THE SANDMEYER REACTION

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I. INTRODUCTION

During an attempt in 1884 to prepare phenylacetylene from benzenediazonium chloride and cuprous acetylide, Sandmeyer (53) obtained chlorobenzene in good yield, and he subsequently established that the active agent in promoting the reaction was cuprous chloride. Sandmeyer explained his result by two equations, *viz.:*

$$C_6H_5N{=}NCl + Cu_2Cl_2 = C_6H_5N(CuCl)N(CuCl)Cl$$

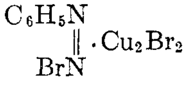
and

$$C_6H_5N(CuCl)N(CuCl)Cl = N_2 + Cu_2Cl_2 + C_6H_5Cl$$

He suggested that the intermediate compound with cuprous chloride might be the ephemeral yellow precipitate obtained when the diazobenzene chloride was added to a solution of cuprous chloride in hydrochloric acid; he stated also that cupric and ferrous chlorides did not act in this way. In analogous fashion, cuprous bromide was found to cause the replacement of the diazo group by bromine in benzenediazonium bromide (54), while cuprous cyanide similarly effected the substitution of the diazo by the cyano group (54). This facilitation by cuprous salts of replacement of the diazo group by halogens or other groups was thought by Sandmeyer to be specific. This viewpoint was held by chemists for well over 50 years and still has its adherents (71); the reaction in consequence became universally known as *The Sandmeyer Reaction.* It is of great interest, however, that although the diazo compounds were decomposed when heated with hydrochloric or hydrobromic acid, with evolution of nitrogen, the yields of halogeno products were poor (nevertheless hydriodic acid appeared to convert aryldiazonium salts to the corresponding aryl iodides even in the cold (19)), and that the replacement of the diazo group by fluorine was either uninfluenced by copper, or, if influenced, the effect may have been unfavorable, since Hantzsch and Vock (28) obtained *p*-bromophenol by acting on *p*-bromobenzenediazonium fluoride with copper. As already noted, Sandmeyer (53) himself tried cupric and iron salts in place of cuprous salts and found them to be without action, while Blumberger (2) reported that cupric salts merely accelerated decomposition. The first real challenge to cuprous chloride or bromide, so far as replacement of the diazo group by chlorine or bromine was concerned, came in 1923, when Contardi and his collaborators (9) found that the decomposition of substituted naphthalenediazonium salts (principally from nitronaphthylamines) was effected by cupric salts, sometimes with better yields than when cuprous salts were used.

II. VIEWS ON THE MECHANISM OF THE SANDMEYER REACTION PRIOR TO 1941

It has already been noted that Sandmeyer (53) attributed the efficacy of cuprous halides or cyanides to their formation of an unstable intermediate compound with the diazonium salts, and although he himself was unable to isolate any such intermediate product (54), yet Hantzsch (25) prepared what he termed the *syn*-diazobenzene cuprobromide,

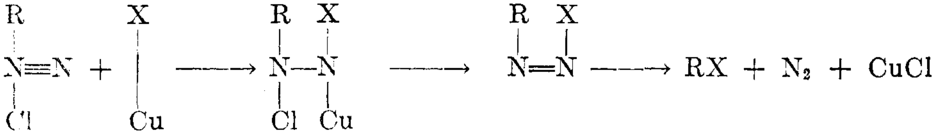


$$\begin{array}{l} C_6H_5N \\ \quad\;\, \| \cdot Cu_2Br_2 \\ BrN \end{array}$$

which was obtained in large, reddish yellow needles and decomposed on addition of water into cuprous bromide, nitrogen, and bromobenzene, no diazonium bromide being re-formed; *p*-bromo-*syn*-diazobenzene cuprobromide, $BrC_6H_4N{=}NBr \cdot Cu_2Br_2$, was similar to the foregoing but of a dark red color. Further, Lellmann and Remy (49) were also successful in isolating a red crystalline substance from *β*-naphthalenediazonium bromide and cuprous bromide, and these double salts all differed from colorless diazonium salts not only in being strongly colored (in contrast likewise to cuprous halides, which are colorless), but also in their stability and ready mode of decomposition to give the aryl or naphthyl halides. In Sidgwick's *Organic Chemistry of Nitrogen* (62), the viewpoint is expressed that in the double salts the diazo nitrogen is probably coördinate to the copper, a union which seems likely to alter the type of decomposition.

The halogen atom which replaces the diazo group was held by Hantzsch and Blagden (27) to be derived from the cuprous halide, on the evidence that *p*-chlorobromobenzene was obtained from *p*-bromobenzenediazonium bromide and cuprous chloride, while conversely *p*-dibromobenzene was obtained from *p*-bromobenzenediazonium chloride and cuprous bromide in methyl sulfide solution. Incidentally, this evidence received some support from experiments by Hodgson and Walker (46), who found that the replacement of the diazo group by chlorine or bromine could be carried out even in concentrated sulfuric acid solution, although in these cases the corresponding halogen acid was also present. Saunders (58) remarks, however, that it is well known that in replacing the diazo group by bromine a higher yield is often obtained if diazotization is carried out with hydrobromic acid than if hydrochloric acid is used; this experience will be dealt with later (Section IV, B).

To explain the above results, Hantzsch (24) proposed a general formulation based on the well-known formation of colored intermediate addition compounds, and analogous to the colored solid diazo halides, which comprehended also the preparation of the nitriles and other analogous derivatives, *viz.*:



$$\begin{array}{c}\text{R}\\ |\\ \text{N}\equiv\text{N}\\ |\\ \text{Cl}\end{array} + \begin{array}{c}\text{X}\\ |\\ |\\ |\\ \text{Cu}\end{array} \longrightarrow \begin{array}{cc}\text{R} & \text{X}\\ | & |\\ \text{N} & \!\!\!-\text{N}\\ | & |\\ \text{Cl} & \text{Cu}\end{array} \longrightarrow \begin{array}{cc}\text{R} & \text{X}\\ | & |\\ \text{N} & \!\!\!=\text{N}\end{array} \longrightarrow \text{RX} + \text{N}_2 + \text{CuCl}$$

Addition complex *syn*-Diazo compound

R = aryl radical; X = halogen, cyano, cyanate, etc.

Groggins (20) has stated that copper is not the only metal that can advantageously be employed for replacement of the diazo group by halogen, and that when precaution is taken to ensure a maximum concentration of chloride ions, saturated solutions of calcium chloride, zinc chloride, and zinc-ammonio chloride often give equally good results. In the corresponding decomposition to form nitriles, when a diazo solution is added to one of cuprous cyanide in potassium cyanide, a complex containing copper separates which decomposes on warming, and, while the yields are usually quite good, nevertheless they are improved by substituting nickel cyanide, $Ni(CN)_2$, for cuprous cyanide; this reaction is apparently specific for copper and nickel, since the cyanides of iron, chromium, zinc, and other metals are stated to be quite useless (48). A good recipe for the preparation of cuprous cyanide for use in the Sandmeyer reaction is given by Barber (1), who employs the reaction

$$2CuSO_4 + 2NaCN + NaHSO_3 + H_2O \longrightarrow 2CuCN + 3NaHSO_4$$

and who states that the cuprous cyanide thus prepared can be kept indefinitely.

Groggins (20) envisaged the mechanism of the Sandmeyer reaction as follows: The aryldiazonium compound first forms an addition compound with cuprous salts, resulting in a complex cation which subsequently undergoes decomposition. In this process, it is not the halogen inherent in the diazonium compound or the halogen ions of the reaction solution, but the halogen of the copper halide by virtue of its closer proximity to the aryl radical that enters the nucleus. That quantitative yields are never obtained in carrying out this reaction is explained by Groggins on the hypothesis that some of the diazonium salt reacts with hydroxyl ions before the addition complex is formed.

The kinetics of the Sandmeyer reaction were first investigated by Waentig and Thomas (68), who found that the reaction was not monomolecular, if the assumption be made that the measurable reaction is the decomposition of the cuprous diazo double compound, but that the acid concentration has considerable influence on the decomposition velocity—in direct contrast to the simple formation of phenols from diazonium compounds. Sandmeyer (56) had further supported his hypothesis of a double compound by the formation of nitrobenzene from aniline, and stronger evidence was obtained by Hantzsch (27), who found that the double salt of benzenediazonium nitrate and mercury nitrite, $(C_6H_5N_2NO_3)_2 \cdot Hg(NO_2)_2$, afforded nitrobenzene almost entirely when decomposed.

More recently Eichenberg (12) pointed out that two factors of decisive importance had to be considered: (*1*) the activation energy required to discharge the chloride ions; (*2*) the operation of the law of mass action. It is evident, he states, that in a solution containing hydroxyl as well as halogen ions, the former will move with a greater velocity and react more readily, and therefore play a prominent rôle in the formation of phenols; on the other hand, from the law of mass action, it would be expected that in a solution containing different ions, each will react in proportion to its concentration. From the consideration of molecular or ionic concentrations alone, practically theoretical yields of aryl halide would be expected when maximum concentrations of hydrochloric acid and zinc chloride were used in the Sandmeyer reaction, but this does not occur, and a discussion of this anomaly is given later in the paper.

Gattermann (17) believed free copper to be as effective as the cuprous salts, but Saunders (58) pointed out that when copper is used to bring about halogen replacement it is the cuprous ions first formed by the action of the acid on the copper which really do the work, and that the reaction only proceeds in acid solution and hence appears to be a reaction of the diazonium salt. On the other hand, Hantzsch considered that any intermediate stages were derived from the *syn*-diazo hydroxide.

This paper will deal only tentatively with the Gattermann reaction, which is still being experimentally studied by the author, but it may be pointed out that *o*- and *p*-dinitrobenzenes are obtained in good yield by the decomposition of *o*- and *p*-nitrobenzene fluoroborates in aqueous solution containing sodium nitrite by means of copper powder and in the absence of acid (63). Naturally, however, in the presence of hydrochloric or any other acid, cuprous salts will be formed incipiently as envisaged by Saunders, so that Hantzsch's viewpoint of a double rôle would appear to have considerable justification.

According to Erdmann (14), the normal decomposition of the diazo cuprous chloride compound takes place rapidly and smoothly only above a certain temperature, which is different for each compound; these temperatures are about 0°, 27°, and 30–40°C. in the case of cuprous chloride derivatives of diazobenzene, *o*-diazotoluene, and *p*-diazotoluene, respectively. Below these points the evolution of nitrogen takes place too slowly and is incomplete, part of the diazo cuprous chloride compound being converted to an azo compound by the liberated cuprous chloride. It has been found that the quantity of cuprous chloride required may be reduced to 1/21 and 1/28 mole per mole of amine without materially reducing the yield of chlorobenzene (66.2–63.5 per cent) and *m*-chloronitrobenzene (78.5–73.2 per cent), respectively (66). This is considered to be due to the diazobenzene chloride becoming first reduced to phenylhydrazine by the cuprous chloride, which subsequently becomes cupric chloride; the phenylhydrazine is then oxidized in the presence of hydrochloric acid to chlorobenzene by the cupric chloride, and the cuprous chloride would then be reformed to play the same part again. In an assumed confirmation of this explanation, it is found that phenylhydrazine is oxidized to chlorobenzene under the conditions named by both cupric and ferric chlorides, but the fact remains that no phenylhydrazine can be detected in the Sandmeyer reaction, and this is ascribed to its momentary existence. Against this viewpoint, it is worthy of emphasis that a copper salt is not necessary in the preparation of iodobenzene by this method, and this is explained by the fact that hydriodic acid is itself a reducing agent (69). Later it will be shown that iodobenzene is not formed in the presence of reducing agents.

III. INDUSTRIAL APPLICATIONS OF THE SANDMEYER REACTION

The Sandmeyer reaction has not as yet received many technical applications, but a few may be cited: (*1*) the preparation of 2,6-dichlorotoluene from 2,6-chlorotoluidine and of 2-chlorobenzaldehyde (15); (*2*) the production of 1-chloro-8-naphthol-3,6-disulfonic acid from H acid (5); and (*3*) the preparation of halogenoanthraquinones (21). An electrolytic process (67) has also been based on the Sandmeyer method, and has been devised to avoid the preparation and recovery of cuprous salts in large-scale technical operations. It consists in electrolyzing a solution of a diazo compound to which cupric chloride has been added, where a thick copper wire is used as the anode and a cylinder of sheet copper as the cathode. With a current density of 2.1 amperes per square decimeter, and an E. M. F. of 10 volts, nitrogen was evolved and a yield of 64 per cent of the theoretical yield of chlorobenzene was obtained. Apparently, however, such processes have not enjoyed wide technical use.

IV. AN INTERPRETATION OF THE SANDMEYER REACTION

A. Foreword

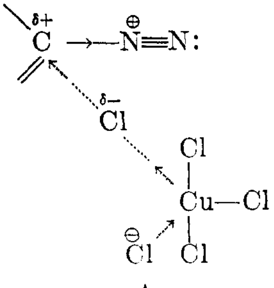
Although various suggestions have been noted in the introduction for the mechanism of the Sandmeyer reaction, all of them are invalid for one reason or another. It is stated by Hammett (23) that "*the characteristic effect of cuprous compounds in the Sandmeyer reaction has no obvious explanation*," and by Sidgwick (61) that the action of metallic copper is not understood. In an attempt to solve this problem, Hodgson, Birtwell, and Walker (34) have submitted 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 destabilized) by cuprous salts acting purely as catalysts, which convert them into nucleophilic (anionoid) reagents by a temporary sharing of their stable octets. This interpretation was then found to explain: (*1*) the similar catalytic action of cupric, iron, and cobalt salts; (*2*) the experimental results of Hantzsch and Blagden (27); (*3*) the anomalous behavior of fluorine compounds; (*4*) the ease of reaction between diazonium compounds and iodides in the absence of copper salts; and (*5*) the action of halogen acids on diazonium compounds. Also, the formation of diaryls (16, 57, 64) in the Sandmeyer reaction was shown to be a consequence of an oxidation-reduction mechanism involving conversion of cuprous into cupric salts.

B. Mixed Sandmeyer reactions

Eight arylamines (2-, 3-, and 4-nitroanilines, *p*-chloro- and *p*-bromoanilines, anthranilic acid, *p*-phenylenediamine, and benzidine) were each diazotized by the glacial acetic acid-nitrosylsulfuric acid procedure of Hodgson and Walker (46), and the solutions of the diazonium salts thus obtained were decomposed in two ways: (*a*) by cuprous chloride dissolved in concentrated hydrobromic acid and (*b*) by cuprous bromide dissolved in concentrated hydrochloric acid. Taking the example of *p*-nitroaniline as typical of the eight, it was found for (*a*) that the weights of 4-chloronitrobenzene and 4-bromonitrobenzene which resulted were in the ratio of *ca.* 4:96, while for (*b*) the ratio had shifted to 60:40. This distribution superficially contradicts the results of Hantzsch and Blagden (27), 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 below, however, that there is complete harmony between all the data.

To interpret these results, the dissolution of cuprous chloride and bromide in hydrobromic and hydrochloric acid, respectively, is assumed to form complex anions, *viz.*, $[CuClBr_3]^{---}$ and $[CuCl_3Br]^{---}$, and in these complexes the bromine (see later) will be more reactive than the chlorine. The reason (35) for this formulation of the anions is that the older formula for cuprous chloride, Cu_2Cl_2, has now been replaced by CuCl, since there is little reliable evidence for the Cu—Cu link in cuprous compounds (because in these compounds where detailed structure is known, the cuprous atoms are too far apart for such direct linkage); moreover, such structures usually enable the cuprous atoms to acquire seven electrons and thus attain the krypton structure (10, 18, 50, 72). The active complex cuprous anion in a solution of cuprous chloride in hydrochloric acid should therefore be represented by $[CuCl_4]^{---}$. This formulation will also be in harmony with the established compound, $K_3Cu(CN)_4$, which Grossmann and van der Forst (22) have shown to represent the most stable type of complex cuprous cyanide.

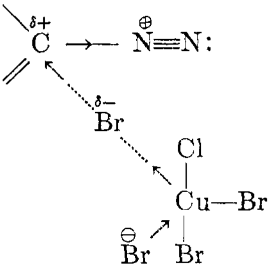
The mechanism of decomposition of aryldiazonium chlorides by cuprous chloride dissolved in hydrochloric acid could then be envisaged as follows: Attraction of the complex anion $[CuCl_4]^{---}$ to the diazonium cation, and then



A

decomposition of the complex A, 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 the rehabilitation of the complex anion by coördination with an external chloride anion.

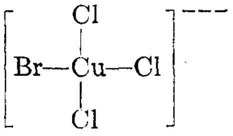
For decomposition (*a*) above, the mixed complex B will react by a bromine atom at the cationoid carbon of the diazonium ion, since bromine is more reactive



B

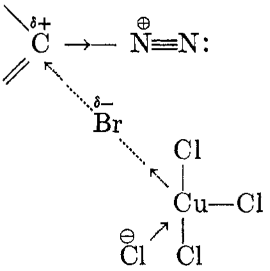
than chlorine, owing to its exterior electrons being less under control by the positive nucleus (*cf.* also Schwechten (60)); moreover, release of a bromide ion from the copper to the cationoid carbon entails immediate replenishment of bromine to the copper from the bromide ions in solution, so that a preponderance of bromo compound will be formed (*ca.* 96 per cent in the case of *p*-nitroaniline). It is reasonable to assume, however, that some of the complex ions will be in an environment where the chlorine can be more reactive than the bromine, and in this case a chloro compound will result (*ca.* 4 per cent for *p*-nitroaniline).

For decomposition (*b*) above, the complex anion



$$\left[\begin{array}{c}\mathrm{Cl}\\ | \\ \mathrm{Br{-}Cu{-}Cl}\\ | \\ \mathrm{Cl}\end{array}\right]^{---}$$

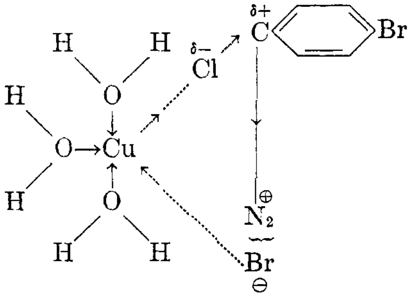
will react by a bromine atom at the cationoid carbon of the diazonium ion, and

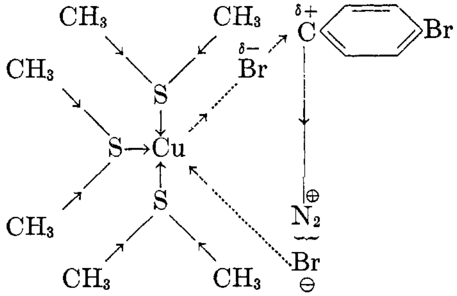


the diazo nitrogen will be displaced initially by bromine, but in this case the depleted copper anions will be replenished by chloride anions from the solution, whereby chloro complexes will now gradually take the place of the cuprous chlorobromo anions and the resulting mixture of chloro- and bromoaryls will in consequence possess a more even distribution of the halogens than in (*a*). Actually, the chloro compound predominates (60–70 per cent), as would be expected.

C. The Hantzsch-Blagden data (27)

The experiments of Hantzsch and Blagden to prove that the halogen came from the complex were as follows: The diazonium salt (1 mole) was treated with cuprous halide (1 mole) in aqueous suspension and also in methyl sulfide 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 present author's point of view (see above), it would appear that an incipient complex anion is formed in each case between the cuprous halide and coördinating solvent ions, *viz.*, water and methyl sulfide, 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 ions from the diazonium salt will then replace the departing halogen of the complex anion, and so tend to form the other halogen derivative in minor yield, as found by Hantzsch and Blagden. The contention of these authors that the halogen came from the cuprous salt is therefore valid, but if they had carried out the mixed Sandmeyer experiments described by the present authors (35), especially where nearly 100 per cent of bromo compound resulted when cuprous chloride was employed in hydrobromic acid solution, an erroneous deduction that the halogen came directly from the acid would have been well nigh irresistible. The more vigorous reaction obtained when methyl sulfide was employed in homogeneous medium would be expected from the greater abundance of the copper complex and from its greater negativity, which is due to the more permanent coördination with methyl sulfide than with the polarized water molecules. A series of experiments (34) 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, a result which is in accordance with the hypothesis now advanced to interpret the Sandmeyer reaction.

D. Copper as catalyst in the Sandmeyer reactions

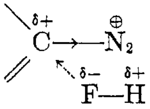
Gattermann's substitution of metallic copper for cuprous halide (17) was tested (34) for mixed halogen acids by: (*a*) diazotizing *p*-nitroaniline in hydrochloric acid, adding the equivalent of hydrobromic acid, and treating the mixture with copper powder; (*b*) diazotizing *p*-nitroaniline in concentrated sulfuric acid, adding concentrated aqueous solutions of sodium chloride and sodium bromide, and then decomposing the mixture with copper powder. For comparison, *p*-nitroaniline was diazotized by the Hodgson–Walker method (46), 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 per cent yield together with *p*-nitrophenol. Almost theoretical yields of halogenonitrobenzenes were obtained in (*c*) and (*d*), the distribution being (*c*) 96 per cent of 4-bromo- and 4 per cent of 4-chloronitrobenzene, (*d*) 94 per cent of 4-bromo- and 6 per cent of 4-chlorobenzene; *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.

E. Mixed Sandmeyer reactions with cuprous iodide

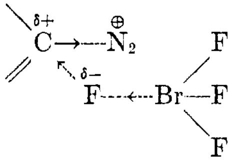
When solutions of *p*-nitroaniline diazotized by the Hodgson–Walker method (46) were poured into suspensions of cuprous iodide in hydrochloric acid and in hydrobromic acid, the yields of 4-iodonitrobenzene were 80 per cent and 75 per cent, respectively. It follows that in the incipiently formed cuprous 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. These experiments are also in accord with those of Hantzsch and Blagden (27), who reported that cuprous iodide furnished iodo derivatives only with various diazo chlorides and bromides.

F. The anomalous case of hydrofluoric acid

In aqueous solution hydrofluoric acid is regarded as being present mainly as molecules of H_2F_2 (largely ionized as $H^+\{HF_2^-)$ with only a small amount of HF (probably non-ionized). These properties account for the ineffectiveness of copper as a catalyst in the ordinary Sandmeyer or Gattermann reactions, since the affinity of fluorine for hydrogen and the stability of the $\overset{\ominus}{HF_2}$ anion apparently prevent cuprous ion formation. The small yield of fluoro compound (about 25 per cent from diazotized *m*-nitroaniline (42)) would therefore appear



to be due to attack of cationoid carbon by non-ionized HF, the $\overset{\ominus}{HF_2}$ anion being unreactive, like the chloride and bromide anions. When, however, a dry bromofluoride is decomposed by heating, e.g., $R\overset{\oplus}{N_2}\}Br\overset{\ominus}{F_4}$. the same kind of process occurs as in the cuprous salt mechanism, *viz.*, a polarized fluorine atom in the



$Br\overset{\ominus}{F_4}$ ion attacks the cationoid carbon, like chlorine in the $[CuCl_4]^{---}$ complex, with resulting evolution of nitrogen and BrF_3, and subsequent replacement of the diazo group by fluorine. 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 (58, page 154).

The poor yields of halogeno compounds obtained when diazonium salts are heated with even the most concentrated hydrochloric and hydrobromic acids would, by analogy with hydrofluoric acid, be due to the simultaneous reaction of water (fast) and non-ionized acid (slow, since the concentration is small). Blumberger's observation (3) 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-ionized 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 bromide ions would exceed the amount of water present.

G. The influence of chloride ion on the decomposition of diazonium salts

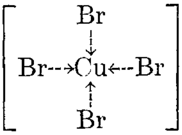
To test the conclusion above that the chloride ion plays little or no part in the decompositions of diazonium salts, Hodgson and Sibbald (44) examined the influence of chloride ions on the decomposition of neutral *p*-nitrobenzenediazonium chloride and of *p*-nitrobenzenediazonium cobaltinitrite. Most of the decompositions of diazonium chlorides hitherto reported have been studied in acid solutions (2, 3, 34, 36, 43), and have been found to vary greatly in the presence of hydrochloric acid either with sodium chloride or with the addition of various catalysts: in particular, when the acid concentration was altered from 29 to 6 per cent, the yield of *p*-chlorobenzene was altered from 56 to 17 per cent. Sodium chloride was present in all these experiments, and in the case of the 56 per cent yield the solution was saturated with it, so that it appeared of interest to ascertain whether metallic chlorides, i.e., the chloride anion, took part in the decomposition, or whether the *p*-chloronitrobenzene formed was mainly due to the unionized hydrogen chloride (36). For this purpose, the acid solution of *p*-nitrobenzenediazonium chloride was exactly neutralized with the appropriate base, and the corresponding metallic chlorides added in equivalent amounts to secure exactly parallel sets of decompositions. Except in the cases of calcium and zinc chlorides, it was not possible to ensure complete neutrality throughout the decomposition on account of the hydrochloric acid formed by the decomposing diazonium chlorides, but in these cases, excess of calcium carbonate and of zinc oxide, respectively, was added to maintain neutrality. Comparison of the data obtained, with and without filtering off the excess base, showed that the acid formed was without significant effect upon the yield, and consequently was ignored in the other experiments where its presence was unavoidable. It was found that in neutral decompositions, the addition of relatively large amounts of metallic chlorides caused no significant rise in the yield of chloro compound above that obtained when no salts were added. There was, however, one exception, *viz.*, that when cupric chloride was added to the solution of diazo compound neutralized with calcium carbonate the yield rose to 85 per cent. This remarkable result was obtained with about one-third of the equivalent amount of chlorine present in solution, which would appear to indicate the presence of a complex hydrated cupric chloride anion in the experiments in acid solution (this will be discussed later (43)). The results indicate quite clearly that the chloride ion plays little if any part in the substitution of chlorine for the diazo group, since the only cases of appreciable substitution are those in which there is the possibility of the existence of covalent (or partly polarized) chlorine, *viz.*, with hydrogen, cupric, and calcium chlorides. The behavior of zinc chloride, which unexpectedly did not follow that of calcium chloride, was probably due to the same cause as that which differentiates it from that of cuprous or cupric salts in the decomposition of its complex salts with diazonium compounds, *viz.*, that bound, anionoid, and therefore reactive water is further from the zinc than the polarized chlorine atoms (i.e., the reverse of the case of crystalline $K_2CuCl_4 \cdot 2H_2O$, which will be discussed later). Support for this view is to be found in Hodgson and Foster's observation (38) that decomposition of the zinc diazonium complexes in phenol results in *ca.* 50 per cent chlorine substitution.

p-Nitrobenzenediazonium cobaltinitrite has been shown by Hodgson and

Marsden (41) to undergo replacement of the diazo by the nitro group when treated with sodium nitrite, copper sulfate, and cuprous oxide. When the decomposition was carried out in the presence of sodium chloride and copper sulfate in neutral solution, the product formed was pure *p*-chloronitrobenzene, showing that the cupric chloride has been more effective than the cobaltinitrite, or alternatively that polarized chlorine is more reactive than the polarized nitro group in the cobalt complex. When the cobaltinitrite was decomposed by sodium nitrite and sodium chloride in the absence of copper, the product was entirely *p*-dinitrobenzene, showing that the fully ionized chlorine was without effect on the decomposition, which took place *via* the polarized nitro group in the complex (see below) and was in accord with the results obtained with metallic chlorides mentioned above. Decompositions with sodium nitrite and sodium chloride in conjunction with copper sulfate gave mixtures of *p*-chloronitro- and *p*-dinitrobenzenes.

H. The action of cupric salts on diazonium compounds

Sandmeyer (53) has reported that cupric salts are without the same action as cuprous salts, and Blumberger (2) that cupric salts merely accelerate decomposition. These statements have long been true only in degree, since good yields of bromo compounds are formed when amines are diazotized in sulfuric acid solution and then treated with a solution of sodium bromide (no action alone) and copper sulfate. Further, Hodgson (32) found that when 3-bromo-4,6-dinitroaniline was diazotized in sulfuric acid solution and then treated with cuprous chloride and hydrochloric acid, 1,6-dichloro-3-bromo-4-nitrobenzene was found in the cold and 1,4,6-trichloro-3-bromobenzene in the hot reaction. However, treatment at or below 0°C. with sodium chloride (no action alone), followed by pure copper sulfate, gave the required 1-chloro-3-bromo-4,6-dinitrobenzene in almost quantitative yield. From these results it would appear to follow 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 able to bring about replacement by chlorine. Further, cupric salts have been shown (9) to react readily like cuprous salts with nitronaphthalenediazonium ions, and thereby provide supporting evidence for the point of view above with respect to positivity and facility of replacement. Germane also is Saunders' opinion (58) that the Sandmeyer reaction is a characteristic of the diazonium salt, based on his viewpoint at the time that it proceeded only in acid solution. Since then, the experiments described in the section above have shown the Sandmeyer reaction to take place with cupric chloride in neutral solution.



$$\left[\begin{array}{c} \mathrm{Br} \\ \downarrow \\ \mathrm{Br}\rightarrow\mathrm{Cu}\leftarrow\mathrm{Br} \\ \uparrow \\ \mathrm{Br} \end{array}\right]$$

The mechanism of the catalytic action of cupric salts can be assumed to differ in no wise from that of cuprous salts, *viz.*, the formation of complex cupric anions, which, while of ephemeral existence, nevertheless serve to activate the otherwise stable halogen ions.

I. The comparative behavior of cuprous, cupric, and ferric chlorides as catalysts in strong acid solution

Experiments have been described by Hodgson, Birtwell, and Walker (36), in which dilute sulfuric acid solutions of *p*-nitrobenzenediazonium sulfate were decomposed in the presence of ferric chloride alone, and also with copper sulfate and sodium chloride, which gave results indicating clearly the catalytic influence of the copper salt and of the chloride-ion concentration in promoting the formation of the complex anion. In the decompositions of *p*-nitrobenzenediazonium chloride, a 41 per cent yield of 4-chloronitrobenzene was obtained in fairly concentrated hydrochloric acid alone, and, under more concentrated conditions, the yield increased to 54.4 per cent (37). Since increase in hydrochloric acid concentration resulted in increased replacement by chlorine, it follows that this must be ascribed to the increase in concentration of the anionoid complex in the stronger acid, the simultaneous reaction by anionoid water with production of *p*-nitrophenol showing a corresponding decrease. This result is in substantial agreement with the earlier views of Hantzsch (26) and the deduction of Waters (70) on the activity of unionized hydrogen chloride in the decomposition of benzenediazonium chloride in very concentrated aqueous solution, or in concentrated hydrochloric acid, where the yield of chlorobenzene falls off very rapidly as the solution is diluted. The experiments with diazonium chlorides in concentrated acid were therefore carried out with a series of metallic chlorides whose metals are prone to form complex halogeno anions, *viz.*, those of aluminum, antimony, chromium, cobalt, copper (cuprous and cupric), iron (ferric), mercury (mercuric), nickel, tin (stannic), and zinc. Since sodium chloride under the concentrated conditions was also present in the solid form by precipitation during diazotization with sodium nitrite, all the solutions were saturated thereby, and all the decompositions were thus carried out under practically the same conditions, except for the small differences in boiling points of the various solutions.

A noteworthy feature of the decomposition of diazotized *p*-nitroaniline in strong acid solution is the efficiency of ferric and cupric chlorides as catalysts, a 77.6 per cent yield of *p*-chloronitrobenzene being obtained, i.e., the same as that with cuprous chloride under like conditions. On the other hand, aluminum chloride only slightly increased the yield over the blank, and calcium, chromium, mercuric, and zinc chlorides had no effect upon it. In marked contrast, antimony trichloride reduced the yield to 37.1 per cent (blank, 54.4 per cent), a similar effect having already been observed under more dilute conditions (41 per cent to 32 per cent), and it would appear that antimony chloride activated anionoid water preferentially to chlorine.

The experiments with cobalt chloride had an interesting bearing on its ionic state. When anhydrous, or in solutions of high chloride-ion concentration, it is blue, owing, it is generally supposed, to the $[CoCl_4]^{--}$ anion; such solutions afforded a 70.9 per cent yield of chloro compound, whereas the more aqueous pink solution, containing $Co(H_2O)_6Cl_2$, gave a yield of only about 10 per cent, i.e., the same as that in hydrochloric acid at the same dilution with no cobalt present. Also, when *p*-nitroaniline was diazotized by the Hodgson and Walker method (46) in concentrated sulfuric–glacial acetic acid solution, and then decomposed by the blue solution of cobalt chloride in concentrated hydrochloric acid, the yield was decreased to that of the blank (40.5 per cent), showing that the dissociation of the complex ion in the composite solution had inhibited its efficiency for replacement of the diazonium group by chlorine. These experiments with cobalt chloride support the interpretation given for the previous results with cupric chloride, and with copper sulfate and sodium bromide (36), that the decomposition is due to the complex $[CuCl_4]^{--}$ or $[CuBr_4]^{--}$ anion. In this connection, it is of interest that anhydrous cupric bromide is black, this color being ascribed to $Cu[CuBr_4]$, and that the addition of sodium bromide to copper sulfate produced a color change from blue to green-brown, due probably to the formation of the $[CuBr_4]^{--}$ anion; in like manner, cupric chloride is held be $Cu[CuCl_4]$ (13). The great efficiency of ferric chloride in concentrated acid solution is also due to the formation of a complex anion, and the older viewpoint that there is considerable evidence for the existence of $HFeCl_4$ has received support from evidence discussed in a later section.

Similar experiments with *m*-nitroaniline (37) usually gave somewhat lower yields of *m*-chloronitrobenzene, but in every case in the same order of efficiency as those with *p*-nitroaniline (37). In these reactions also, ferric and cupric chlorides proved to be as efficient as cuprous chloride, and the decreased yields were to be anticipated in view of the lower positivity of the significant carbon atom to which the diazonium group is attached.

J. The comparative behavior of cuprous, cupric, and ferric chlorides as catalysts over a wide range of hydrochloric acid concentrations

Experiments have been carried out by Hodgson and Sibbald (43) in which *p*-nitrobenzenediazonium chloride was decomposed over a range of hydrochloric acid concentrations with cuprous, cupric, and ferric chlorides as catalysts, and with cuprous and cupric chlorides together. With ferric chloride, an almost proportional decrease in yield of *p*-chloronitrobenzene occurs on dilution.

When the percentage yield according to the amount of water present is plotted, the plot for cuprous chloride has a maximum at *ca.* 18.6 per cent of acid, while that for cupric chloride has maxima at 26.9 per cent and 4 per cent, the latter after the plot has crossed that for cuprous chloride. When cuprous and cupric chlorides are used in combination the curve is approximately a straight line, the effect of the cuprous chloride being inappreciable at high dilutions; incidentally, the curve for the combination is tangential to the peak of the cupric chloride curve. The remarkable increase in activity of cupric chloride at 4 per cent strength suggests the existence of a complex hydrated cupric chloride anion in which the chlorine is much more active than the bound water. This preferential activity of the chlorine may be due to its actual distance from the copper being greater than that of the bound water, as in the known example of crystalline $K_2CuCl_4 \cdot 2H_2O$ (8, 29, 30). The active amount of this complex would appear to be only slowly changed with increasing dilution. (*Cf.* the previous discussion on the non-reactivity of the chlorine in the zinc chloride complexes as possibly due to the water being further from the zinc than the chlorine.)

A further study by Hodgson (33) has shown that while cupric chloride is an effective catalyst for the replacement of the diazo nitrogen in strongly positive diazonium cations (such as are furnished by the nitroanilines) by chlorine, and in both weakly acid and neutral solutions saturated with sodium chloride, it is much less efficient for weak cations such as are given by aniline and the three toluidines, although it is superior to cuprous chloride under these conditions. At the slight acidity of the acid reactions, the catalytic power of the cupric chloride is generally somewhat inferior to that in neutral solutions, a result which confirms an earlier observation of Hodgson and Sibbald (43). In solutions of the less positive diazonium cations the main reaction is phenol formation, and the phenol in neutral solution then tends to couple with undecomposed diazonium compound, a reaction which is very pronounced in benzidine decompositions. It is of interest that neutral solutions of *o*- and *p*-nitrobenzenediazonium chlorides saturated with sodium chloride gave no chloronitrobenzene, and that *m*-nitrobenzenediazonium chloride gave only 6 per cent of *m*-chloronitrobenzene, whereas when hydrochloric acid was present small yields of the chloronitro compounds were obtained in all three cases; these results suggest the viewpoint above (34), that unionized hydrogen chloride is the active reagent and not the chloride ion (44). In similar decompositions with diazotized *o*- and *p*-anisidines there is a surprisingly large replacement of the diazonium group by chlorine, which indicates that the negative $(-I)$ inductive effect of the methoxyl group has appreciably increased the positivity of the significant carbon to which the diazonium group is attached.

K. A limitation of the Sandmeyer reaction as shown by the behavior of diazotized 2,4,6-trichloro- and 2,4,6-tribromoanilines

In some experiments carried out by Hodgson and Mahadevan (40), it was found that whereas 2,4,6-trichloro- and 2,4,6-tribromoanilines were smoothly diazotized by the nitrosylsulfate–glacial acetic acid procedure of Hodgson and Walker (46) and then behaved normally towards the Sandmeyer reagent (cuprous halide) in concentrated mineral acid solution with formation of tetrahalogenobenzenes, they were reduced in dilute acid (3–4 per cent) to 1,3,5-trichloro- and 1,3,5-tribromobenzene, respectively. In these cases, the cuprous halide has reacted as a reducing agent and not as a catalyst, since cupric chloride or bromide, respectively, was found in the ultimate reaction mixture. This reducing behavior of cuprous salts recalls the somewhat analogous behavior of 2-nitro-1-naphthalenediazonium sulfate towards cuprous hydroxide in glacial acetic–sulfuric acid (39) to form β-nitronaphthalene, when other reaction products might have been anticipated, *viz.*, 2,2′-dinitro-1,1′-azonaphthalene and 2,2′-dinitro-1,1′-dinaphthyl. With potassium iodide, however, both 2,4,6-trichloro- and 2,4,6-tribromobenzenediazonium sulfates gave normal replacement of the diazo group by iodine, whether in concentrated or dilute mineral acid or in neutral solution. Chattaway's observation (6) that potassium perbromide gave 2,4,6-tribromobenzenediazonium perbromide, which on heating with glacial acetic acid gave 1,2,3,5-tetrabromobenzene, has been confirmed.

L. The formation of complex salts between aryldiazonium chlorides and ferric chloride, and the decomposition of p-nitrobenzenediazonium chloride by ferrous salts

It is generally agreed that an unstable intermediate product is formed in the solution during the usual Sandmeyer reaction with cuprous chloride. The work of the author and his collaborators in this field has been based so far on the existence, however ephemeral, of intermediate complex anions; while none have hitherto been actually isolated, ocular demonstration of their existence has been shown (37) for the cases of blue complex anions with cobalt chloride of the type $(RN_2)_2^{++}\}CoCl_4^{--}$. It was then suggested that the efficiency of ferric chloride as a catalyst in concentrated hydrochloric acid was due to the formation of complex salts of the type $R\overset{+}{N}_2\}FeCl_4^-$. Incidentally, Schmidt and Maier (59) have previously obtained double salts of *p*-diethylaminobenzenediazonium chloride with mercurous, ferric, zinc, and cadmium chlorides.

Hodgson and Sibbald have since found (45) that complex salts of aryldiazonium chlorides with ferric chloride of the general formula $R\overset{+}{N}_2\}FeCl_4^-$ were readily prepared, owing to their sparing solubility in concentrated hydrochloric acid. Eight examples of these salts are described from aniline, *m*-nitro- and *p*-nitroanilines, *p*-toluidine, α- and β-naphthylamines, benzidine, and 4,4′-diaminodiphenyl disulfide, a set sufficiently versatile to indicate their ease of formation. These ferri-complexes decomposed when heated with concentrated hydrochloric acid similarly to the original solutions of diazonium chlorides when they were treated with ferric chloride (43), and so furnished strong evidence of intermediate compound formation preceding decomposition in concentrated hydrochloric acid. When the ferrichloride was treated with concentrated hydrobromic acid the chlorine was replaced by bromine, and the ferribromide, $R\overset{+}{N}_2\}FeBr_4^-$, was isolated; it decomposed in hydrobromic acid solution to give excellent yields of RBr.

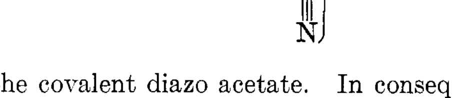
When the ferrichloride from diazotized *p*-nitroaniline was decomposed by boiling hydrobromic acid, a mixture was obtained of *p*-bromonitrobenzene (93 per cent) and *p*-chloronitrobenzene (7 per cent), a decomposition exactly analogous to those already referred to (34) of diazonium salts with cuprous chloride and cuprous bromide in hydrobromic and hydrochloric acid, respectively. The corresponding ferribromide, however, when decomposed by boiling hydrochloric acid gave a mixture of *p*-bromonitrobenzene (50 per cent) and *p*-chloronitrobenzene (50 per cent). As well as substantiating the general interpretation advanced above for the mixed Sandmeyer reactions, the data indicated that in the competitive introduction of chlorine and bromine, where the bromo complex is being decomposed by hydrochloric acid, ferric iron is more favorable to the introduction of bromine than is cuprous copper, since the latter provided a mixture of *p*-bromonitrobenzene (36 per cent) and *p*-chloronitrobenzene (64 per cent).

p-Nitrobenzenediazonium ferrichloride is very rapidly decomposed by ethanol and, while *p*-chloronitrobenzene is the main product, some nitrobenzene is also formed, owing to the usual reduction of diazonium salts by ethanol. In the analogous case of zinc chloride double salts (38), nitrobenzene was the main product (*ca.* 66 per cent) of decomposition with ethanol.

Ferrous chloride and ferrous sulfate also decompose, very efficiently, concentrated hydrochloric acid solutions of *p*-nitrobenzenediazonium chloride, giving *p*-nitrochlorobenzene in about 81 per cent yield; whereas the yield falls only slightly (*ca.* 6 per cent) even at great dilutions, the difference between the two yields when the ferrous salt is present and absent rises appreciably with dilution, thereby proving that the mechanism of decomposition involves the presence of a complex anion containing iron and chlorine.

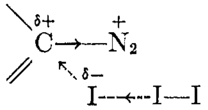
M. The action of iodides on acid solutions of diazonium salts

Experiments have been made (34) to test whether the facile direct replacement of the diazo group by iodine was due to the iodide anion, as was generally supposed, or was bound up with the oxidizing action of the diazo group. For this purpose *p*-nitroaniline was diazotized in hydrochloric acid and treated with sodium bisulfite; *p*-nitrophenylhydrazine hydrochloride then resulted. When, however, the mineral acid was first replaced by acetic acid, sodium bisulfite or sodium thiosulfate was without immediate effect, and subsequent addition of potassium iodide produced no 4-iodonitrobenzene in either case. On addition of the mild oxidizing agent copper sulfate, 4-iodonitrobenzene was immediately precipitated. Further, potassium iodide decomposed a diazo compound much more slowly in dilute acetic acid than in dilute mineral acid, a result which would indicate an equilibrium



$$RN{=}NOCOCH_3 \rightleftharpoons \left.\begin{array}{c}R\overset{+}{N}\\ |||\\ N\end{array}\right\}OCOCH_3^-$$

greatly in favor of the covalent diazo acetate. In consequence, since it is the positive diazonium ion which oxidizes 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. By 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 I_3^-, and this complex anion reacts with a diazonium ion to form the iodo compound, iodine is liberated, more iodine is regenerated, and so on.



Further, if the reaction between diazonium ion and hydriodic acid were 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. This interpretation of the direct action of potassium iodide on acid solutions of diazonium salts is strictly analogous to the formation of bromoaryls from aryldiazonium perbromides, $\mathrm{Ar}\overset{+}{\mathrm{N}_2}\}\mathrm{Br}_3^-$, without the intervention of copper as catalyst, but merely by heating with ethanol.

N. Diaryl formation in the Sandmeyer reaction

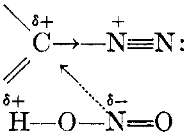
When benzenediazonium chloride was added below 10°C. to a solution of cuprous chloride which had been so diluted with water that the cuprous chloride was just precipitating, the main product was chlorobenzene; but when the sequence of addition was reversed, the chlorobenzene was now accompanied by considerable amounts of diphenyl and 4-hydroxydiphenyl. These experiments indicated that, when the complex anion was in excess, the main attack was at the cationoid carbon to which the diazo group was attached, whereas when the diazonium salt was in excess, a considerable oxidation by the diazonium salt occurred. These experiments also fall into line with the observation of Hodgson and Walker (46), that when *o*- or *p*-nitroaniline was diazotized in sulfuric–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, whereby it is oxidized to the cupric ion, nitrogen is evolved, the carbon to which the nitrogen was linked is now in the radical state, and diaryl formation takes place.

The cuprous chloride in the last case was no longer a catalyst but a reducing agent. To test the effect of substituents in the nucleus on diaryl formation, aniline, *p*-bromoaniline, *p*-toluidine, and *o*-nitroaniline were diazotized 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 gram-mole, respectively, of diaryl formation per gram-mole of amine taken, while *o*-nitroaniline gave 0.56 gram-mole of 2,2′-dinitrodiphenyl. This indicated that the more positive the diazonium ion, the more readily it was reduced and the copper oxidized. The similar results of *p*-bromoaniline and *p*-toluidine may be ascribed to the mesomeric (resonance) effect (33) of the bromine counteracting its negative $(-I)$ inductive effect, since if only the inductive effect had operated, there would have been much greater diaryl formation than that realized.

O. The replacement of the diazonium by the nitro group. A general method analogous to the Sandmeyer reaction based on the decomposition of the aryldiazonium cobaltinitrites (41)

Previous work on the replacement of the diazonium by the nitro group has been carried out by Sandmeyer (55), Veselý and Dvořák (65), Orton (51), Bucherer and van der Recke (4), Hantzsch and Blagden (27), and Contardi (9). In every case, however, the reactions were of limited application (58).

Since diazonium nitrites decompose in nitrous acid solution to form nitro compounds, the mechanism of the reaction would appear to be attack of the



carbon atom to which the diazonium group is attached by anionoid nitrogen (due to resonance) of the nitrite group; otherwise, attack by oxygen would form the hitherto unknown, and probably therefore very unstable, phenyl nitrite, wherein the nitrite group must immediately isomerize into the stable nitro group. This mechanism follows on the analogy of the much greater reactivity of anionoid nitrogen (due to resonance) in nucleophilic nitrous acid (47) than of either of its oxygens for the cationoid carbon atom. Accordingly, complex salts with diazonium cations and metallic nitrite anions were expected to offer a means of preparing nitro compounds by a mechanism analogous to that of the Sandmeyer reaction (34).

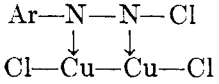
For this purpose, the aromatic diazonium cobaltinitrites were prepared by the simple addition of sodium cobaltinitrite to a solution of a diazonium salt previously neutralized by calcium carbonate (41). They were yellow to orange crystalline substances which, when obtained from the nitro- and chloroanilines, were stable when dry; those from the toluidines, anisidines, and α-naphthylamine were less stable. These cobaltinitrites decompose on heating (sometimes with explosive violence), couple with β-naphthol in alkaline solution, and with α- and β-naphthylamines in acetic acid solution, but in hydrochloric acid they diazotize amines and nitrosate phenols by the nitrous acid formed during decomposition of the complex salt by mineral acid. They have the general formula $[RN_2]_3^{+++}\ [Co(NO_2)_6]^{---}$.

When the solid diazonium cobaltinitrites from aniline, *o*-, *m*-, and *p*-nitroanilines, and *p*-chloroaniline were added to a suspension of cuprous oxide in concentrated aqueous sodium nitrite, a vigorous evolution of nitrogen took place in the cold, and excellent yields of nitro compounds were obtained. However, with the cobaltinitrites from *o*- and *p*-toluidines, *o*- and *p*-anisidines, and α- and β-naphthylamines, the yields were poor, nor did the further addition of freshly precipitated copper effect any appreciable improvement; when copper sulfate was also present, however, all the cobaltinitrites as yet prepared decomposed to give very favorable yields (mostly above 60 per cent). In the absence of sodium nitrite, cuprous oxide, either alone or in conjunction with copper sulfate, would not decompose the cobaltinitrite in the cold, although on heating there was a reaction without, however, the production of a nitro compound; addition of sodium nitrite to the cold mixture immediately brought about formation of the relevant nitro compound.

The results confirmed the expectations noted above, the anionoid (nucleophilic) nitrite group of the complex cobalt anion attacking the cationoid (electrophilic) carbon atom of the diazonium compound. The simpler mechanism of nitrogen attack, however, would imply that the cobaltinitrite anion contained at least some of its nitrito groups attached to the central cobalt atom by oxygen. This appears a reasonable assumption in view of the facts: (*1*) that the nitrito groups in the metallic cobaltinitrites are indicated by magnetic data to be covalently linked (52); (*2*) by analogy, the mixed inorganic cobalt complex salts containing both NH_3 and NO_2 groups are found in two forms, *viz.*, the red unstable nitritopentammine salts, e.g., $[Co(NH_3)_5(ONO)]X_2$, and the more stable nitropentammines, e.g, $[Co(NH_3)_5(NO_2)]X_2$ (13). Further, both NH_3 and NO_2 are themselves anionoid, but the introduction of NH_3 into the cobalt complex renders it cationoid, whereas the nitrito group renders the complex anionoid. It is reasonable, therefore, to assume that reaction occurs *via* a feebly linked nitrito group, in view of the direct formation of a nitro compound upon the decomposition of a diazonium cobaltinitrite. The function of the copper compounds is to bring about the elimination of the diazonium nitrogen, and the rôle of the sodium nitrite would appear to be the re-formation of stable sodium cobaltinitrite, which would in consequence be the main driving force of the decomposition, since the copper compounds did not themselves effect reaction in the cold.

P. Discussion of Waters' complex cuprous cation theory (71)

Subsequent to the publication by Hodgson, Birtwell, and Walker (34) of their interpretation of the Sandmeyer reaction, Waters (71) suggested a different mechanism for the Sandmeyer reaction and limited that of Hodgson *et al.* as cogent for the thermal decomposition of solid diazonium salts, which, he stated, should be classed as an ionic reaction. The Waters' mechanism, which is almost identical with that for the reduction of a diazonium compound to a diaryl, is based on his statement that Hodgson *et al.* have not been able to suggest why the cuprous salts decomposed in a way which is so very different from the double salts which diazonium halides readily form with the halides of other metals such as zinc, cadmium, mercury, arsenic, antimony, or bismuth which he formulates as $(ArN_2)_2^{++}\}ZnCl^{--}$. He assigns to Hodgson *et al.* the rôle of giving strong support for Hantzsch's view (27) that Sandmeyer reactions are essentially decompositions of complex cuprous diazonium salts formulated by Hantzsch (25) as $(ArN_2,Cu_2)X_3$. It must be pointed out that Hodgson *et al.* did not adopt Hantzsch's formula at all, but emphasized that the catalytic reagent was a cuprous halogeno anion which, in a later paper (35)—submitted for publication nearly three months before the appearance of Dr. Waters' polemic and therefore in entire ignorance of its nature—was definitely formulated by them as CuX^{---}, where X is a halogen atom. It was this cuprous halogeno anion which first formed a salt with the diazo cation, to be followed by the rearrangements already described. Hantzsch's complex had very little in common with the complex anion concept, and it has already been pointed out into what a dilemma Hantzsch would have fallen had he obtained the data which Hodgson *et al.* received from their mixed Sandmeyer reactions. By a curious circumstance, both Hantzsch and Hodgson *et al.* arrived at the same conclusion as to the source of the halogen which replaces the diazo group, though the last-named authors claim validity for their line of argument. Waters himself points out, what is really a criticism of Hantzsch's viewpoint, that while cuprous salts will form addition complexes with covalent azo compounds such as azomethane (11) and for which in consequence it could be suggested that the cuprous diazonium halides are structurally different from all other metal diazonium halides, e.g., that they contain a covalent azo group,



$$\begin{array}{ccccccc} \mathrm{Ar} & — & \mathrm{N} & — & \mathrm{N} & — & \mathrm{Cl} \\ & & \downarrow & & \downarrow & & \\ \mathrm{Cl} & — & \mathrm{Cu} & — & \mathrm{Cu} & — & \mathrm{Cl} \end{array}$$

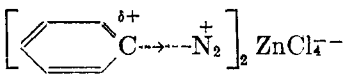
which might decompose to give neutral aryl radicals, nevertheless, the fact that metallic copper can be used instead of a cuprous salt greatly weakens the plausibility of this *ad hoc* suggestion.

The isolation, however, by Hodgson *et al.* of stable complex salts of the type $\overset{+}{R}N_2\}FeCl_4^-$ (45), and $(RN_2)_3^{+++}\}Co(NO_2)_6^{---}$ (41), should leave no possible shadow of doubt as to their conception of what the complex salt would be in the classical Sandmeyer reaction *viz.*, $(RN_2)_3^{+++}\}CuCl_4^{---}$, a conception never put forward either by Hantzsch or by any other author prior to 1941. Further, in reply to Waters' challenge, Hodgson *et al.* (36) reaffirmed emphatically that, far from being unable to suggest why cuprous salts were almost unique as Sandmeyer catalysts, they held the belief (implicit in the very first paragraph of their paper (34)) that there was no justification for such a point of view as that advanced by Waters; in support thereof examples were quoted from both the benzene and the naphthalene series where cupric salts act as efficiently (or nearly so) as cuprous salts, i.e., examples for which the Waters' explanation (71) could have no validity whatever. Moreover, Waters did not mention these reactions, although it is obvious that if cupric salts could behave under identical circumstances like cuprous salts, his whole argument for an oxidation-reduction mechanism involving a complex cation of a cuprous diazonium double salt becomes invalid. In like manner, Sandmeyer's own statement (53) that cupric salts were without the same action as cuprous salts was based on insufficient evidence. Throughout his paper (70) Waters argued for the unique or almost unique character of cuprous salts for replacement of the diazo group by halogens under the conditions of the Sandmeyer reaction, i.e., in aqueous acids, but this unique character does not exist in actual fact (despite Waters' assertion to the contrary, page 268), and the whole argument of a single electron-transfer mechanism from the cuprous copper collapses when the electron comes from the anionoid (nucleophilic) halogen loosely attached to the copper in the complex anion and not from the copper itself. To clinch the argument, it has been shown (33, 43) that below a certain acid strength, cupric chloride is superior as a catalyst to cuprous chloride.

It was pointed out by Hodgson *et al.* in their original paper (34) that the Sandmeyer reaction appeared to be dependent on the degree of positivity of the diazonium ion, which, when of sufficient magnitude, enabled the more ephemeral cupric halogen complexes to react like their more abundant cuprous analogues. This dependence has been subsequently illustrated by the data given above for decomposition by cupric salts, which indicated that when the significant carbon had only a relatively small positive charge (as in diazotized aniline or *p*-toluidine) the yield of chloro compound was only small, but with increase of positivity, as in *p*-chlorobenzenediazonium chloride, and still more so in *p*-nitrobenzenediazonium chloride, owing to the $(-I)$ inductive effect of the chloro and nitro groups, respectively, yields as ample as those with cuprous chloride were obtained. Incidentally, but important for the argument, no diaryl formation was observed in the decompositions with cupric salts, the usual by-product being the corresponding phenol. Waters implicitly concedes this point, since he depicts [71, page 268, Fig. 1] the positive centers of a complex cation of a cuprous diazonium double salt as attracting each other, an attraction which could only result in electron release to the significant carbon of the aryl group when this is at a higher positive potential than the cuprous copper. Hodgson *et al.* suggested that attraction was far more likely to occur between the reactive anionoid center of a complex anion (such as is generally acknowledged to be formed when cuprous salts are dissolved in mineral acids) and the positive significant carbon, than between positive centers in a complex structure such as that depicted by Waters.

Q. Halogen replacements by metallic complexes other than those of copper

A statement by Groggins (20) that copper is not the only metal that can advantageously be employed for the replacement of the diazo group by halogen has already been quoted above. Further, recent work by Hodgson and Foster (38) has established that zinc chloride double salts of diazonium chlorides are decomposed by molten phenols, and, in the cases where a nitro group was not present in the aromatic nucleus of the diazonium chloride, three simultaneous reactions occurred, *viz.:* (*a*) replacement of the diazo group by chlorine, which is the main reaction and affords yields of chloro compounds up to 50 per cent; (*b*) formation of a hydroxydiphenyl; and (*c*) formation of a diphenyl ether. The three different mechanisms involved may be illustrated from the complex involving benzenediazonium chloride,



The cationoid carbon to which the diazo group is attached reacts: (*a*) with anionoid chlorine in the complex, whereby electron release to the carbon occurs with separation of neutral chlorine, evolution of nitrogen, and subsequent linkage of the aryl radical with neutral chlorine to form chlorobenzene in 40 per cent yield, a mechanism analogous to that of the Sandmeyer reaction (34); (*b*) with the anionoid *p*-carbon atom of the phenol to form, by similar release of electrons, etc., the 4-hydroxydiphenyl in 26 per cent yield; (*c*) with the anionoid oxygen of the hydroxyl group of the phenol, whereby the diphenyl ether is produced in 20 per cent yield. The zinc chloride double salts of *o*-, *m*-, and *p*-nitrobenzenediazonium chlorides all coupled with the phenol to form *o*-, *m*-, and *p*-nitrobenzeneazophenols. This enhanced coupling power is due to the well-known stabilizing effect of the nitro on the diazo group. The anionoid (nucleophilic) phenol in the reaction above plays a rôle identical with that of anionoid water.

When the double salts of diazonium chlorides with lead tetrachloride are heated with alcohol, the diazo group is replaced by chlorine (7), the reaction being analogous to the decomposition of the perbromides and indicating the function of the metal to be that of host for the formation of the reactive complex anion.

R. The dual rôle of cuprous compounds

Hodgson *et al.* (36) consider that it is more rational to postulate distinct mechanisms (*1*) for halogen substitution and (*2*) for diaryl formation than a single mechanism such as that proposed by Waters (71) for both. Hodgson and Walker found (46) that when the amount of water was reduced, i.e., the concentration of the complex cuprous ion increased, diaryl formation could be prevented altogether in the decomposition of *o*- and *p*-nitrobenzenediazonium chlorides by cuprous chloride in hydrochloric acid solution. The Waters' mechanism does not explain the complete absence of diaryl formation in such cases, which is due not to the high concentration of chloride ions, since this may be very moderate, but to conditions which favor the maximum production of a complex anion. Likewise, when the water content was increased, the formation of diaryl was also increased but was accompanied by that of nitrophenol, indicating that anionoid water now competed with the cuprous reducing agent for the diazonium salt.

The Waters' mechanism, moreover, differs only in elaboration from that already proposed by Groggins (20), who also introduces hydroxyl anions as competitors with the cationoid complex. Hodgson *et al.* submit that it is more reasonable to assume competition for the diazonium cation between a complex cuprous anion and anionoid water (since there are no hydroxyl ions present in such strong acid solutions, in a realistic sense of the term), than to assume a competing cuprous cation. The fact that by reducing the amount of anionoid copper complex by dilution of the solution with water the yield of halogen compound is decreased, whereas that of phenol is increased, supports this viewpoint.

S. Decompositions by copper sulfate, with and without other oxidizing agents

Reactions between nitroaryldiazonium sulfates, copper sulfate, and sodium chloride or bromide in sulfuric acid solution to give chloro- or bromoaryls in 90–100 per cent yields were discovered by Hodgson (31). Benzenediazonium sulfate itself gives a 38 per cent yield of bromobenzene under similar conditions. To eliminate any chance of cuprous salt formation (in view of Waters' statement as to the unique character of cuprous salts (71)), a number of reactions were carried out with *p*-nitrobenzenediazonium sulfate, copper sulfate, and sodium bromide, in the presence of ammonium persulfate and also of ferric chloride. Although the yields of halogenoaryl were not much affected, nevertheless in the ferric chloride experiment a mixture of about equal parts of 4-chloro- and 4-bromonitrobenzenes resulted. When hydrogen peroxide was used as the supplementary oxidizing agent, the yield of 4-bromonitrobenzene was reduced, and the reaction included the initial formation of a yellow precipitate (probably of a perbromide), which, on heating, decomposed with evolution of bromine and separation of 4-bromonitrobenzene. The last experiment might suggest that when oxidizing agents are present, bromine replacement occurs *via* intermediate formation of a perbromide, but in the decompositions with sodium bromide and copper sulfate alone, the by-product was always the corresponding phenol, which was never found to have been brominated. Further, a mixture of copper sulfate, sodium bromide, and phenol, in the presence of dilute sulfuric acid, gave no precipitate of tribromophenol, even when heated under reflux on the water bath for an hour and subsequently kept for 24 hr. Initial formation of the perbromide does not therefore take place in the copper sulfate and sodium bromide experiments, and the mechanism of decomposition of the diazonium salt is *via* a cupric copper anionoid complex as originally suggested by Hodgson *et al.* (34, 35).

V. CONCLUSIONS

The experimental evidence proves: (*a*) cuprous salts do not possess the unique (or almost unique) character claimed for them first by Sandmeyer (53) and recently by Waters (71). (*b*) In cases where the diazonium cation possesses sufficient positivity, cupric salts can function with efficiencies comparable to those of cuprous salts and, under certain conditions, even superior to them. (*c*) Metals other than copper, such as iron, cobalt, and zinc, can form anionoid complexes with halogens which decompose diazonium cations in like manner to the copper salts. (*d*) The Sandmeyer reaction is an oxidation–reduction process involving an electrophilic diazonium cation and a nucleophilic (anionoid) halogen which is part of a cuprous copper halogeno complex anion, the formula of the intermediate salt, by analogy with the isolable iron salts, $(\mathrm{Ar\overset{+}{N}})\}\mathrm{FeCl_4^-}$, and with the aryldiazonium cobaltinitrites, $(\mathrm{ArN_2})_3^{+++}\}\mathrm{Co(NO_2)_6^{---}}$, being $(\mathrm{ArN_2})_3^{+++}\}$ $\mathrm{CuCl_4^{---}}$. (*e*) There are no fundamental differences in the mechanism of formation of halogen compounds during the decomposition of complex salts of diazonium chlorides with cuprous chloride, cupric chloride, cobalt chloride, ferric chloride, zinc chloride, or any other chloride including hydrogen chloride (similarly for hydrogen fluoride) in aqueous or other media; such differences as do occur, e.g., in the distribution of yield, are due to differences in structure, stability, and concentration of the complex anion, whereby the competing action of anionoid water can become negligible (cuprous salts) or predominant (zinc salts). (*f*) The decomposition of diazonium cations by potassium iodide proceeds *via* the formation of KI_3, and it is the complex anion I_3^- which enters into the mechanism of decomposition, by analogy with the similar decomposition of aryldiazonium perbromides, $Ar\overset{+}{N_2}\}Br_3^-$, and both are in accordance with the mechanism of the Sandmeyer reaction. (*g*) All the reactions discussed in this paper can be interpreted by the simple anionoid mechanism proposed (34, 35). The older theories of Hantzsch, Erdmann, Gattermann, Groggins, etc., are obviously inadequate, and in the cases of Hantzsch, Erdmann, and Groggins, an unnecessary covalent union of copper and nitrogen is assumed.

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VI. REFERENCES

(1) BARBER, H. J.: J. Chem. Soc. **1934,** 79.
(2) BLUMBERGER, J. S. P.: Rec. trav. chim. **49,** 267 (1930).
(3) BLUMBERGER, J. S. P.: Rec. trav. chim. **49,** 1420 (1930).
(4) BUCHERER, H. T., AND VAN DER RECKE, G.: J. prakt. Chem. **132,** 121 (1931).
(5) CASSELLA & Co.: British patent 1920 of 1894; French patent 235,271; German patent 29,055; U. S. patent 535,037.
(6) CHATTAWAY, F. D.: J. Chem. Soc. **95,** 869 (1909).
(7) CHATTAWAY, F. D.: J. Chem. Soc. **125,** 1981 (1924).
(8) CHROBAK, L.: Z. Krist. **88,** 30 (1934).
(9) CONTARDI, A.: Ann. chim. applicata **7,** 13 (1923).
CONTARDI, A., AND MOR, G. G.: Rend. ist. lombardo sci. **57,** 646–54 (1924); *cf.* Chem. Abstracts **17,** 2109.
(10) DAVEY, W. P.: Phys. Rev. **19,** 248 (1922).
(11) DIELS, O., AND KOLL, W.: Ann. **443,** 262 (1925).
(12) EICHENBERG, E.: Dissertation, E. T. H. Zürich, 1929.
(13) EMELÉUS, A. J., AND ANDERSON, J. S.: *Modern Aspects of Inorganic Chemistry,* p. 144. G. Routledge & Sons, Ltd., London (1938).
(14) ERDMANN, H.: Ann. **272,** 141 (1893).
(15) FIERZ-DAVID, H. E.: *The Fundamental Processes of Dye Chemistry,* p. 93. J. and A. Churchill, London (1921).
(16) GATTERMANN, L.: Ber. **23,** 1218 (1890).
(17) GATTERMANN, L., AND CANZLER, A.: Ber. **25,** 1091 (1892); *cf.* also GATTERMANN, L.: Ber. **23,** 738, 1218, 1223 (1890); **32,** 1136 (1899); LANDSBERG, Z.: Ber. **23,** 1454 (1890); ULLMANN, F.: Ber. **29,** 1878 (1896); Ann. **332,** 28 (1904); VORLÄNDER, D., AND MEYER, F.: Ann. **320,** 122 (1902); ULLMANN, F., AND FRENTZEL, L.: Ber. **38,** 725 (1905).

(18) Goldschmidt, V. M.: Z. Elektrochem. **34,** 459 (1928).

(19) Griess, P.: Ann. **137,** 56 (1886); Ber. **1,** 190 (1868); **18,** 961 (1885).

(20) Groggins, P. H.: *Unit Processes in Organic Syntheses*, pp. 198–9. McGraw-Hill Book Company, Inc., New York and London (1938).

(21) Reference 20, p. 228.

(22) Grossmann, H., and von der Forst, P.: Z. anorg. Chem. **43,** 94 (1905).

(23) Hammett, L. P.: *Physical Organic Chemistry*, p. 295. McGraw-Hill Book Company, Inc., New York and London (1940).

(24) Hantzsch, A.: Ber. **27,** 1702 (1894).

(25) Hantzsch, A.: Ber. **28,** 1751 (1895); *cf.* also Neumann, G.: Monatsh. **15,** 492 (1894).

(26) Hantzsch, A.: Ber. **33,** 2534 (1900).

(27) Hantzsch, A., and Blagden, G. W.: Ber. **33,** 2544 (1900).

(28) Hantzsch, A., and Vock, R.: Ber. **36,** 2060 (1903).

(29) Harker, D.: Z. Krist. **93,** 136 (1936).

(30) Hendricks, S. B., and Dickinson, R. G.: J. Am. Chem. Soc. **49,** 2149 (1927).

(31) Hodgson, H. H.: J. Soc. Dyers Colourists **42,** 365 (1926).

(32) Hodgson, H. H.: J. Soc. Dyers Colourists **42,** 367 (1926).

(33) Hodgson, H. H.: J. Chem. Soc. **1946,** in press.

(34) Hodgson, H. H., Birtwell, S., and Walker, J.: J. Chem. Soc. **1941,** 770.

(35) Hodgson, H. H., Birtwell, S., and Walker, J.: J. Chem. Soc. **1942,** 376.

(36) Hodgson, H. H., Birtwell, S., and Walker, J.: J. Chem. Soc. **1942,** 720.

(37) Hodgson, H. H., Birtwell, S., and Walker, J.: J. Chem. Soc. **1944,** 18.

(38) Hodgson, H. H., and Foster, C. K.: J. Chem. Soc. **1942,** 581.

(39) Hodgson, H. H., Leigh, E., and Turner, G.: J. Chem. Soc. **1942,** 744.

(40) Hodgson, H. H., and Mahadevan, A. P.: J. Chem. Soc. **1947,** in press.

(41) Hodgson, H. H., and Marsden, E.: J. Chem. Soc. **1944,** 22.

(42) Hodgson, H. H., and Nixon, J.: J. Chem. Soc. **1928,** 1879.

(43) Hodgson, H. H., and Sibbald, D. D. R.: J. Chem. Soc. **1944,** 393.

(44) Hodgson, H. H., and Sibbald, D. D. R.: J. Chem. Soc. **1945,** 545.

(45) Hodgson, H. H., and Sibbald, D. D. R.: J. Chem. Soc. **1945,** 819.

(46) Hodgson, H. H., and Walker, J.: J. Chem. Soc. **1933,** 1620.

(47) Kenner, J.: Chemistry & Industry **60,** 443 (1941).

(48) Korczynski, A., and Fandrich, B.: Compt. rend. **183,** 421 (1926).

(49) Lellmann, E., and Remy, L.: Ber. **19,** 810 (1886).

(50) Mann, F. G., Purdie, D., and Wells, A. F.: J. Chem. Soc. **1936,** 1503.

(51) Orton, K. J. P.: J. Chem. Soc. **83,** 806 (1903).

(52) Pauling, L.: *The Nature of the Chemical Bond*, p. 116. Cornell University Press, Ithaca, New York (1940).

(53) Sandmeyer, T.: Ber. **17,** 1633 (1884).

(54) Sandmeyer, T.: Ber. **17,** 2650 (1884).

(55) Sandmeyer, T.: Ber. **20,** 1945 (1887).

(56) Sandmeyer, T.: Ber. **20,** 1945 (1887); **23,** 1630 (1890).

(57) Sandmeyer, T.: Ber. **23,** 1881 (1890).

(58) Saunders, K. H.: *The Aromatic Diazo Compounds and their Technical Applications*, p. 155. Edward Arnold & Co., London (1936).

(59) Schmidt, J., and Maier, O.: J. prakt. Chem. **133,** 153 (1931).

(60) Schwechten, H. W.: Ber. **65,** 1605 (1932).

(61) Sidgwick, N. V.: *The Organic Chemistry of Nitrogen*, p. 407. The Clarendon Press, Oxford (1937).

(62) Sidgwick, N. V.: *The Organic Chemistry of Nitrogen* (revised by T. W. J. Taylor and W. Baker), p. 406. The Clarendon Press, Oxford (1938).

(63) Starkey, E. B.: J. Am. Chem. Soc. **59,** 1427 (1937); *cf. Organic Syntheses* **19,** 40–2, John Wiley and Sons, Inc., New York (1939).

(64) Tobias, G.: Ber. **23,** 1628 (1890).
(65) Veselý, V., and Dvorǎk, K.: Bull. soc. chim. **31,** 421 (1922).
(66) Votoček, E.: Chem. Listy **20,** 1 (1896); Chem.-Ztg. **20,** 70 (1896).
(67) Votoček, E., and Zeníšek, E.: Z. Elektrochem. **5,** 458 (1899).
Veselý, V.: Ber. **38,** 136 (1905).
(68) Waentig, P., and Thomas, J.: Ber. **46,** 3923 (1913); *cf.* also Heller, G., and Tischner, W.: Ber. **44,** 250 (1911).
(69) Walter, J.: J. prakt. Chem. **53,** 427 (1896).
(70) Waters, W. A.: J. Chem. Soc. **1939,** 868.
(71) Waters, W. A.: J. Chem. Soc. **1942,** 266.
(72) Wyckoff, R. W. C., and Posnjak, E.: J. Am. Chem. Soc. **44,** 30 (1922).