g. lost 0·0309 g. in 14 days in a vacuum over phosphoric oxide. Loss of $1H_2O$ requires 0·0299 g. The specially dry material so obtained melted at 84—86°).

2 : 4-*Dibromo*-5-*aminophenyl* o-*Amino*-p-*toluenesulphonate*.—The corresponding dinitro-compound was added with shaking to a hot solution of stannous chloride (1·5 times the calculated quantity) in a mixture of glacial acetic acid and concentrated hydrochloric acid. After the mixture had been heated at 100° for a few minutes, vigorous reduction set in, and was allowed to become complete during an hour at 100°. The resulting solution was poured into excess of 20% potassium hydroxide solution, and the suspension was cooled and filtered (asbestos). The washed and dried precipitate crystallised from dilute acetone in colourless leaflets, m. p. 174—175° (Found : Br, 37·5. $C_{13}H_{12}O_3N_2Br_2S$ requires Br, 36·7%).

2 : 4 : 5-*Tribromophenyl* o-*Bromo*-p-*toluenesulphonate*.—The diamino-compound was diazotised at 20—25°, in a mixture of equal parts of concentrated hydrochloric acid and water, with a solution of sodium nitrite. The diazo-perbromide was precipitated by means of a solution of bromine in aqueous potassium bromide, collected, washed, and decomposed in glacial acetic acid, the temperature of the latter being slowly raised until the b. p. was reached. Water was added, and the precipitate crystallised from alcohol, colourless leaflets, m. p. 107—108°, being obtained (Found : Br, 56·9. $C_{13}H_8O_3Br_4S$ requires Br, 56·7%).

2 : 4 : 5-*Tribromophenol*.—(*a*) A solution of the preceding compound in excess of piperidine was boiled under reflux for an hour; the solution was then strongly acidified and submitted to steam distillation. The tribromophenol passed over rapidly, and crystallised from light petroleum (b. p. 40—60°) in long colourless needles, m. p. 85—86° (Found : Br, 73·0. $C_6H_3OBr_3$ requires Br, 72·5%).

(*b*) 2 : 4 : 5-Tribromoaniline, prepared for the purpose from *p*-dibromobenzene, was converted into the corresponding phenol by adapting the method of Noelting and Kopp (*loc. cit.*). The product was identical with that from process (*a*).

Kohn and Pfeifer (*Monatsh.*, 1927, **48**, 211) obtained what was evidently mainly 2 : 4 : 5-tribromophenol, m. p. 79°, by heating pentabromophenol with zinc dust and glacial acetic acid. We failed to trace this work for some time, since in the original paper and in the British abstracts the substance was incorrectly called 3 : 4 : 6-tribromophenol.

Nitration of 2 : 4-Dibromo-2′ : 4′-dinitrodiphenyl Ether.—The ether, described by Le Fèvre, Saunders, and Turner (J., 1927, 1168), is more conveniently obtained as follows : 21 g. of 2 : 4-dibromophenol were added to 4·6 g. of potassium hydroxide previously fused with 0·5 c.c. of water. To the still hot mixture were added 17·5 g. of 1-chloro-2 : 4-dinitrobenzene. After a few minutes' shaking, potassium chloride began to separate, and after an hour's heating at 100°, interaction was complete. Excess of dilute alkali was added, and the mixture cooled and shaken. The solid mealy product was collected, washed with water, and crystallised from glacial acetic acid (23 g., m. p. 133°).

The ether was added rapidly to 10 parts of nitric acid (*d* 1·5). After 0·5 hour, the solution was poured into water. The precipitated solid was collected, washed, and crystallised from glacial acetic acid, 2 : 4-*dibromo*-5 : 2′ : 4′-*trinitrodiphenyl ether* being obtained in very pale yellow needles, m. p. 142° (Found : Br, 35·1. $C_{12}H_5O_7N_3Br_2$ requires Br, 34·9%).

Scission of 2 : 4-Dibromo-5 : 2′ : 4′-trinitrodiphenyl Ether.—(a) *With piperidine.* The trinitro-compound was heated with twice its weight of piperidine at 100° for an hour. The solution was treated with alkali and extracted several times with benzene. The benzene layer was extracted first with hydrochloric acid and then with alkali. Acidification of the alkaline solution gave 2 : 4-dibromo-5-nitrophenol, identical with the above product, and the benzene layer yielded 2 : 4-dinitrophenylpiperidine.

(b) *With aniline.* The trinitro-compound was heated for an hour at 100° with excess of aniline. On addition of much dilute hydrochloric acid, 2 : 4-dinitrodiphenylamine separated in almost quantitative yield.

Nitration of 2 : 4-Dibromophenyl Benzoate.—The benzoate was added slowly to 10 parts of nitric acid (*d* 1·5), kept below 30°. After a further 15 minutes, the solution was poured into excess of cold water. The gummy precipitate was separated, and heated with water until it became hard. It crystallised from alcohol in colourless needles, m. p. 155—156° (Found : Br, 36·2. $C_{13}H_6O_6N_2Br_2$ requires Br, 35·9%). The nitro-compound was heated for an hour at 100° with excess of piperidine. The excess of piperidine was removed by extraction with benzene in presence of alkali. The 2 : 4-dibromo-5-nitrophenol obtained, after crystallisation from light petroleum, had m. p. 77—78°, and did not depress the m. p. of the dibromo-compound described above.

The *m*-nitrophenol used in these experiments was prepared as described in Adams's "Organic Syntheses," Vol. VIII, p. 80, but it was found advisable to remove all traces of sulphuric acid from the crude product by dissolving it in alkali and reprecipitating it with hydrochloric acid before distilling it under reduced pressure; otherwise, towards the end of the distillation, explosive decomposition set in. From 212 g. of *m*-nitroaniline, 135—140 g. of pure *m*-nitrophenol were consistently obtained.

m-*Nitrophenyl* p-*toluenesulphonate*, obtained in the usual way, separated from alcohol in prisms, m. p. 112—113° (Found: S, 10·7. $C_{13}H_{11}O_5NS$ requires S, 10·9%).

Experiments on the Dibromination of m-*Nitrophenol.*—(A) *Dry.* (1) The method described by Lindner (*loc. cit.*) led to mixtures, the examination of which proved unprofitable.

(2) A current of carbon dioxide laden with bromine vapour was passed through *m*-nitrophenol in a bath at 120—140° until the desired increase in weight had occurred. The product was worked up by Lindner's method. Precipitation of the barium-salt fraction gave a solid, m. p. 82—98°. A mixture of this with 2 : 4 : 6-tribromo-3-nitrophenol melted below 75°, and one with 4-bromo-3-nitrophenol melted at 76—135°. On the assumptions that the product, m. p. 82—98°, is approximately 50% of 4-bromo- and 50% of tribromo-3-nitrophenol, and that the mixed melting-point curve is of the simplest type, these results are explicable, as is also the bromine content of the bromination product (51·3%; a 1 : 1 mixture of mono- and tri-bromo-compounds requires Br, 53·9%).

(3) On one occasion, by Schlieper's method of monobromination, a product was obtained corresponding very closely to that just described. It had m. p. 85—95°, and Br, 51·2%.

(B) *Wet.* (1) A solution of *m*-nitrophenol (1 mol.) and bromine (2 mols.) in 90% acetic acid was left in the cold for an hour. Since bromination did not begin, the solution was heated at 100° for 0·5 hour and then boiled for 0·5 hour. The product was worked up by Lindner's method and gave no substance corresponding to his dibromo-derivative.

(2) A solution of *m*-nitrophenol (1 mol.) and anhydrous sodium acetate (2 mols.) in glacial acetic acid was treated with a solution of bromine (2 mols.) in glacial acetic acid. A number of experiments were carried out, with variation of concentrations, temperature, and time of mixing. In every case the main product was 2 : 4 : 6-tribromo-3-nitrophenol, m. p. 89—90° (Found: Br, 63·4. Calc.: Br, 63·8%).

2 : 4 : 6-*Tribromo-3-nitrophenyl* p-*Toluenesulphonate*.—The tribromo-compound was readily converted into the p-*toluenesulphonyl* derivative, which crystallised from alcohol in colourless needles, m. p. 146—147° (Found : Br, 45·2 ; S, 6·0. $C_{13}H_8O_5NBr_3S$ requires Br, 45·3 ; S, 6·0%).

2 : 4 : 6-*Tribromo-3-aminophenyl* p-*Toluenesulphonate*.—Reduction of the preceding compound was effected by West's method (J., 1925, **127**, 494). The *amino*-compound separated from alcohol or dilute acetic acid in colourless prisms, m. p. 146—147° (mixture with the nitro-compound, m. p. 120—125°) (Found : Br, 47·9. $C_{13}H_{10}O_3NBr_3S$ requires Br, 48·0%).

2 : 3 : 4 : 6-*Tetrabromophenol*.—A solution of the preceding amino-compound in concentrated sulphuric acid was diazotised at 15° with a solution of sodium nitrite in concentrated sulphuric acid (made at — 10°). When the resulting solution was poured on ice, a yellow crystalline precipitate of the diazo-compound separated. Addition of water produced a clear solution, to which was added a solution of bromine in potassium bromide until no further precipitate was obtained. The diazo-perbromide was collected, washed with water, and decomposed in hot glacial acetic acid. On cooling, a crystalline product separated, which was washed with water and then heated with excess of piperidine at 100° for 4 hours. Addition of water precipitated 2 : 3 : 4 : 6-tetrabromophenol, which soon became solid and crystallised from dilute alcohol in colourless needles, m. p. 113—114°. An identical specimen was obtained by using the Sandmeyer instead of the perbromide process (Found : Br, 76·8. Calc. : Br, 78·0%).

N-p-*Bromophenylphthalimide*.—A mixture of *p*-bromoaniline (1 mol.) with finely ground phthalic anhydride (1 mol.) was heated at 250—300° for 2 hours. The molten mass was poured into cold alcohol and the solid product was ground and extracted with a large volume of boiling alcohol. The residual solid and the long silky needles that separated from the extract both melted at 204° (Found: Br, 26·8. $C_{14}H_8O_2NBr$ requires Br, 26·5%). Yield, 88%.

Nitration of N-p-*Bromophenylphthalimide*.—The imide (1 mol.) was dissolved in 10 parts of warm concentrated sulphuric acid. To the solution, cooled in running water, 1 mol. of nitric acid (d 1·5), dissolved in 5 vols. of concentrated sulphuric acid, was added slowly, with stirring. After an hour, the solution was poured on ice, and the resulting gummy precipitate collected. It was heated for an hour at 130° with 90% sulphuric acid, and the resulting solution was much diluted and then basified. The product was mainly 4-bromo-2-nitroaniline, and did not contain more than 20% of 4-bromo-3-nitroaniline (fractional crystallisation of the mixed sulphates).

Nitration of *p*-bromoaniline in excess of sulphuric acid as described by Noelting and Collin (*loc. cit.*) gave 4-bromo-3-nitroaniline in good yield, but an attempt to effect replacement of the amino-group by hydroxyl by the diazo-method proved unsuccessful.

Mononitration of ON-*Diacetyl*-p-*aminophenol.*—Hähle (*loc. cit.*) recommends nitration at 0° with fuming nitric acid. We have found that the best results are obtained when 50 g. of the diacetyl compound are added gradually to 75 c.c. of nitric acid (*d* 1·5) kept at about 5°. (Only partial nitration occurs at temperatures just below 0°, and the diacetyl compound may be recovered unchanged from its solution in a mixture of equal volumes of acids of *d* 1·5 and *d* 1·42, kept at 0° to – 5°.) The solution is poured on ice, and the precipitate obtained is crystallised from alcohol.

4-*Bromo*-3-*nitrophenol.*—*ON*-Diacetyl-3-nitro-4-aminophenol was slowly added to 10 times its weight of boiling hydrobromic acid (*d* 1·49). Boiling was continued for ¼ hour and the suspension of 3-nitro-4-aminophenol hydrobromide was then diluted and diazotised : diazotisation was slow. The excess of nitrous acid was removed by addition of urea and the solution obtained was poured into a suspension of copper powder in 25% hydrobromic acid. The copper slowly dissolved and needles separated. These crystallised from water in brown needles, m. p. 146·5—147·5°, and from dilute hydrochloric acid in yellow needles having the same m. p.

4-Chloro-3-nitrophenol was obtained in a precisely similar manner from diacetyl-3-nitro-4-aminophenol. The diazotisation proceeded more easily than with the bromo-compound. The product crystallised from dilute hydrochloric acid in yellow needles, m. p. 127—128°.

3-Bromo-2-nitrophenol was prepared by Hodgson and Moore's method (J., 1926, 157). In the intermediate sulphonation we obtained good results with 20% oleum, but with acid of the composition (27% oleum) used by Hodgson and Moore, our sulphonation mixture set almost solid and would not dissolve even in a large quantity of concentrated sulphuric acid.

3-*Bromo*-2-*nitrophenyl* p-*toluenesulphonate*, readily obtained in the usual way, crystallised from alcohol, in which it was very sparingly soluble, in colourless rectangular plates, m. p. 136·5—137·5° (Found : Br, 21·4. $C_{13}H_{10}O_5NBrS$ requires Br, 21·5%).

3-*Bromo*-2-*aminophenyl* p-*Toluenesulphonate.*—The preceding nitro-compound was reduced with a mixture of 2 parts of crystalline stannous chloride, 2 parts of concentrated hydrochloric acid, and 7 parts of glacial acetic acid at 100°. Much alkali was added and the suspension produced was extracted with ether. Evaporation of the dried ethereal extract, followed by crystallisation from alcohol, gave colourless needles of the *amino*-compound, m. p. 120—121° (Found : Br, 23·6. $C_{13}H_{12}O_3NBrS$ requires Br, 23·4%).

2 : 3-*Dibromophenol.*—The amino-compound was diazotised in concentrated sulphuric acid at 15—20°, with a solution of sodium nitrite in concentrated sulphuric acid prepared at − 10°. The reaction mixture was poured on ice. A small portion was found to couple normally with alkaline β-naphthol, and the main portion was added to cuprous bromide–hydrobromic acid. The resulting solution was heated on a boiling water-bath under reflux for ¾ hour and then distilled in steam. The white solid that passed over was dried over concentrated sulphuric acid (desiccator) and crystallised from light petroleum (b. p. 40—60°). The 2 : 3-*dibromophenol* obtained formed stout prisms, m. p. 68—69° (Found : Br, 63·6. $C_6H_4OBr_2$ requires Br, 63·6%). It is much less soluble in light petroleum than 2 : 3-dichlorophenol and is very much less volatile.

Monobromination of Wet m-*Nitrophenol.*—(a) When a dilute solution of bromine (1 mol.) was added to a cold dilute solution of *m*-nitrophenol (1 mol.) and anhydrous sodium acetate (1 mol.) in glacial acetic acid, a mixture of substances was formed, the examination of which led to no positive results.

(b) A solution of 20 g. of *m*-nitrophenol and 8·8 c.c. of bromine in 30 c.c. of glacial acetic acid was gently boiled under reflux for 2 hours; it then became almost colourless. The solvent was evaporated on a boiling water-bath and the residue, which became crystalline on cooling, was dissolved in dilute aqueous alkali. Addition of acid precipitated an almost colourless solid which, after being crystallised from dilute hydrochloric acid, melted at 117—120°, and after a further crystallisation from light petroleum (b. p. 80—100°), at 118·5—121° (Found : Br, 36·4. $C_6H_4O_3NBr$ requires Br, 36·7%). The following experiments show that this substance is 2-*bromo*-5-*nitrophenol.*

2-*Bromo*-5-*nitrophenyl* p-*toluenesulphonate* was formed in good yield by the usual process; it crystallised from alcohol in colourless plates, m. p. 131·5—132·5° (Found : Br, 21·6. $C_{13}H_{10}O_5NBrS$ requires Br, 21·5%).

2-*Bromo*-5-*aminophenyl* p-*toluenesulphonate*, obtained by the reduction of the nitro-compound with stannous chloride, hydrochloric acid, and acetic acid, crystallised from alcohol in colourless bunches of prisms, m. p. 135—136° (Found : Br, 23·3. $C_{13}H_{12}O_3NBrS$ requires Br, 23·4%).

2 : 5-*Dibromophenol.* (*a*) The last-named amino-compound was diazotised in concentrated sulphuric acid exactly as described under the preparation of 2 : 3-dibromophenol. The steam-distilled 2 : 5-*dibromophenol* was dried over concentrated sulphuric acid

(desiccator) and then crystallised from light petroleum (b. p. 40—60°); it formed prismatic needles, m. p. 73—74° (Found: Br, 63·4. $C_6H_4OBr_2$ requires Br, 63·6%). It was readily converted into 2 : 5-*dibromophenyl* p-*toluenesulphonate*, which separated from alcohol in colourless prisms, m. p. 109—110° (Found: Br, 39·7. $C_{13}H_{10}O_3Br_2S$ requires Br, 39·4%).

(*b*) 2 : 5-Dibromoaniline (44 g.), obtained in good yield by reducing 2 : 5-dibromonitrobenzene by West's method, was dissolved in 150 c.c. of warm concentrated sulphuric acid. The solution was cooled to room temperature and treated with a solution of 13 g. of sodium nitrite in 150 c.c. of concentrated sulphuric acid (prepared at − 10°). After an hour, 150 c.c. of water were added and the resulting solution, after addition of purified sand, was heated under reflux over a small flame for 2 hours. (A small portion of the diluted diazo-solution coupled readily with alkaline β-naphthol.) The whole was then distilled in steam, 37 g. of 2 : 5-dibromophenol, containing a trace of 2 : 5-dibromoaniline, passing over. The phenol was freed from the base by solution in alkali and filtration and then recovered by acidification; it had m. p. 73—74°, b. p. 256—257° (corr.)/755 mm. The *p*-toluenesulphonyl derivative melted at 109—110°.

Mixtures of the phenols or of their *p*-toluenesulphonyl derivatives obtained by methods (*a*) and (*b*) had the same m. p. as those of the single substances.

Monobromination of Dry m-*Nitrophenol.*—(1) A current of dry carbon dioxide was passed through bromine and then through 10·5 g. of *m*-nitrophenol heated at 120—140°. When the calculated increase of weight had occurred, the product was freed from the excess of bromine by a rapid current of carbon dioxide and at once dissolved in excess of dilute sodium hydroxide solution. After addition of dilute hydrochloric acid, yellow needles of 4-bromo-3-nitrophenol separated for some time, and later, an oil made its appearance. At this stage the liquid was filtered and the solid was crystallised from dilute hydrochloric acid, 7 g. of the 4-bromo-compound, m. p. 146·5—147·5°, being obtained.

(2) *m*-Nitrophenol (28 g.) was brominated, the weight being allowed to increase to 43 g. When the product was worked up as before, 22 g. of pure 4-bromo-3-nitrophenol were obtained.

The products from both experiments did not depress the m. p. of 4-bromo-3-nitrophenol prepared from diacetyl-*p*-aminophenol.

Attempted Monobromination of 4-*Bromo*-3-*nitrophenol.*—When the monobromo-compound (1 mol.), dissolved together with 1 mol. of anhydrous sodium acetate in glacial acetic acid, was treated with 1 mol. of bromine dissolved in the same solvent, a mixture was obtained containing unchanged 4-bromo-3-nitrophenol.

Attempted Monobromination of 2-Bromo-5-nitrophenol.—This appeared to proceed readily. The acetic acid was evaporated, and the hard solid obtained (on cooling) crystallised from light petroleum (b. p. 80—100°). The product had the appearance of an individual substance, but melted at 68—108°.

Monochlorination of m-*Nitrophenol.*—Chlorine was passed into *m*-nitrophenol (42 g.) at 120—140° until the weight increased by 9·5 g. A rapid current of carbon dioxide was passed through the molten product until the excess of chlorine had disappeared and the whole was then dissolved in dilute alkali solution. Dilute hydrochloric acid was added until no further evident precipitation occurred and the yellow needles produced were washed and dried (14 g.). After crystallisation from dilute hydrochloric acid, 12 g. of pure 4-chloro-3-nitrophenol, m. p. 127—128°, were obtained. The mother-liquor from the first filtration was strongly acidified, and filtered after some time: the yellow precipitate obtained, having been washed and dried, weighed 16 g. and after crystallisation from dilute hydrochloric acid gave 10 g. of 2-chloro-3-nitrophenol, m. p. 120° (Found: Cl, 19·6. Calc.: Cl, 20·0%). The mother-liquor from the second precipitation was evaporated to a small bulk under reduced pressure and then extracted with ether. Evaporation of the extract gave 12·5 g. of an oily mixture of chloro-compounds. The total yield of crude chloro-compounds was 85% of the theoretical yield.

The 4-chloro-3-nitrophenol obtained produced no depression of the m. p. of the material prepared from *ON*-diacetyl-*m*-nitro-*p*-aminophenol.

The 2-chloro-3-nitrophenol was reduced with iron, hydrochloric acid, and alcohol, and the filtered solution evaporated to dryness. Diazotisation, followed by addition of copper powder and hydrochloric acid, gave 2 : 3-dichlorophenol, m. p. 56—57°: this depressed the m. p. of 2 : 5-dichlorophenol (m. p. 57°). 2 : 3-Dichlorophenol is extraordinarily volatile, and vacuum desiccation over sulphuric acid and phosphoric oxide was accompanied by considerable loss. This property and the intense odour of the compound appear to differentiate this dichlorophenol from its isomerides (compare Holleman, *Rec. trav. chim.*, 1917, **37**, 96), and the volatility accounts for the poor analytical figure obtained (Found in air-dried specimen: Cl, 41·7. Calc.: Cl, 43·6%).

Some of the preliminary work on the dibromodinitrodiphenyl ether was carried out by Miss G. I. Sharp, B.Sc.

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