XXIX.—*On the Influence of the Amido-group upon the Orientation of Bromine or NO_2 in the Benzene-nucleus, as illustrated by the preparation of the six possible Dibromotoluenes, the six possible Tribromotoluenes, the three possible Tetrabromotoluenes, and various other Bromo- and Bromonitro-derivatives of Toluene.*

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IN the table given in his memoir on the "Isomerism of the Aromatic Compounds containing Six Atoms of Carbon," Körner (*Gazzetta chim. ital.*, 1874, 305; *Chem. Soc. J.* [2], **14**, 204; *Jahresb.*, 1875, 364) lays down the rule that when one of the halogens or the nitro-group is introduced into aniline, it takes the para-position. Körner's paper deals only with the substitution of the second hydrogen-atom in mono-derivatives of benzene, and consequently in this case only with aniline. But it appears to us for various reasons that the rule is of more general application, and that if bromine or another halogen, or the nitro-group,

be directly introduced into aniline or any of its homologues, such as toluidine or xyloidine, and very probably other amido-compounds, the acid-group nearly always, if possible, takes the para-position to the amido-group; or if the para-position be occupied by any other group that it then takes one of the ortho-positions, but that under no circumstances can one of the above groups be directly introduced into a position meta to the amido-group.

We have investigated this question carefully only so far as relates to the monamido-compounds. We are inclined to think that the same rule will hold good with reference to diamido-compounds and others, but the data we have at the present time are not sufficient to enable us to arrive at a definite conclusion on this point.

The only experiments that we have noticed which appear to point to conclusions at variance with the above theory, are some experiments of E. Wroblewsky's (*Jahresb.*, 1870, 528; 1871, 450; summary in *Liebig's Annalen*, **168**, 147) on the formation of the six possible isomeric dibromotoluenes. As some of these results point to a conclusion directly opposed to the above theory in both its branches, we have thought it wise to repeat the experiments, and have done so with results which seem to us to establish the correctness of the above conclusion as against the experiments of Wroblewsky.

We will consider first the two possible ortho-meta-dibromotoluenes, viz., 1 : 2 : 3 and 1 : 2 : 5.

Wroblewsky states that he has succeeded in preparing both of these, and in the following ways:—The first from the diazoperbromide of metabromorthotoluidine; the second from the diazoperbromide of orthobromometatoluidine, by heating them respectively with absolute alcohol.

He describes them as different substances, and says that the first is a liquid boiling at 238–239°, and giving on nitration a mononitro-compound melting at 86–87°, and convertible by reduction into an amido-compound melting at 83°; and he says further that a similar compound can be obtained by brominating metabromotoluene. As to the product of the second reaction, he says that it is solid (m. p. 42·5°, b. p. 239°). Further that he gets the same compound by removing the amido-group from dibromorthotoluidine, and that this latter gives a nitro-compound melting at 59°. He assigns to the former the constitution 1 : 2 : 3, and to the latter the constitution 1 : 2 : 5, without, as far as we have been able to ascertain, giving any reasons.

Now it is clear that the above results, if true, are opposed to the theory enunciated before as to the bromine taking the para-position to the amido-group, as if it did so the two dibromotoluenes would evidently be identical, as in fact we believe them to be.

We prepared the dibromotoluene both from orthobromometatoluidine

and from metabromorthotoluidine (we also obtained the dibromotoluene from dibromorthotoluidine, but found it quite different, and shall speak of it later). As to the former we proceeded as follows:—

By acting upon acetorthotoluid with a single molecular proportion of bromine suspended in water, we obtained a monobromacetotoluid, which, by decomposition with alcoholic potash, gave a monobromotoluidine, which, after separation from small quantities of dibromotoluidine, formed by solution in *dilute* hydrochloric acid and reprecipitation with sodic carbonate and purification by distillation with steam, melted at 55—56° (Wroblewsky gives 58°). This monobromotoluidine was converted into diazoperbromide, and decomposed by warming it gently with glacial acetic acid. We thus obtained the dibromotoluene.

We proceeded in the same way to obtain it from metatoluidine, also, however, boiling the hydrochloric acid solution of monobromometatoluidine to expel any dibromotoluidine that had been formed, as we found that, although it is far more soluble in dilute acids than the corresponding dibromorthotoluidine, it nevertheless distils away freely from the solution.

Here, however, we find a divergence from Wroblewsky's results. He states that the monobromometatoluidine obtained by the decomposition of the monobromacetometatoluid with alcoholic potash is an oil. We, however, found it to be a solid of m.p. 77—78°:—

Analysis:—

Employed .. 0.2005 AgBr = 0.2031 = 43.10 per cent. Br.

„ .. 0.2497 AgBr = 0.2536 = 43.21 „

The theory for $C_6H_3.CH_3.NH_2.Br$ requires 43.01 per cent. Br.

On converting this into diazoperbromide and decomposing it in the same way as the compound from orthotoluidine, we likewise obtained a dibromotoluene. We also prepared the monobromometatoluidine in the following way:—Taking metanitroorthotoluidine, we converted it into diazoperbromide, and decomposed it with warm acetic acid. In this way we obtained metanitroorthobromotoluene, which, after distillation with steam and frequent recrystallisation from alcohol, melted at 76.3°:—

Analysis:—

Employed .. 0.3217 AgBr = 0.2783 = 36.81 per cent. Br.

Theory for $C_6H_3.CH_3.Br.NO_2$ requires 37.04 per cent. Br.

On reducing this with tin and hydrochloric acid and distilling the product with steam, we obtained a monobromometatoluidine, melting at 76—78.5°.

We consider the dibromotoluenes prepared by either of the methods given above as identical, for the following reasons:—

1st. They are both fluid at ordinary temperatures, and do not solidify in a freezing mixture of ice and salt.

2nd. On nitrating them with fuming nitric acid, sp. gr. 1520 :—

That from metatoluidine gave a compound, m. p. 87·6—88·5°.

That from orthotoluidine gave a compound, m. p. 88·2—88·6°.

3rd. On reducing these nitro-compounds with iron and acetic acid, they gave amido-compounds :—

That from metatoluidine melted at 84—85°.

That from orthotoluidine „ 84·5—85·1°.

These experiments, as we consider, establish without doubt that the dibromotoluenes produced either from metabromortho-diazotoluene perbromide or orthobromo-meta diazotoluene perbromide are identical, and must consequently be ortho-meta-derivatives, viz., either 1 : 2 : 5 or 1 : 2 : 3, showing also that when bromine is introduced into orthotoluidine, it takes the meta-position relatively to CH_3 , and when introduced into metatoluidine, it takes the ortho-position.

As these two methods give only one dibromotoluene, we next endeavoured to prepare the other one of the orthometa-constitution. We proceeded thus :—Taking metanitroorthotoluidine (m. p. 128°), we suspended it in water, and added a solution of bromine in water to the amount of slightly more than a single molecular proportion, leaving the mixture to itself for some time, and finally warming it slightly. By then filtering off the liquid, washing, and drying the residue, we obtained a substance, which, after recrystallisation from alcohol, melted at 180·3—181·3° (corr.) :—

Analysis :—

Employed .. $0\cdot1957 \text{ AgBr} = 0\cdot1577 = 34\cdot29 \text{ per cent. Br.}$

Theory for $\text{C}_6\text{H}_4\cdot\text{CH}_3\cdot\text{NH}_2\cdot\text{Br}\cdot\text{NO}_2$ requires 34·63 per cent. Br.

This substance is therefore bromonitroorthotoluidine, and is different from that which Wroblewsky obtained, by nitrating metabromortho-acetatoluid, and taking out the acetyl group, for which he gives the melting point 139°.

We investigated the constitution of this substance as follows :—We prepared also the compound described by Wroblewsky as of m. p. 139°, and also the bromonitroparatoluidine in two ways, viz., by first nitrating and then brominating, and also by first brominating and then nitrating. (It is probably unnecessary to mention that one must use the acetyl-compound for nitration, but that the aceto-group must be taken out before bromine can be introduced into the nitro-compound.) We treated the above four compounds with nitrous gas and alcohol, to remove the amido-group, and then reduced the bromonitrotoluene thus produced with tin and hydrochloric acid. The bromotoluidine thus

produced was also converted into an aceto-compound by boiling with glacial acetic acid for seven or eight hours, with the results tabulated below :—

	From ortho- toluidine by first nitrating and then bromi- nating.	From ortho- toluidine by first brominating and then nitrating.	From para- toluidine by first nitrating and then brominat- ing.	From para- toluidine by first bromi- nating and then nitrat- ing.
Nitrobromotolui- dine	m.p. 180·3—181·3°	m.p. 143·0°	m.p. 64—65°	m.p. unpurified, 63°
Nitrobromotoluene	81·4—81·8°	81·4—81·8°	81·4—81·8°	81—81·5°
Bromotoluidine ..	35·6—36°	34·5—37°	36·6°	35—35·2°
Aceto-compound of the bromotolui- dine	167—168°	167—168°	167—168°	168°

Hence it is clear, as we think, that the bromonitrotoluenes, as obtained by the four methods above mentioned, are identical. As to the bromotoluidine, the melting points differ slightly, and Wroblewsky says that this compound (as obtained from the bromnitroparatoluidine) is a liquid. Ours remained liquid for a long time, and at last solidified only after a very cold night. We then found, however, that the smallest particle of the crystalline substance was sufficient to make any quantity crystallise at once. We found it, however, pretty nearly impossible to recrystallise it from alcohol, as it declined to crystallise at all until nearly all the alcohol had evaporated, and then generally the whole became solid at once. This will account for the slight differences in the melting points. Now we have already shown that bromine assumes the meta-position to CH_3 in orthotoluidine, and it is known that the nitro-group also takes up the meta-position relatively to CH_3 in both ortho- and para-toluidine. Hence the bromonitrotoluene must have the constitution 1 : 3 : 5. This shows also that on the introduction of bromine into paratoluidine, it takes a position meta to CH_3 .

We see, then, that of the first two bromonitrotoluidines, one must have the constitution $\text{CH}_3\text{NH}_2\text{Br}\text{NO}_2$, and the other the constitution $\text{CH}_3\text{NH}_2\text{NO}_2\text{Br}$. We now proceeded to convert the meta-bromometanitrorthotoluidine, melting at 180·3—181·3°, into meta-bromometanitrorthobromotoluene by decomposing the diazoperbromo-

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mide by warming it with glacial acetic acid. We thus obtained dibromonitrotoluene melting at $105\cdot4^{\circ}$.

Analysis :—

Employed . . $0\cdot2378 \text{ AgBr} = 0\cdot3025 = 54\cdot13 \text{ per cent. Br.}$

Theory for $\text{C}_6\text{H}_2\cdot\text{CH}_3\cdot\text{Br}_2\cdot\text{NO}_2$ requires $54\cdot23 \text{ per cent. Br.}$

On reducing this with iron and acetic acid, and distilling the separated base with steam, we obtained a dibromotoluidine, melting at $86\cdot4^{\circ}$. This compound dissolves in hot dilute hydrochloric acid with tolerable facility, and the salt crystallises out on cooling in small white needles.

Analysis for free HCl :—

Employed . . $0\cdot0808 \text{ AgCl} = 0\cdot0382 = 11\cdot69 \text{ per cent. Cl.}$

Theory for $\text{C}_6\text{H}_2\cdot\text{CH}_3\cdot\text{Br}_2\cdot\text{NH}_2\cdot\text{HCl}$ requires $11\cdot77 \text{ per cent. Cl.}$

On heating this dibromotoluidine with glacial acetic acid for six or seven hours, it is converted into an acetyl-compound, which, after purification with animal charcoal and recrystallisation from alcohol, melts at $204\text{--}205^{\circ}$.

On treating the dibromotoluidine with nitrous gas and alcohol to remove the amido-group, we obtained a substance which, after distillation with steam, melted at $27\cdot4\text{--}27\cdot8^{\circ}$; and on dissolving this in a mixture of three volumes of nitric acid of sp. gr. 1520 and one volume of sp. gr. 1450, and precipitating with water, we obtained a nitro-compound melting at $51\text{--}62^{\circ}$.

Following up our theory that bromine will take up a position para to the amido-group, we now endeavoured to prepare the above substance (which we shall show to be in all probability 1 : 2 : 3 dibromotoluene) from the aceto-metabromometatoluid described above as of m. p. $167\text{--}168^{\circ}$. We acted upon it with a single molecular proportion of bromine in aqueous solution. The bromine was at first absorbed with tolerable rapidity, but towards the end of the reaction it became necessary to apply heat in order to cause complete absorption. Thus we obtained a dibromacetoluid of m. p. $204\text{--}205^{\circ}$. On heating this with a mixture of equal volumes of hydric sulphate and water, it was decomposed, and on diluting with water and cooling, the sulphate of a dibromotoluidine crystallised out. On decomposing this with sodic carbonate, we obtained the dibromotoluidine, melting, after recrystallisation from alcohol, at $83\text{--}85^{\circ}$. On decomposing this with nitrous gas and alcohol, and distilling the product with steam, we obtained a substance, melting at $27\cdot4\text{--}28^{\circ}$.

Analysis :—

Employed . . $0\cdot2675 \text{ AgBr} = 0\cdot4 = 63\cdot63 \text{ per cent. Br.}$

Theory for dibromotoluene requires 64·00 per cent. Br.

On nitrating this with a mixture of three volumes 1520, and one volume 1450, nitric acid, we obtained a nitro-compound, which, after several recrystallisations from alcohol, melted at 56·5—57·5°.

Analysis:—

Employed.. $0\cdot2048 \text{ AgBr} = 0\cdot2613 = 54\cdot29$ per cent. Br.

Theory for $\text{C}_6\text{H}_2\cdot\text{CH}_3\cdot\text{Br}\cdot\text{Br}\cdot\text{NO}_2$ requires 54·24 per cent. Br.

This, reduced with tin and hydrochloric acid, gave an amido-compound, which, after crystallisation from alcohol, melted at 52—53°.

From the above it is clear that the two methods employed by us give identically the same results, and that this is the other ortho-meta-dibromotoluene.

There now only remains the question, which of the two dibromotoluenes we have described has the constitution $\text{CH} : \text{Br} : \text{Br} = 1 : 2 : 5$, and which $1 : 2 : 3$.

We endeavoured to decide this point by converting them into dibromobenzoic acids by heating them with dilute nitric acid (one vol. 1360 to three of water) for about three days. In this way we obtained from the one first described:—From the portion prepared from metatoluidine a dibromobenzoic acid, melting at 149—151°. (On analysis this gave 57·49 per cent. Br; theory requiring for dibromobenzoic acid 57·14 per cent. Br.) From the portion prepared from orthotoluidine, a dibromobenzoic acid, melting at 151—153°. (On analysis this gave 58·40 per cent. Br.) From the dibromotoluene last described, we obtained a dibromobenzoic acid, melting at 146—148°.

Analysis:—

Employed.. $0\cdot1372 \text{ AgBr} = 0\cdot1847 = 57\cdot35$ per cent. Br.

The first agrees very closely with that described by V. v. Richter (*Ber.*, 1875, 1422; *Jahresb.*, 1875, 293), as obtained from paradibromobenzene, and melting at 151—152°; and on distilling some of it with lime, we obtained a very small quantity (unfortunately not sufficient for analysis) of a solid, resembling in outward appearance paradibromobenzene, and melting at 85—86°, the melting point of paradibromobenzene when pure being 89°.

Although the above differences in the melting points of the benzoic acids taken by themselves would not, in our opinion, be sufficient to settle the question as to the constitution of the two dibromotoluenes from which they are obtained, yet, taken in connection with the fact that from the former, on distillation with lime, the above solid was obtained, we think we may safely conclude that the former has the two bromine-atoms in a position para to each other, and consequently has the constitution $1 : 2 : 5$, and the latter consequently the consti-

tution 1 : 2 : 3; more especially as if we assign to them the opposite constitutions, we must imagine that both in orthotoluidine and in metatoluidine both the bromine and also the nitro-group when introduced takes a position ortho to NH_2 rather than para, which would be exactly contrary to Körner's results in the case of aniline, and could not be the result of the influence of the CH_3 -group, inasmuch as the negative group is in either case meta thereto.

If, then, we accept the above theory of the constitution of the two compounds, it will be seen that throughout the above reactions the bromine and nitro-groups follow the laws indicated in the theory at the commencement of this paper, the bromonitrotoluidine obtained by us (m. p. $180-183^\circ$) having the constitution $\text{CH}_3.\text{NH}_2.\text{Br}.\text{NO}_2$,
 $\begin{array}{ccccccc} & & & & 1 & 2 & 3 & 5 \\ & & & & | & | & | & | \end{array}$
 and that obtained by Wroblewsky (m. p. 139°) the constitution $\text{CH}_3.\text{NH}_2.\text{NO}_2.\text{Br}$, and ordinary nitrothotoluidine the constitution $\text{CH}_3.\text{NH}_2.\text{NO}_2$.
 $\begin{array}{ccccccc} & & & & 1 & 2 & 3 & 5 \\ & & & & | & | & | & | \end{array}$

We next consider what we may call symmetrical dibromotoluene, in which both the bromine-atoms are meta to the CH_3 -group.

This we obtained, contrary to the observation of Wroblewsky, both from dibromortho- and from dibromo-paratoluidine.

Our results were as follows :—

1st. With orthotoluidine. By acting upon this either in alcoholic or in acid aqueous solution with a slight excess of bromine, we obtained (after precipitation with water in the former case, and after distillation with steam) a white crystalline dibromotoluidine, which melted constantly at $45-46^\circ$ (the melting point given by Wroblewsky is 50°).

Analysis :—

Employed .. $0.4472 \text{ AgBr} = 0.6328 = 60.19 \text{ per cent. Br.}$

Theory for $\text{C}_6\text{H}_4.\text{CH}_3.\text{Br}_2.\text{NH}_2$ requires $60.37 \text{ per cent. Br.}$

Wroblewsky states that this compound does not combine with acids. We found that it did not unite with dilute acids; but by heating it with strong acids we formed the sulphate, nitrate, and chloride, and found that at all events the latter could be recrystallised from alcohol or suspended in cold water, without apparent decomposition. Heating with water at once caused the resolution of the salt into the base and free acid.

Acting in a similar manner with bromine on paratoluidine we obtained a dibromotoluidine melting at 73° (Wroblewsky gives 76°).

Analysis :—

Employed .. $0.3237 \text{ AgBr} = 0.4549 = 59.79 \text{ per cent. Br.}$

On acting upon the above dibromotoluidines with a solution of nitrous

acid in alcohol, the first gave, after distillation with steam, at once a substance melting at 39° .

Analysis:—

Employed .. 0.4761 $\text{AgBr} = 0.7194 = 64.29$ per cent. Br.

Theory for $\text{C}_6\text{H}_3\text{CH}_3\text{Br}_2$ requires 64.00 per cent. Br.

The second, obtained from paratoluidine, gave a substance which generally melted a little higher, viz., at $40-42^{\circ}$, but could be easily separated by recrystallisation into two substances, one of which melted at 39° , and was in all appearances exactly similar to the one above described.

Analysis:—

Employed .. 0.4728 $\text{AgBr} = 0.7121 = 64.09$ per cent. Br.

The other (present only in very small quantities) melted at or above 121° . This latter was probably a bye-product of the action of the nitrous gas, probably an amidoazo-compound, but the quantity obtained was not sufficient to enable us to make any examination of it.

On treating the dibromotoluenes with fuming nitric acid, and precipitating the products with water, they both gave nitro-compounds, melting at first from $120-125^{\circ}$; by several recrystallisations from alcohol these were separated into two compounds:—

	(a) From orthotoluidine.	(b) From paratoluidine.
1. Melting point	$157.8-158.3^{\circ}$	$157.6-158^{\circ}$
2. "	105°	105°

These both proved on analysis to be dinitro-compounds.

Analysis:—

1. α . Employed.. 0.2192 $\text{AgBr} = 0.2417 = 46.92$ per cent. Br.

Theory for dibromodinitrotoluene requires 47.05 per cent. Br.

1. β . Employed.. 0.2356 ; $\text{N} = 16.5$ c.c.; $b = 758.4$; $t = 17.1$
 $= 8.1$ per cent. N.

2. β . Employed.. 0.1351 ; $\text{N} = 9.25$ c.c.; $b = 755.7$; $t = 17.0$
 $= 7.89$ per cent. N.

Theory for dibromodinitrotoluene requires 8.23 per cent. N.

Further, in both cases the dibromotoluene, melting at 39° , gave on oxidation with chromic and acetic acids a benzoic acid melting between 207° and 210° .

Analyses—

From ortho. Employed.. 0.1551 $\text{AgBr} = 0.2117 = 58.08$ per cent. Br.

From para. Employed .. 0.1603 $\text{AgBr} = 0.2187 = 58.05$ per cent. Br.

All the above results seem to show conclusively that in the action of bromine upon either ortho- or para-toluidine, the bromine-atoms

take up the same positions, one of which we already know to be meta to CH_3 . As to the position of the second, it must either be the other meta-position or the ortho-position, and the dibromotoluene must have either the constitution 1 : 2 : 3; 1 : 2 : 5; or 1 : 3 : 5. We have already described the first two, and their characteristics are quite different, and therefore the only constitution remaining is 1 : 3 : 5.

Further, the dibromobenzoic acid agrees with that described by V. v. Richter (*Ber.*, 1875, 1423), as obtained from metadibromobenzene of melting point 208—209°.

It may be well here to notice a statement made by Gerver (*Jahresb.*, 1873, 674), who says in a footnote, that he obtains from orthotoluidine, by the action of 3 molecules of bromine, a tribromotoluidine which melts at 105—106°, and from a weak alcoholic solution with 1 molecule of bromine, a mixture of di- and tri-bromotoluidines melting at 85—89°.

Owing to this statement we have made most careful experiments, both in alcoholic and ethereal solutions, as well as in aqueous acid solutions, but we could never obtain from ortho- or para-toluidine any more highly brominated toluidine than a dibromotoluidine. Any further bromine either remained uncombined or acted upon the solvents, generally producing a pitch which entirely declined to distil with steam or to give any crystals on extraction with dilute alcohol. In fact, when sufficient bromine was added, the whole of the dibromotoluidine was destroyed if in aqueous solution.

We also tried the same substance without any solvents with similar results, the excess of bromine remaining uncombined.

We can only account for Gerver's statement by supposing that the orthotoluidine he used was impure, and with reference to this point we would observe that the melting point of the aceto-compound of orthotoluidine seems to be by no means a sufficient proof of its purity, inasmuch as Hübner and Wallach (*Jahresb.*, 1869, 678) find 105—106° for the melting point of an acetotoluid, which Rosenstiehl considers to be a mixture of orthotoluid with about 30 per cent. of paratoluid, and which, from the method of preparation given by H. and W., we should imagine to be anything but a pure orthotoluidine. It is, therefore, by no means impossible that the compound used by Gerver may have contained metatoluidine or aniline, which do give with bromine tribromo-compounds.

We now come to the parabromometabromotoluene (1 : 3 : 4).

This we prepared from monobromoparatoluidine by means of the diazoperbromide reaction. We found this monobromotoluidine to be, as described by Wroblewsky, an oil, and we can also confirm his results as to the dibromotoluene. It was fluid.

Analysis :—

Employed .. 0.2666 AgBr = 0.4031 = 64.34 per cent. Br.

On nitrating it with fuming nitric acid, we got a crystalline compound (as well as a very small quantity of an oil) melting, after frequent recrystallisations from alcohol, at 86.6—87.5°.

Analysis :—

Employed .. 0.1240 AgBr = 0.1586 = 54.42 per cent. Br.

On reducing this with iron and acetic acid we obtained a compound which, after distillation with steam, dissolution in dilute hydrochloric acid, and reprecipitation with sodic carbonate, melted at 96.8—98°.

Analysis :—

Employed .. 0.2942 AgBr = 0.4185 = 60.53 per cent. Br.

We also converted this dibromotoluene into a dibromobenzoic acid by oxidation with chromic and acetic acids; this, after purification by conversion into barium salt, washing with ether, and reprecipitation with hydrochloric acid, melted at 232—233°.

Analysis of the barium salt :—

Employed .. 0.3119 AgBr = 0.3300 = 45.02 per cent. Br.

Theory for dibromobenzoate of barium 46.04 per cent. Br.

The melting point given by Burghardt (*Ber.*, 1875, 558) is 229—230°.

We now come to the last two, viz., 1 : 2 : 4 and 1 : 2 : 6. Here again our results differ from those of Wroblewsky. He prepares the latter from the dibromometatoluidine resulting from the action of two molecular proportions of bromine on acetometatoluidine and subsequent decomposition with alcoholic potash. He describes the dibromotoluidine as of melting point 92.5°; and the dibromotoluene resulting from it by elimination of the amido-group as liquid and boiling at 246°. By nitration of the dibromotoluene he obtains a mononitro-compound melting at 79°.

We find that on acting upon the aceto-compound of metatoluidine with two molecular proportions of bromine, the first one is readily absorbed, forming a monobromaceto-compound, but the last one is absorbed with much greater difficulty, giving at last a dibromaceto-compound which, however, on the removal of the acetyl-group with alcoholic potash was proved to give, not one, but a mixture of two dibromotoluidines; a small quantity of tri-bromotoluidine was also always formed at the same time.

We separated these as follows :—The di- and tri-bromotoluidines were distilled off from dilute acid which retained the monobromotoluidine.

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This, after separation from the acid solution by means of sodic carbonate, melted at 76—77°.

The mixed di- and tri-bromotoluidines were then extracted with hot strong hydrochloric acid. The liquid on cooling deposited crystals.

Analysis:—

Employed .. 0.1993 AgBr = 0.3117 = 66.54 per cent. Br.

Theory for dibromotoluidine 60.38 per cent.

„ tribromotoluidine 69.76 „

Whence it appears that the crystals consist of a mixture of di- and tri-bromotoluidine; on distilling them with steam, a distillate of lower melting point (78—84°) came over first, followed by a portion of higher melting point (98—99°). We found the melting point of the tribromometatoluidine, prepared by the direct action of bromine upon an acid solution of metatoluidine, after purification, to be 100—101.6°. (Wroblewsky gives 97°.) The portion which had remained undissolved in hydrochloric acid was repeatedly distilled with steam, rejecting the last portions. The distillate thus purified was recrystallised from alcohol, and thus we obtained one portion (the largest by far) of m. p. 74.6—75.5°. This appeared to consist of a single dibromotoluidine.

Analysis:—

Employed .. 0.2241 AgBr = 0.3207 = 60.89 per cent. Br.

Theory requires 60.38 per cent. Br.

On boiling it with glacial acetic acid for 30 or 40 hours, it gave an acetyl-compound which, after purification and recrystallisation, melted at 168—168.6°.

The mother-liquids contained a substance of lower melting point, 33—35°.

According to the theory laid down at the beginning of this paper, two different dibromotoluidines could be produced, viz.,

and we concluded that in all probability these were the two, although we could not be sure of their purity.

We now converted them into dibromotoluenes, and from the first (m. p. 74.6—75.5°) we obtained an oil which did not solidify at -20°.

Analysis:—

Employed .. 0.1871 AgBr = 0.2834 = 64.32 per cent. Br.

On nitration at ordinary temperatures without cooling, this gave a mixture of nitro-compounds separable by recrystallisation from alcohol into one of melting point 80—80.6°, crystallising in white needles.

Analysis :—

Employed .. 0.2512 AgBr = 0.3248 = 55.01 per cent. Br.

Analysis of a portion melting lower, 75—80° :—

Employed .. 0.1396 AgBr = 0.1741 = 53.06 per cent. Br.

Theory for mononitrodibromotoluene being 54.23 per cent. Br, and another of higher melting point, 128—129°, which proved on analysis to be a mixture of di- and tri-nitrodibromotoluene : this crystallised in scales.

Analysis :—

Employed .. 0.1685 AgBr = 0.1765 = 44.57 per cent. Br.

„ .. 0.0762 AgBr = 0.0787 = 43.94 „

Theory for dinitrodibromotoluol requires 47.05 per cent. Br; theory for trinitrodibromotoluol requires 41.04 per cent. Br. Also a substance in small quantity melting below 80°.

We also converted this dibromotoluene into a dibromobenzoic acid by heating it with dilute hydric nitrate, and thus obtained one which after purification melted at 167—169°.

Analysis :—

Employed .. 0.0722 AgBr = 0.0959 = 56.52 per cent. Br.

Theory for dibromobenzoic acid requires 57.14 per cent. Br.

If the dibromotoluene was kept cool by cold water during nitration the trinitro-compound did not appear to be formed.

From the other substance (m. p. 33—35°) we also obtained by removal of the amido-group, an oil which did not solidify at -20°. This gave on nitration a mixture which by recrystallisation from alcohol we separated into a compound melting at 159—161°, and not freely soluble in alcohol, from which it crystallised in long fine needles; and another in small quantity melting below 80°. This dibromotoluene when heated with nitric acid also gave a dibromobenzoic acid melting at 150—167°.

The behaviour of these two dibromotoluenes with fuming nitric acid shows that they are different from any of the four above described, and therefore that their constitutions must be 1 : 2 : 4 and 1 : 2 : 6. The question remains as to which is which. To determine this we endeavoured to prepare them in other ways. For the preparation of 1 : 2 : 4 we took ordinary dinitrotoluene (m. p. 70°) which is known to have this constitution; from it we prepared orthonitroparatoluidine (m. p. 77—78°) by reduction with alcoholic ammonium sulphide; from this we obtained orthonitroparabromotoluene (m. p. 44.4—45.2°) by the diazoperbromide reaction. This crystallised in beautiful large monoclinic tables, which on reduction gave parabromorthotoluidine

(m. p. 30—31°); and this by the diazoperbromide reaction gave us 1 : 2 : 4 dibromotoluene. This, after removal of some adhering cresol by potassic hydrate and distillation with steam, proved to be an oil not solidifying at -20°. On nitrating it with fuming nitric acid, and recrystallising the product from alcohol, needles were obtained melting at 80·5—81·3°.

Analysis:—

Employed .. 0·1596 AgBr = 0·2059 = 54·32 per cent. Br.

Another lot. The portion melting at 74—80° gave—

Employed .. 0·1472 AgBr = 0·1873 = 54·14 per cent. Br.

Some crystals in scales were also obtained, m. p. 128—129°.

Analysis:—

Employed .. 0·1314 AgBr = 0·1545 = 50·03 per cent. Br.

The dibromotoluene was also converted into dibromobenzoic acid by heating it with nitric acid. It crystallised from the acid solution in colourless tables in the same manner as the dibromobenzoic acid obtained from the first of the two above-described dibromotoluenes, and melted after purification at 168—170°.

Analysis:—

Employed .. 0·2461 AgBr = 0·3319 = 57·38 per cent. Br.

Theory requires 57·14 per cent.

This result agrees then very well with that obtained from the larger portion of the dibromometatoluidine, and points to the conclusion that the second atom of bromine takes up principally the position para to CH₃, a certain amount taking the ortho-position, and forming 1 : 2 : 3 : 6 dibromotoluidine.

To test the theory further, we endeavoured to prepare the 1 : 2 : 4 dibromotoluene in another way, viz., from 1 : 3 : 4 monobromotoluidine. This we prepared by the diazoperbromide reaction from mononitroparatoluidine. The metanitroparabromotoluene melted at 31—32°. This reduced with tin and hydrochloric acid gave an amido-compound which, after distillation with steam and recrystallisation from alcohol, melted at 30·6—32°.

Analysis:—

Employed .. 0·2063 AgBr = 0·2067 = 42·63 per cent. Br.

Theory for monobromotoluidine = 43·01.

Wroblewsky (*Jahresb.*, 1870, 527) says that it melts at 67°, but he also finds the bromnitrotoluene from which it is derived to be a liquid, and not solid at -20°. Hübner and Roos (*Ber.*, 1873, 800) say that it melts at 75°, although, they find the same melting point for the nitro-

bromotoluene as we do. We, however, prepared it several times, and always got very nearly the same melting point, and we cannot help thinking it possible that the parabromotoluene from which Hübner and Roos prepared their nitro-compound may have been mixed with some other bromotoluene, which may possibly have given metanitro-orthobromotoluene, and although this may not much have affected the melting point of the metanitroparabromotoluene, yet on reduction the amido-compound may have had a greater effect.

We next converted the bromotoluidine into aceto-compound by 30 or 40 hours' heating with the strongest glacial acetic acid with a reversed condenser. The product washed with water, freed from toluidine by extraction with hydrochloric acid, and recrystallised from water, melted at $113.7-114.6^{\circ}$. This was suspended in water, and two atomic proportions of bromine in aqueous solution added; the mixture was heated on a water-bath, but this was not found sufficient to cause complete absorption, and it was found necessary to redissolve the aceto-compound in alcohol and reprecipitate it with water, in order to get it into a sufficiently fine state of division; it then absorbed the bromine better. It was then decomposed by heating it with 2 vols. of sulphuric acid and one of water, precipitated with water, filtered, and the salt decomposed with sodic carbonate and distilled with steam. We thus obtained a dibromotoluidine which, after recrystallisation from alcohol, melted at $74.5-75.8^{\circ}$, and by boiling with glacial acetic acid for 30 to 40 hours, and subsequent purification, we obtained from it an aceto-compound melting at $168-168.6^{\circ}$.

The dibromotoluidine was now treated with nitrous gas and alcohol for the removal of the amido-group; an oil was thus obtained, which when heated with nitric acid gave a dibromobenzoic acid, m. p. $166-168^{\circ}$.

Analysis :—

Employed .. $0.2667 \text{ AgBr} = 0.3608 = 57.56 \text{ per cent. Br.}$

Theory requires 57.14 per cent.

On nitrating the dibromotoluene, needles were obtained melting at $78-80^{\circ}$.

These experiments then seem to confirm clearly the purity and constitution of the substance m. p. $74.5-75.5^{\circ}$ obtained from metatoluidine.

Fittig describes a dibromotoluene melting at $107-108^{\circ}$, which Wroblewsky considers to be 1 : 2 : 4. We have been unable to obtain any dibromotoluene melting at this point or anywhere near it.

We now endeavoured to prepare the dibromotoluene 1 : 2 : 6. We first tried to obtain it from dinitroparatoluidine, hoping to obtain therefrom a dinitrotoluene of the constitution 1 : 3 : 5, and then by a

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reduction, first of one and then of the other nitro-group, and intermediate bromination, to get first nitrometatoluidine ($\text{CH}_3.\text{NO}_2.\text{NH}_2$) then $\text{CH}_3.\text{Br}.\text{NO}_2.\text{NH}_2$ by introduction of bromine; then $\text{CH}_3.\text{Br}.\text{NO}_2$; then $\text{CH}_3.\text{Br}.\text{NH}_2$; next $\text{CH}_3.\text{Br}.\text{NH}_2.\text{Br}$; and finally $\text{CH}_3.\text{Br}.\text{Br}$.

In this, however, we were not successful, as up to the present we have not been able to get beyond the first step, as we have failed in taking out the amido-group from the dinitroparatoluidine. We have heated it with alcohol saturated with nitrous gas under a pressure of two atmospheres, and although a small quantity of substance has been obtained melting at $68-75^\circ$, yet the quantity is far too small to hold out any prospect of obtaining in this manner the desired dibromotoluene, except at an expenditure of time and material quite incommensurate with the object to be attained.

The second plan we tried promised better results. We took the acetyl compound of orthobromometatoluidine. This we nitrated by solution in a mixture of 1 volume nitric acid 1520 and 2 volumes 1450. It was then precipitated with water, washed, recrystallised from alcohol, m. p. $110-121^\circ$, and dissolved in a mixture of 2 vols. sulphuric acid and one of water by the aid of heat. This when cold was precipitated by water containing 1 molecular proportion of bromine in solution; in this way we obtained a dibromonitrometatoluidine which after crystallisation from alcohol melted at $124-130^\circ$.

Analysis:—

Employed .. 0.1220 AgBr = 0.1465 = 51.09 per cent. Br.
 „ .. 0.1975 AgBr = 0.2381 = 51.29 „

Theory, $\text{C}_6\text{H}_4.\text{CH}_3.\text{Br}_2.\text{NO}_2.\text{NH}_2$ = 51.61 per cent. Br.

In order to determine the constitution of the bromonitro-compound first obtained before the bromination (m. p. $110-121^\circ$) we dissolved it in a mixture of 2 volumes hydric sulphate and 1 volume water, precipitated with water, and recrystallised it from alcohol, thereby obtaining a compound of m. p. $179-181^\circ$.

Analysis:—

Employed .. 0.2060 AgBr = 0.1668 = 34.45 per cent. Br,
 together with a much smaller quantity of a substance of m. p. $102-103^\circ$.

Analysis:—

Employed .. 0.1587 AgBr = 0.1257 = 33.70 per cent. Br.

Theory for bromonitrotoluidine requires 34.63 per cent.

The portion melting at $179-181^\circ$ was treated with nitric acid and a current of nitrous acid, and gave on precipitation with a

solution of bromine in potassic bromine a yellow perbromide getting scarlet on drying. This decomposed with acetic acid and precipitated by water, and recrystallised from alcohol, melted at 87°.

Analysis:—

Employed .. 0.1076 AgBr = 0.1360 = 53.78 per cent. Br.

Theory for dibromonitrotoluene = 54.23 per cent.

This was reduced with iron and acetic acid, and gave on distillation an amido-compound which after crystallisation from alcohol melted at 84.6—85°.

Analysis:—

Employed .. 0.0895 AgBr = 0.1257 = 59.76 per cent. Br.

Theory for dibromotoluidine = 60.37 per cent. Br.

Some of this was converted into perbromide and decomposed with acetic acid, and thus gave crystals which after recrystallisation from alcohol melted at 110—111.5°.

Analysis:—

Employed .. 0.1158 AgBr = 0.1974 = 72.53 per cent. Br.

Theory for tribromotoluene = 72.94 per cent.

This agrees with a tribromotoluene which we shall show later to have the constitution 1 . 2 . 4 . 5.

This shows that inasmuch as the positions 2 and 5 were occupied originally by bromine and the amido-group respectively, the nitro-group must have taken the position 4. Hence the constitution of the dibromonitrotoluene m. p. 87° must be $\text{CH}_3 \cdot \underset{1}{\text{Br}} \cdot \underset{2}{\text{Br}} \cdot \underset{4}{\text{NO}_2} \cdot \underset{5}{\text{Br}}$, and of the amido-compound m. p. 84.6—85° $\text{CH}_3 \cdot \underset{1}{\text{Br}} \cdot \underset{2}{\text{Br}} \cdot \underset{4}{\text{NH}_2} \cdot \underset{5}{\text{Br}}$.

These compounds agree very closely with the dibromonitrotoluene and dibromotoluidine obtained from the dibromotoluene 1 . 2 . 5, and thus seem to show us that on nitrating that compound the NO₂ takes the position para to CH₃.

This, then, shows us that the compound which we obtain by nitrating monobromometatoluidine must have the constitution $\text{CH}_3 \cdot \underset{1}{\text{Br}} \cdot \underset{2}{\text{NO}_2} \cdot \underset{4}{\text{NH}_2} \cdot \underset{5}{\text{Br}}$. On brominating this the two positions 3 and 6 are open, and therefore the compound produced must either be $\text{CH}_3 \cdot \underset{1}{\text{Br}} \cdot \underset{2}{\text{Br}} \cdot \underset{3}{\text{Br}} \cdot \underset{4}{\text{NO}_2} \cdot \underset{5}{\text{NH}_2}$ or $\text{CH}_3 \cdot \underset{1}{\text{Br}} \cdot \underset{2}{\text{Br}} \cdot \underset{4}{\text{NO}_2} \cdot \underset{5}{\text{NH}_2} \cdot \underset{6}{\text{Br}}$.

We now took out the amido-group by treating the dibromonitrotoluidine (m. p. 124—130°) with ethyl nitrite, and thus obtained a dibromonitrotoluene (1 . 2 . 3 . 4 or 1 . 2 . 4 . 6), melting at 56.8—57°.

Analysis:—

Employed .. 0.1489 AgBr = 0.1886 = 54.89 per cent. Br.

Theory requires 54.23 per cent. Br.

This, reduced with tin and hydrochloric acid, gave a dibromamido-compound melting at 87—88°.

Analysis:—

Employed .. 0.1376 AgBr = 0.1931 = 59.71 per cent. Br.

Theory for dibromotoluidine = 60.37 per cent.

On treating this with ethyl nitrite a dibromotoluene was obtained as an oil (not solidifying at -10°).

On dissolving it in nitric acid 1520 it became slightly warm and slowly dissolved. After some time strong colourless needles crystallised out. These, crystallised from alcohol, after purification with animal charcoal, melted at 161.6—162.2.

Analysis:—

Employed .. 0.1185 AgBr = 0.1303 = 46.78 per cent. Br.

„ .. 0.1690 AgBr = 0.1880 = 47.33 „

Mean = 47.05 per cent.

Theory for $C_6H_5CH_3.Br_2(NO_2)_2$ is 47.06 per cent.

Now the above described dibromotoluene must, as we have shown, have either the constitution 1 : 2 : 3 or 1 : 2 : 6, and, as will be easily seen, it is quite different in its characteristics from the dibromotoluene 1 : 2 : 3 above described; it must therefore have the constitution 1 : 2 : 6. Moreover it agrees very closely with the dibromotoluene obtained from the dibromotoluidine of lower melting point, obtained from dibromometatoluidine, which we showed above must in all probability have this constitution.

TRIBROMOTOLUENES.

We have also prepared the six isomeric tribromotoluenes as follows:—

$C_6H_3Br_3.Br.Br.H.Br.H$, from the diazoperbromide of dibromorthotoluidine. It crystallises from alcohol in long flat colourless needles, m. p. 52—53°.

Analysis:—

Employed .. 0.0993 AgBr = 0.1703 = 72.97 per cent. Br.

Theory for tribromotoluene requires 72.94 per cent.

Dissolved in nitric acid sp. gr. 1520 and precipitated with water, it gives a nitro-compound, which after crystallisation from alcohol melts at 95—170°.

$C_6H_3.H.Br.Br.Br.H$, from the diazoperbromide of dibromopara-dine, m. p. 88—89°.

Analysis :—

Employed .. 0.5161 $AgBr = 0.8866 = 73.07$ per cent. Br.

$C_6H_3.H.Br.Br.H.Br$, from the diazoperbromide of the dibromometatoluidine m. p. 74—75.5°, which we showed before to have the constitution $C_6H_3.H.NH_2.Br.H.Br$. It crystallises from alcohol in colourless long shining needles, m. p. 111.2—112.8°.

Analysis :—

Employed .. 0.4052 $AgBr = 0.6920 = 72.66$ per cent. Br.

$C_6H_3.Br.Br.Br.H.H$. This was obtained as follows :—Metabromometanitroparatoluidine was converted into diazoperbromide, and from this metabrommetanitroparabromotoluene prepared—

This melted at 62—63.6°, and crystallised from alcohol in colourless leaves.

Analysis :—

Employed .. 0.3565 $AgBr = 0.4564 = 54.47$ per cent. Br.

Theory for dibromonitrotoluene = 54.24 per cent. Br.

This was reduced with iron and acetic acid, and gave an amido-compound which crystallised from alcohol in long colourless needles or flat prisms, m. p. 58—59°.

Analysis :—

Employed .. 0.3551 $AgBr = 0.5014 = 60.08$ per cent. Br.

Theory for dibromotoluidine = 60.37 per cent.

This was converted into aceto-compound of m. p. 162—163° by 24 hours' boiling with the strongest glacial acetic acid. It was then suspended in water and brominated. We thus obtained a tribromacetotoluid, m. p. 171—173°, crystallising from alcohol in white needles. This decomposed with alcoholic potash gave a tribromotoluidine, m. p. 96—96.8°.

Analysis :—

Employed .. 0.0914 $AgBr = 0.1485 = 69.13$ per cent. Br.

Theory for tribromotoluidine = 69.76 per cent. Br.

This decomposed with nitrous acid and alcohol gave us a tribromotoluene m. p. 44.4—44.7°.

Analysis :—

Employed .. 0.0965 $AgBr = 0.1636 = 72.14$ per cent. Br.

Theory for tribromotoluene = 72.94 per cent. Br.

On nitrating this by solution in nitric acid, sp. gr. 1.520, and pre-

cipitating with water, a nitro-compound is obtained, melting at first at $97-98^{\circ}$, but by frequent recrystallisations giving about $106-107^{\circ}$ as m. p.

This sufficiently distinguishes this tribromotoluene from the one above described of m. p. $52-53^{\circ}$, and which gives a nitro-compound m. p. $95-170^{\circ}$.

$C_6H_3Br_3.H.H.Br.$ —This we obtained from Wroblewsky's bromonitrothotoluidine, m. p. 143° , which we showed above had the constitution $C_6H_3NH_2.NO_2.H.Br.H$, by converting it into dibromonitrotoluene by the diazoperbromide reaction. This melted at $69.5-70.2^{\circ}$.

Analysis:—

Employed.. $0.3090 \quad AgBr = 0.3959 = 54.51$ per cent. Br.

Theory 54.24 per cent. Br.

This we reduced with tin and hydrochloric acid, and thus obtained an amido-compound easily soluble in alcohol, m. p. $72.5-73.1^{\circ}$.

Analysis:—

Employed.. $0.1208 \quad AgBr = 0.1711 = 60.26$ per cent. Br.

Theory for dibromotoluidine = 60.37 per cent. Br.

This, boiled with glacial acetic acid, gave us an acetyl-compound, m. p. $144-145^{\circ}$. By suspending this in a state of fine division in water, and adding 2 atomic proportions of bromine, we obtained a tribromaceto-compound melting at $179-181^{\circ}$. On taking out the aceto-group from this by eight hours' boiling with alcoholic potash, we obtained a tribromotoluidine melting at $93-94^{\circ}$.

Analysis:—

Employed.. $0.1328 \quad AgBr = 0.2159 = 69.18$ per cent. Br.

Theory for tribromotoluidine requires 69.76 per cent. Br.

On treating this with nitrous gas and alcohol we obtained the tribromotoluene in flat needles melting at $58-59^{\circ}$.

Analysis:—

Employed.. $0.1238 \quad AgBr = 0.2128 = 73.13$ per cent. Br.

Theory for tribromotoluene = 72.94 per cent. Br.

Now, from the method of formation of this tribromotoluene it will be seen that it must have the constitution $C_6H_3Br_3.H.H.Br.Br.H$, or $C_6H_3Br_3.H.H.Br.Br.$ The former of these is the one obtained from dibromometatoluidine perbromide, and described above, m. p. $111.2-112.8^{\circ}$; therefore this one must have the latter constitution.

This tribromotoluene gives on nitration with nitric acid sp. gr. 1.520 a nitro-compound of m. p. $89-91^{\circ}$; recrystallised, $91-91.4^{\circ}$.

$C_6H_3Br_3.H.H.Br.H.Br.$ —This was prepared from tribromometatoluidine, melting at $100-101.6^{\circ}$.

Analysis:—

Employed .. 0.1629 AgBr = 0.2650 = 69.22 per cent. Br.

Theory for tribromotoluidine = 69.76 per cent. Br.

As this tribromotoluidine can be obtained by the bromination of the dibromometatoluidine, which we showed must have the constitution $C_6H_3Br_2H$, it must have either the constitution $C_6H_3Br_3H$, or $C_6H_3Br_2H$; on decomposing it with alcohol and nitrous gas it gives a tribromotoluene which melts at 66° .

Analysis:—

Employed .. 0.1442 AgBr = 0.2476 = 73.06 per cent. Br.

Theory for tribromotoluene = 72.94 per cent. Br. This shows that it cannot have the constitution $C_6H_3Br_3H$, for the tribromotoluene which would be derived from this is described above as melting at 44.4 — 44.7° .

On nitrating this tribromotoluene it gives a dinitro-compound melting at 217 — 220° .

Analysis:—

Employed .. 0.1106 AgBr = 0.1499 = 57.66 per cent. Br.

Theory for dinitrotribromotoluene = 57.28 per cent. Br.

TETRABROMOTOLUENES.

We have also prepared the three possible tetrabromotoluenes.

$C_6H_3Br_4H$.—This we prepared from tetrabromometatoluidine, which we obtained by acting with bromine in aqueous solution upon a hydrochloric acid solution of metabromometatoluidine (m. p. 35 — 37°), we thus obtained a copious white flocculent precipitate which, after purification by boiling with animal charcoal in alcohol, in which it is not very soluble, crystallised therefrom in white needles, melting at 223 — 224° . This decomposed by boiling with alcohol and nitrous gas gave us a tetrabromotoluene melting at 105 — 108° .

Analysis:—

Employed .. 0.0763 AgBr = 0.1403 = 78.24 per cent. Br.

Theory requires for tetrabromotoluene 78.43 per cent. Br. This was also prepared from tribromometatoluidine perbromide, and was thus obtained of melting point 106.8 — 108° .

Analysis:—

Employed .. 0.2191 AgBr = 0.4015 = 77.97 per cent. Br.

On nitration with nitric acid, sp. gr. 1.520, precipitation with water and recrystallisation from alcohol, a nitro-compound was obtained melting at 215 — 216° .

$C_6H_3Br_4H$.—This was obtained from tribromometatolu-

idine ($\text{C}_6\text{H}_3\text{Br}_2\text{NH}_2$, m. p. 93—94°, described on page 448) by the diazoperbromide reaction. In this way it was obtained of m. p. 116—117°.

Analysis:—

Employed.. 0.1041 $\text{AgBr} = 0.1924 = 78.64$ per cent. Br.

This nitrated with nitric acid, sp. gr. 1.520, precipitated with water and recrystallised from alcohol, gave a nitro-compound melting at 213°.

$\text{C}_6\text{H}_3\text{Br}_3$.—This was obtained from tribromometatoluidine ($\text{C}_6\text{H}_3\text{Br}_2\text{NH}_2$, m. p. 96—96.8°, described on page 447) by the diazo-perbromide reaction, and melted at 111.0—111.5°.

Analysis:—

Employed.. 0.1230 $\text{AgBr} = 0.2255 = 78.01$ per cent. Br.

This gave a nitro-compound melting at 212°.

Pentabromotoluene was obtained from the diazo-perbromide of tetrabromometatoluidine (m. p. 223—224°). After crystallisation from either acetic acid or alcohol, in neither of which is it freely soluble, and from both of which it crystallises in white needles, it melts at 283—285°.

Analysis:—

Employed.. 0.0918 $\text{AgBr} = 0.1782 = 82.59$ per cent. Br.

Theory requires 82.14 per cent. Br.

This agrees with the melting point (282—283°) given by Gustavson (*Bull. Soc. Chim.* [2], 28, 347).

In volume viii of Watts' Chemical Dictionary, p. 221, after some remarks on the melting points of the different nitro-, bromo-, and other derivatives of benzene, it is said "that the more symmetrical the constitution of a benzene-derivative, the greater is the resistance which it offers to the passage from the liquid to the solid state." This remark seems not to apply to the derivatives of toluene,* as the tribromotoluene ($\text{C}_6\text{H}_3\text{Br}_3$) which, according to this, should melt the highest of the six tribromotoluenes, melts at 66°, while ($\text{C}_6\text{H}_3\text{Br}_2\text{H}$) and ($\text{C}_6\text{H}_3\text{Br}_2\text{H}$) both melt considerably higher.

We subjoin to this a table of the various bromine-derivatives of toluene, and hope to give in a future communication a further table of the other derivatives above described, together with some derivatives which we have not described.

In conclusion, we should like to make a few remarks upon some of the processes which we have used.

* The remark in question was intended to apply only to benzene-derivatives containing 6 atoms of carbon, the melting points of which are given in the volume above referred to (pp. 217—220).—H. W.

TABLE.

1	2	3	4	5	6		Product of nitration with HNO ₃ . Sp. gr. 1.520.	Product by reduction of above.	Benzoic Acid.
CH ₃	Br	—	—	—	—	Fluid, b. p. 182–183°.	<p>These monobromotoluenes have not been investigated by us, as they appear to have been sufficiently previously investigated.</p> <p>Mononitro, 88–89°</p> <p>Mononitro, 56·5–57·5°</p> <p>Two dinitro, 157·5–158° and 105° ..</p> <p>Mononitro, 86·6–87·5°</p> <p>Mononitro, 80–81° and others ..</p> <p>Dinitro, 161·6–162·2°</p> <p>M. p. 95–170°</p> <p>—</p> <p>M. p. 106–107°</p> <p>M. p. 91–91·4°</p> <p>M. p. 217–220° dinitro</p> <p>M. p. 215–216°</p> <p>M. p. 213°</p> <p>M. p. 212°</p> <p>—</p>	<p>84–85°</p> <p>52–53</p> <p>—</p> <p>97–98</p> <p>—</p> <p>—</p> <p>—</p> <p>—</p> <p>—</p> <p>—</p> <p>—</p>	<p>With HNO₃, 151–153°</p> <p>With HNO₃, 147–149°</p> <p>With CrO₃, 208–210°</p> <p>With CrO₃, 232–233°</p> <p>With HNO₃, 168–170°</p> <p>—</p> <p>—</p> <p>—</p> <p>—</p> <p>—</p> <p>—</p>
CH ₃	—	Br	—	—	—	Fluid, b. p. 184°			
CH ₃	—	—	Br	—	—	M. p. 28·5°, b. p. 185° ..			
CH ₃	Br	—	—	Br	—	Fluid			
CH ₃	Br	Br	—	—	—	M. p. 27·4–27·8°			
CH ₃	—	Br	—	Br	—	M. p. 39°			
CH ₃	—	Br	Br	—	—	Fluid			
CH ₃	Br	—	Br	—	—	Fluid			
CH ₃	Br	—	—	Br	Br	Fluid			
CH ₃	Br	Br	—	Br	—	M. p. 52–53°			
CH ₃	—	Br	—	Br	—	M. p. 88–89°			
CH ₃	Br	—	Br	Br	—	M. p. 111·2–112°			
CH ₃	Br	—	Br	—	—	M. p. 44·4–44·7°			
CH ₃	Br	Br	Br	—	Br	M. p. 58–59°			
CH ₃	Br	—	—	—	—	M. p. 66°			
CH ₃	Br	—	Br	—	Br	M. p. 106·8–108°			
CH ₃	Br	Br	Br	—	Br	M. p. 116–117°			
CH ₃	Br	Br	—	Br	Br	M. p. 111–111·5°			
CH ₃	—	Br	Br	Br	Br	M. p. 283–285°			

In the first place, as to the diazoperbromide reaction for the substitution of bromine for the amido-group. We have always proceeded thus: first taking the toluidine, we have treated it with a mixture of about two volumes of nitric acid, sp. gr. 1360, to one of water. We have then introduced nitrous gas until the substance was nearly or completely dissolved. After filtering we have then added bromine dissolved in potassic or sodic bromide. After filtering out the perbromide which, in every case with which we have dealt, was precipitated either as a solid or as an oil quickly becoming so, and slightly washing with ether, we always decomposed it by means of glacial acetic acid at as low a temperature as was found capable of causing the decomposition. We adopted this method, as we found that absolute alcohol gave very untrustworthy results; in one case, on decomposing the perbromide of orthodiazodibromotoluene with alcohol, we got the whole simply as dibromotoluene. We also found that by *boiling* the perbromide with acetic acid we frequently caused the introduction of bromine into other places than that to which the diazo-group was connected.

It appeared to us, however, that by simply warming the acetic acid in a water-bath, just sufficiently to keep up a brisk reaction, the operation succeeded well.

The acetic acid we used was supplied by Messrs. Hopkin and Williams, and described as glacial at 60°. Some that we tried, described glacial at 50°, did not appear to us to answer so well.

For the elimination of the amido-group we generally acted thus:—The substance was first treated with a solution of nitrous gas in absolute alcohol, slightly warmed till gas was freely given off, allowed to cool, and then resaturated with nitrous gas, this being repeated until no considerable amount of gas was evolved on heating.

To dry the nitrous gas we used sulphuric acid kept warm in a water-bath to prevent the chamber crystals formed from becoming sufficiently solid to stop the passage of the gas.

We found the use of calcium chloride to be attended with grave objections, in some instances producing chlorinated compounds in the substances submitted to the action of the nitrous gas.

For reduction of the nitro-group tin and hydrochloric acid were mostly used. Here, however, we found it to be necessary not to use the hydrochloric acid too strong, as some substances, metanitrotoluene for example, were acted upon in such a way as to produce a chlorotoluidine instead of the substance desired. Sometimes we found iron and acetic acid to act better.

To form the dibromobenzoic acids where a mixture of chromic and acetic acids was not available, we used a mixture of 1 vol. nitric acid, sp. gr. 1360, to 3 vols. of water; sometimes boiling the dibromo-

toluene simply in a retort with a condenser, but more often heating it in a sealed tube to whatever temperature was found necessary.

To form acetyl-compounds we always found it sufficient to heat the amido-compound for at the most two or three days with the strongest acetic acid (glacial at 60°), never finding it necessary to use acetyl chloride or acetic anhydride.

In order to purify amido-compounds whose salts were decomposed by water, from any unchanged nitro-compound which might accompany them, the substance obtained by distilling with water was dissolved in ether, and precipitated with hydrochloric or sulphuric acid. The ether was then poured off, and the residue washed once or twice with ether, the salt being finally decomposed with sodic carbonate.

We wish to take this opportunity of expressing our sense of the care and diligence with which Mr. F. W. Streatfield has carried out the innumerable bromine-determinations required in the above research.