138. *An Interpretation of the Sandmeyer Reaction.*

By HERBERT H. HODGSON, STANLEY BIRTWELL, and JOHN WALKER.

Cuprous halides react with diazonium salts mainly by two mechanisms: (1) The formation of a complex anion with halogen acid; attack by the anionoid halogen of this complex at the kationoid aryl-carbon atom to which the diazonium group is linked; release of an electron from the halogen to the nitrogen *via* the carbon; and final covalent linking of halogen to the carbon.

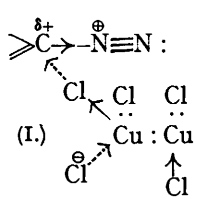
(2) Oxidation of the cuprous halide to the cupric state by the kationoid diazonium ion, which involves release of an electron by the copper to the nitrogen, with subsequent linkage of the aryl radicals produced, to form diaryls.

The direct action of hydriodic acid on diazonium salts is explicable by mechanism (1).

IT is stated by Hammett (" Physical Organic Chemistry," McGraw-Hill Book Co., New York and London, 1940, p. 295) that " the *characteristic* effect of cuprous compounds in the Sandmeyer reaction has no obvious explanation," and by Sidgwick (" Organic Chemistry of Nitrogen," Oxford, Clarendon Press, 1937, p. 407) that the action of metallic copper is not understood. In an attempt to solve this problem the present authors submit an interpretation of the Sandmeyer reaction and its variations based on a mechanism whereby the exceedingly stable halogen ions involved are rendered reactive (*i.e.*, are somewhat destabilised) by cuprous salts acting purely as catalysts, which convert them into nucleophilic (anionoid) reagents by a temporary sharing of their stable octets. This interpretation is subsequently extended to explain the similar catalytic action of cupric salts, the experimental results of Hantzsch and Blagden (*Ber.*, 1900, **33**, 2544), the anomalous behaviour of fluorine compounds, and the sole exception to the general reaction of iodides with diazonium compounds reported by Cumming and Muir (*J. Roy. Tech. Coll.*, 1936, **3**, 562). Finally, the formation of diaryls in the Sandmeyer reaction is shown to be a consequence of an oxidation-reduction mechanism involving conversion of cuprous into cupric salts.

Mixed Sandmeyer Reactions.—Eight arylamines (see Table I) were diazotised by the Hodgson–Walker method (J., 1933, 1620), and the products decomposed in two ways: (*a*) By cuprous chloride dissolved in concentrated hydrobromic acid; the weights of 4-chloro- and 4-bromo-1-nitrobenzene which resulted were in the ratio of *ca.* 4 : 96. (*b*) By cuprous bromide dissolved in concentrated hydrochloric acid; the ratio then shifted to 60 : 40. This distribution superficially contradicts the results of Hantzsch and Blagden (*loc. cit.*) which indicated the halogen to come from the cuprous salt, since in (*a*) the halogen apparently comes directly from the acid. It will be shown, however, that there is complete harmony between all the data.

To interpret these results, the dissolution of cuprous chloride and bromide in hydrobromic acid and hydrochloric acid respectively is assumed to form a complex anion, *e.g.*, $[Cu_2Cl_2Br_2]^{--}$ (cf. Saunders, " The Aromatic Diazo-Compounds," E. Arnold and Co., London, 1936, p. 154 *et seq.*, for a resumé of the literature on the subject) and in this complex the bromine (see later) will be more reactive than the chlorine.

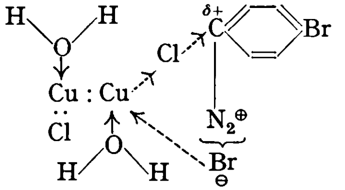

(I.)

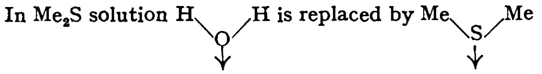
The mechanism of decomposition of aryldiazonium chlorides by cuprous chloride dissolved in hydrochloric acid could be then envisaged as follows: Attraction of the complex anion $[Cu_2Cl_4]^{--}$ to the diazonium kation, decomposition of the complex (I) in the sequence ----- release of an electron at the carbon with separation of neutral chlorine, evolution of nitrogen and linkage of neutral chlorine to the aryl radical -----, followed by rehabilitation of the complex anion by co-ordination with an external chloride anion.

For decomposition (*a*) the mixed complex will react by a bromine atom at the kationoid carbon of the diazonium ion, since bromine is more reactive than chlorine owing to its exterior electrons being less under control by the positive nucleus (cf. also Schwechten, *Ber.*, 1932, **65**, 1605). Moreover, release of a bromine ion from the copper to the kationoid carbon entails immediate replenishment of bromine to the copper from the bromine ions in solution, so that a preponderance of bromo-compound will be formed (*ca.* 96% in the case of *p*-nitroaniline). It is reasonable to assume, however, that some of the complex anions will be in an environment where chlorine can be more reactive than bromine and in this case chloro-compound will result (*ca.* 4% for *p*-nitroaniline).

For decomposition (*b*) the same complex anion will be formed and bromine as before will displace the group initially, but in this case the depleted copper anions will be replenished by chlorine anions from the solution, whereby chloro-complexes will now gradually take the place of the chloro-bromo-cuprous anions and the resulting mixture of chloro- and bromo-aryls will in consequence possess a more even distribution of the halogens than in (*a*). Actually the chloro-compound predominates (60—70%), as would be expected.

The Hantzsch–Blagden Data.—In these experiments (*loc. cit.*), the diazonium salt (1 mol.) was treated with cuprous halide (1 mol.) in aqueous suspension and also in methyl sulphide solution. When (*a*) cuprous chloride reacted with *p*-bromobenzenediazonium bromide, the main product was *p*-chlorobromobenzene, and (*b*) when cuprous bromide reacted with *p*-bromobenzenediazonium chloride, the main product was *p*-dibromobenzene. From the above point of view it would appear that an incipient complex anion is formed in each case (II) between the cuprous halide and co-ordinating solvent ions, *viz.*, water and methyl sulphide respectively. Reaction would then occur *via* (*a*) chlorine, and (*b*) bromine, with formation of *p*-chlorobromobenzene in (*a*), and *p*-dibromobenzene in (*b*). The halogen atoms from the diazonium salt will then replace the departing halogen of the complex (II) and so tend to form the other halogen derivative in minor yield, as found by Hantzsch and Blagden. The contention of Hantzsch that the halogen came from the cuprous salt is therefore valid, but if he had carried out the mixed Sandmeyer experiments described by the present authors, especially where nearly 100% of bromo-compound resulted when cuprous chloride was employed in hydrobromic acid solution, the erroneous deduction that the halogen came directly from the acid would have been well nigh irresistible. The more vigorous reaction obtained when methyl sulphide was employed in homogeneous medium would be expected from the greater abundance of the copper complex and its greater negativity due to the more permanent co-ordination with methyl sulphide than with the polarised water molecules.


(II.)


In Me$_2$S solution is replaced by

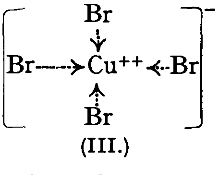
A series of experiments (Table III) with *p*-nitrobenzenediazonium chloride and a constant weight of cuprous bromide dissolved in various amounts of concentrated hydrochloric acid showed that, as the cuprous bromide concentration decreased, the amount of replacement by chlorine increased, though not proportionately, as would be expected.

Copper as Catalyst in the Sandmeyer Reaction.—Gattermann's substitution of metallic copper for cuprous halide was tested for mixed halogen acids by (*a*) diazotising *p*-nitroaniline in hydrochloric acid, adding the equivalent of hydrobromic acid, and treating the mixture with copper powder; (*b*) diazotising *p*-nitroaniline in concentrated sulphuric acid, adding concentrated aqueous solutions of sodium chloride and sodium bromide, and then decomposing the mixture with copper powder. For comparison, *p*-nitroaniline was diazotised by the Hodgson–Walker method (*loc. cit.*), and the product treated separately with a solution of (*c*) cuprous bromide and (*d*) cuprous chloride in a mixture of hydrochloric and hydrobromic acids. In both (*a*) and (*b*), 4-bromonitrobenzene was formed in over 85% yield together with *p*-nitrophenol. Almost theoretical yields of halogenonitrobenzenes were obtained in (*c*) and (*d*), the distribution being (*c*) 96% of 4-bromo- and 4% of 4-chloro-nitrobenzene, (*d*) 94% of 4-bromo- and 6% of 4-chloro-nitrobenzene; *p*-nitrophenol was absent in both experiments. The overwhelming replacement of the diazo-group by bromine was thus in accord with previous experience. The effect of the water content in (*a*) and (*b*) is shown by the formation of *p*-nitrophenol.

Mixed Sandmeyer Reactions with Cuprous Iodide.—When solutions of *p*-nitroaniline diazotised by the Hodgson–Walker method were poured into suspensions of cuprous iodide in hydrochloric acid and in hydrobromic acid, the yields of 4-iodonitrobenzene were 80% and 75% respectively. It follows that in the incipiently formed cuprous chloroiodo- and cuprous bromoiodo-complexes, the iodine is much more reactive than bromine or chlorine, and the bromine is more reactive than the chlorine, since the yield of 4-bromonitrobenzene exceeded that of 4-chloronitrobenzene under equivalent conditions.

The Action of Cupric Salts on Diazonium Compounds.—Sandmeyer has reported that cupric salts are without the same action as cuprous salts, and Blumberger (*Rec. Trav. chim.*, 1930, **49**, 26) that cupric salts merely accelerate decomposition. These statements have long since been true only in degree, since good yields of bromo-compounds are formed when amines are diazotised in sulphuric acid solution and then treated with solutions of sodium bromide (no action alone) and copper sulphate. Further Hodgson (*J. Soc. Dyers and Col.*, 1926, **42**, 367) found that, when 3-bromo-4 : 6-dinitroaniline was diazotised in sulphuric acid solution and then treated with cuprous chloride and hydrochloric acid, 1 : 6-dichloro-3-bromo-4-nitrobenzene was formed in the cold and 1 : 4 : 6-trichloro-3-bromobenzene in the hot reaction. However, treatment at or below 0° with sodium chloride (no action alone), followed by pure copper sulphate, gave the required 1-chloro-3-bromo-4 : 6-dinitrobenzene in almost quantitative yield. From these results it would appear that the Sandmeyer reaction is dependent on the degree of positivity of the diazonium ion, and that when this positivity is superlatively intense, as in the 3-bromo-4 : 6-dinitrobenzene-1-diazonium ion, cupric salts are enabled to bring about replacement by chlorine.

Finally, cupric salts readily react like cuprous salts with nitronaphthalenediazonium ions (Contardi and Mor, *Rend. Ist. Lombardo*, 1924, **57**, 646) and thereby provide supporting evidence for the point of view above with respect to positivity and facility of replacement. Germane also is Saunders' opinion (*loc. cit.*, p. 155) that the Sandmeyer reaction is a characteristic of the diazonium salt, since it only proceeds in acid solution.

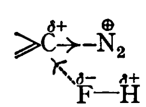


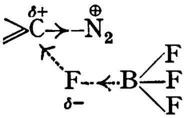
(III.)

The mechanism of the catalytic action of cupric salts can be assumed to differ in nowise from that for cuprous salts, *viz.*, the formation of complex cupric anions (III), which, while of ephemeral existence, nevertheless serve to activate the otherwise stable halogen ions.

The Anomalous Case of Hydrofluoric Acid.—In aqueous solution hydrofluoric acid is regarded as being present mainly in molecules of H_2F_2 (largely ionised as $\overset{+}{H}\}\overset{-}{HF_2}$) with only a small amount of HF (probably non-ionised). These properties account for the ineffectiveness of copper as a catalyst, since the affinity of fluorine for hydrogen and the stability of the $\overset{\ominus}{HF_2}$ anion apparently prevent complex cuprous ion formation. The small yield of fluoro-compound (*ca.* 25% from diazotised *m*-nitroaniline; Hodgson and Nixon, J., 1928, 1879) would therefore appear to be due to attack of kationoid carbon by non-ionised HF (IV), the $\overset{\ominus}{\mathrm{H}}\mathrm{F_2}$ ion being unreactive like the chloride and bromide anions. When, however, a dry borofluoride is decomposed by heating, *e.g.*, $\mathrm{R{\cdot}\overset{\oplus}{N}_2\}\overset{\ominus}{B}F_4}$, the same kind of process occurs as in the cuprous salt mechanism, *viz.*, a polarised fluorine atom in the $\overset{\ominus}{\mathrm{B}}\mathrm{F_4}$ ion attacks the kationoid carbon (V) like chlorine in the $[Cu_2Cl_4]^{--}$ complex, with resulting evolution of nitrogen and BF_3, and subsequent replacement of diazo-group by fluorine.

(IV.)



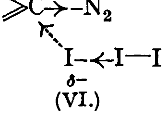


(V.)

Such a reaction is exactly analogous to the heating of dry diazo-perbromides which affords improved yields of bromo-compounds over those obtained in aqueous solution (Saunders, *loc. cit.*, p. 154).

The poor yields of halogeno-compounds obtained when diazonium salts are heated with even the most concentrated hydrochloric and hydrobromic acids would on analogy with hydrofluoric acid be due to the simultaneous reactions of water (fast) and non-ionised acid (slow, since the concentration is small). Blumberger's observation (*Rec. Trav. chim.*, 1930, **49**, 1420) that the addition of chlorides to decomposing dilute hydrochloric acid solutions of diazobenzene chloride somewhat increased the yield of chlorobenzene gives supporting evidence of the previous point of view, since the concentration of the non-ionised but very unstable hydrogen chloride would be slightly increased. The enormous excess of chloride anions present would indicate direct attack by them to be improbable, and, in the case of very concentrated hydrobromic acid, the bromine ions would exceed the amount of water present.

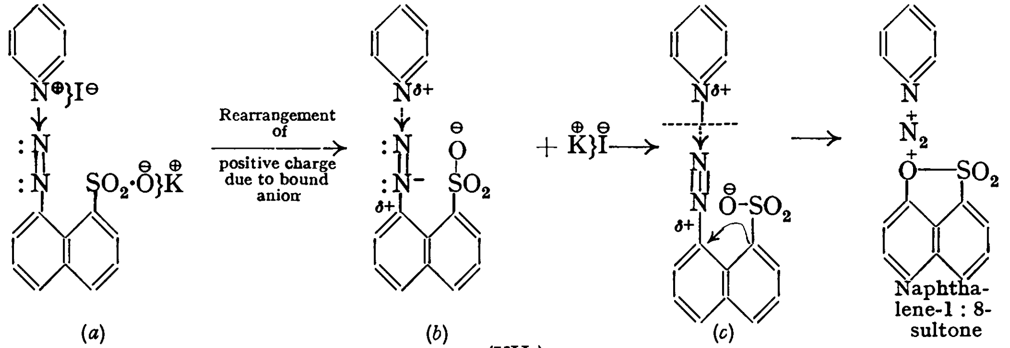
The Action of Iodides on Acid Solutions of Diazonium Salts.—Experiments have been made to test whether the facile direct replacement of the diazo-group by iodine was due to the iodide anion as generally supposed or was bound up with the oxidising action of the diazo-group. For this purpose *p*-nitroaniline was diazotised in hydrochloric acid and treated with sodium bisulphite; *p*-nitrophenylhydrazine hydrochloride then resulted; when, however, the mineral acid was first replaced by acetic acid, sodium bisulphite or sodium thiosulphate was without immediate effect, and subsequent addition of potassium iodide produced no 4-iodonitrobenzene in either case. On addition of the mild oxidising agent copper sulphate, 4-iodonitrobenzene was immediately precipitated. Further, potassium iodide decomposed a diazo-compound much more slowly in dilute acetic acid than in dilute mineral acid, which would indicate an equilibrium of $\mathrm{R{\cdot}N{:}N{\cdot}O{\cdot}CO{\cdot}CH_3 \rightleftharpoons R{\cdot}\overset{\oplus}{N}{\equiv}N\}\,O{\cdot}\overset{\ominus}{C}O{\cdot}CH_3}$ greatly in favour of the covalent diazo-acetate. In consequence, since it is the positive diazonium ion which oxidises the iodide ion to the iodine radical (neutral atom) initially, the reaction in acetic acid will be slow, whereas in mineral acid, where the diazonium ion is in great excess, reaction will be rapid. On analogy with the action of cuprous salts (as halogen carriers), it is reasonable to assume that the iodine acts also in its familiar rôle as halogen carrier, *via* a mechanism in which the iodine radical first formed by oxidation unites with another to form the molecule I_2, which then by combination with an iodide ion forms $\overset{\ominus}{I_3}$, and this complex anion reacts with a diazonium ion (VI) to form the iodo-compound. I is liberated, more I_2 is regenerated, and so on.



(VI.)

Further, if the reaction between diazonium ion and hydriodic acid was purely the simpler one of straight reduction-oxidation with immediate combination of the aryl and iodine radicals formed, it would be reasonable to expect some diaryl formation (see later), whereas this has not been observed.

The Exception reported by Cumming and Muir.—1-Diazonaphthalene-8-sulphonic acid, when treated with potassium iodide in pyridine solution, afforded naphthalene-1 : 8-sultone and not the iodo-compound. This may readily be explained by initial formation of complex (*a*) (VIII), which then undergoes the changes (*b*) and (*c*) :



(VII.)

This exception to the general rule of iodo-substitution illustrates the whole scheme of interpretation employed in this paper, since it is the anionoid sulphonic bound-ion which seeks the kationoid carbon to which the diazo-group is attached, while the iodide ion never departs from its anionic condition, and so remains non-reactive. The latter fact also gives support to the mechanism of iodine replacement of the diazo-group advanced above.

Diaryl Formation in the Sandmeyer Reaction.—When benzenediazonium chloride is added below 10° to a solution of cuprous chloride which has been so diluted with water that the cuprous chloride is just precipitating, the main product is chlorobenzene, but when the sequence of addition is reversed the chlorobenzene is now accompanied by considerable amounts of diphenyl and 4-hydroxydiphenyl. These experiments show that, when the complex anion is in excess, the main attack is at the kationoid carbon to which the diazo-group is attached, whereas when the diazonium salt is in excess a considerable oxidation by the diazonium salt occurs. These experiments are in line with the observation of Hodgson and Walker (*loc. cit.*), who found that when *o*- or *p*-nitroaniline was diazotised in sulphuric–acetic acid and treated with a concentrated hydrochloric acid solution of cuprous chloride, *i.e.*, with a minimum of water present, no diaryl formation occurred, whereas under more aqueous conditions considerable quantities of 2 : 2'- and 4 : 4'-dinitrodiphenyl were formed. In the former case the chlorine in the cuprous ion complex was undoubtedly the active agent while the cuprous chloride functioned solely as a catalyst (halogen carrier), whereas in the latter case, with more water and therefore with more free cuprous chloride present, the copper donates an electron to the diazonium ion; it is thereby oxidised to the cupric ion, nitrogen is evolved, the carbon to which it was linked is now in the radical state, and diaryl formation takes place.

The cuprous chloride in the last case is no longer a catalyst but a reducing agent, and to test the effect of substituents in the nucleus on diaryl formation, aniline, *p*-bromoaniline, *p*-toluidine, and *o*-nitroaniline were diazotised in hydrochloric acid solution in an atmosphere of carbon dioxide. From the estimation of the cupric chloride formed, the first three indicated 0·2, 0·15, and 0·17 g.-mol. respectively of diaryl formation per g.-mol. of amine taken, while *o*-nitroaniline gave 0·56 g.-mol. of 2 : 2'-dinitrodiphenyl. This shows that the more positive the diazonium ion, the more readily it oxidises the cuprous chloride. The similar results of *p*-bromoaniline and *p*-toluidine must be due to the mesomeric effect (Baddeley, Bennett, Glasstone, and Jones, J., 1935, 1827) of the bromine counteracting its negative inductive (— *I*) effect, since, if only the inductive effect had operated, there should have been much greater diaryl formation than that realised.

EXPERIMENTAL.

Decomposition of Diazotised Amines by the Sandmeyer Reaction. General Procedure.—The amine (1/40 g.-mol.), dissolved in glacial acetic acid (usually 1 g. of amine to 12 c.c. of acid), was stirred gradually below 20° into a solution of sodium nitrite (2 g.) in sulphuric acid (14 c.c., *d* 1·84), and the mixture kept for 1 hour and then added dropwise to a solution of freshly prepared cuprous chloride (1/40 g.-mol., *i.e.*, 5 g. of Cu_2Cl_2) in 35% hydrobromic acid [75 c.c., made from hydrobromic acid (35 c.c., *d* 1·7) and water (40 c.c.)]. When reaction ceased (1 hour), the mixture was diluted with water and steam-distilled should the halogen products be volatile. When the products were not steam-volatile, they were collected, washed with aqueous sodium hydroxide and with water, dried, and analysed for mixed halogens.

The procedure was repeated as above except that the diazotised amine was added to a solution of freshly prepared cuprous bromide in hydrochloric acid (75 c.c., *d* 1·16) so as to get parallel conditions. The detailed results are in Table I.

TABLE I.

Decompositions with the Solution of Cuprous Chloride in Hydrobromic Acid.

	Mixed product.				
			Analysis, calc. as halogeno-compounds.		
Amine (1/40 g.-mol.).	M. p.	Yield, g.	% Bromo.	% Chloro.	Remarks.
2-Nitroaniline (3·5 g.)	41·5°	4·1	90	10	Product from first steam-distillation was redistilled from aqueous sodium hydroxide, since any *o*-nitrophenol formed would be present. Only a small amount was found in the flask liquor.
4-Nitroaniline (3·5 g.)	124·5	4·2	96	4	
3-Nitroaniline (3·5 g.)	52—54	4·1	96	4	Small amount of *m*-nitrophenol in liquors after steam-distillation.
p-Phenylenediamine (1·35 g.)	85	1·9	96	4	The analytical data relate to actual halogen contents and not to their distribution, *i.e.*, 1-chloro-4-bromobenzene might be present as well as the 1 : 4-dichloro- and 1 : 4-dibromo-benzene.
Benzidine (2·3 g.)	146—150	3·2	93	7	Not isolated by steam-distillation.
p-Chloroaniline (3·2 g.)	65	4·0	94	6	
p-Bromoaniline (4·3 g.)	88	4·5	92	8	

Decompositions with the Solution of Cuprous Bromide in Hydrochloric Acid.

Amine (1/40 g.-mol.).	M. p.	Yield, g.	% Bromo.	% Chloro.	Remarks.
4-Nitroaniline (3·5 g.)	96	3·0	36	64	
3-Nitroaniline (3·5 g.)	41—45	3·6	32	68	Liquor after steam-distillation contained some hydroxy-compound.
2-Nitroaniline (3·5 g.)	31—34	3·6	31	69	
p-Phenylenediamine (1·35 g.)	55—65	1·4	31	69	The analytical data relate to actual content of halogens, and not to their distribution, *i.e.*, 1-chloro-4-bromobenzene might be present as 1 : 4-dichloro- and 1 : 4-dibromo-benzene.
Benzidine (2·3 g.)	120—140	2·7	35	65	
p-Chloroaniline (3·2 g.)	58	2·6	35	65	
p-Bromoaniline (4·3 g.)	74	3·4	37	63	
Anthranilic acid (3·2 g.)	136—138	2·6	20	80	

TABLE II.

Thermal Data for Mixtures of p-*Chloro- and* p-*Bromo-nitrobenzene.*

% Bromo..................	100	90	80	70	60	50	45
% Chloro	0	10	20	30	40	50	55
M. p.........................	126·5°	122°	118°	113°	108°	102°	99·5°

The graph of these data is practically a straight line as far as 45% of *p*-bromonitrobenzene and then becomes irregular, so that only these results were used for interpreting mixed m. p.'s and checking the analytical data of Tables I and III.

Variation in the Proportion of Halogen Acid to Cuprous Salt and its Effect on the Sandmeyer Distribution. Procedure.—Excess of halogen acid and excess of cuprous salt were maintained throughout and the experiments were limited to *p*-nitroaniline, which was diazotised by the Hodgson–Walker method (see Table III).

Experiments on Gattermann's Copper Powder Modification of the Sandmeyer Reaction in Mixtures of Hydrochloric and Hydrobromic Acids.—(*a*) *p*-Nitroaniline (3·5 g., 1/40 g.-mol.) was

TABLE III.

Amount of *p*-nitroaniline used.	Proportion of cuprous bromide to halogen acid Cu_2Br_2 : HCl (c.c.), *d* 1·16.	Mixed product. M. p.	Yield, g.	% Chloro.	% Bromo.
1/80 G.-mol., 1·75 g.	1/80 G.-mol. : 12·5	101°	1·6	53	47
,, ,,	,, : 25·0	99	1·5	56	44
,, ,,	,, : 50·0	94·5	1·5	61	39
,, ,,	,, : 75·0	87·5	1·5	65	35
1/40 G.-mol., 3·5 g.	1/40 G.-mol. : 75·0	93	3·4	62	38
,, ,,	,, : 150·0	96	3·0	60	40

dissolved in hydrochloric acid (50 c.c., *d* 1·16) and diazotised at 0° (external cooling) by sodium nitrite (3 g.) in water (15 c.c.). 35% Hydrobromic acid was then added, followed by excess of freshly prepared copper powder, and the temperature raised to 50° and maintained for 30 minutes. On steam-distillation, 2·6 g. of mixed products were obtained, m. p. 121° (Found : *p*-chloronitrobenzene, 12·5% ; *p*-bromonitrobenzene, 87·5%).

(*b*) *p*-Nitroaniline (3·5 g., 1/40 g.-mol.) was dissolved in sulphuric acid (50 c.c., *d* 1·84), ice (50 g.) added, and the mixture diazotised at 0° by the addition of finely powdered sodium nitrite (3·0 g.). The diazo-solution was then mixed with one of sodium chloride (30 g.) and sodium bromide (30 g.) in water (100 c.c.), and freshly prepared copper powder added (made from 25 g. of crystallised copper sulphate). To accelerate the reaction the mixture was heated at *ca.* 50° for 30 minutes; the volatile halogeno-compounds were then removed by steam-distillation as before. Yield of mixed products, 1·9 g., m. p. 120° (Found : *p*-chloronitrobenzene, 15% ; *p*-bromonitrobenzene, 85%).

In (*a*) and (*b*), *p*-nitrophenol formation was much larger than in the experiments previously described.

(*c*) *p*-Nitroaniline (3·5 g., 1/40 g.-mol.), dissolved in glacial acetic acid (42 c.c.), was added to a solution of sodium nitrite (2·0 g,) in sulphuric acid (14 c.c., *d* 1·84) at 0°, and the mixture after the completion of the diazotisation was poured into a solution of cuprous bromide (1/40 g.-mol.) in hydrochloric acid (25 c.c., *d* 1·16), hydrobromic acid (25 c.c., *d* 1·7), and water (20 c.c.). Steam-distillation removed 4·2 g. of mixed products, m. p. 124·5° (Found : *p*-chloronitrobenzene, 4% ; *p*-bromonitrobenzene, 96%).

(*d*) Repetition of (*c*) with cuprous chloride (5 g., 1/40 g.-mol.) instead of the cuprous bromide gave 4·2 g. of mixed products, m. p. 123·5° (Found : *p*-chloronitrobenzene, 6% ; *p*-bromonitrobenzene, 94%).

Action of Cuprous Iodide in Hydrochloric and Hydrobromic Acids on Diazotised p-*Nitroaniline.*—*p*-Nitroaniline (1/40 g.-mol.) was diazotised by the Hodgson–Walker method, and the solution poured into suspensions of cuprous iodide (1/20 g.-mol.) in hydrochloric acid (150 c.c., 35%) or in hydrobromic acid (150 c.c., 35%). The products, extracted with benzene, consisted of 80% of iodonitrobenzene and 20% of chloronitrobenzene, and 75% of iodonitrobenzene and 25% of bromonitrobenzene respectively.

Determination of the Amount of Cupric Chloride formed in the Sandmeyer Reaction.—Accurate estimation of the extent of oxidation of the cuprous chloride was impossible unless the complete operation was carried out in absence of air.

Procedure. Cuprous chloride (1 g.) was introduced into the flask, through which carbon dioxide was passing, and when all the air had been expelled, 10 c.c. of hot concentrated hydrochloric acid were introduced inside the flask to dissolve the cuprous halide. This was followed by the dropwise addition of the diazonium solution, in which the excess of nitrous acid had been destroyed by urea, containing *ca.* 1/200 g.-mol. per 30 c.c. used. The hot mixture was kept for 1 hour for completion of the reaction, the current of carbon dioxide being continued throughout. The hydrochloric acid was then neutralised by the addition of 25 c.c. of a solution containing sodium carbonate and sodium acetate (in the proportion of 50 g. and 25 g. respectively per 200 c.c.), and the cupric copper then estimated by the determination of iodine liberated from potassium iodide.

Results :	1 G.-mol. of	aniline	produced	0·20 g.-mol. of	cupric chloride
	,,	*p*-bromoaniline	,,	0·15	,,
	,,	*p*-toluidine	,,	0·17	,,
	,,	*o*-nitroaniline	,,	0·56	,,

The authors thank Imperial Chemical Industries (Dyestuffs) Ltd. for various gifts.

TECHNICAL COLLEGE, HUDDERSFIELD.

[*Received, July* 18*th*, 1941.]