SANDMEYER AND RELATED REACTIONS

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The diversity of compounds that may be prepared by replacement of the diazonium group has often been a matter for comment. Just as remarkable, perhaps, is the fact that nearly all of these reactions have at some time been found to be catalysed by metallic salts or even by metals themselves : copper is the element most frequently mentioned in this connection. The purpose of this Review is to note the most important observations on this type of catalysis and to see how far they can be accommodated into a simple and coherent theory.

These reactions fall into two classes. In the first, a simple nucleophilic replacement occurs, in which the N_2 belonging to the diazonium ion separates with the pair of electrons from the Ar–N bond, and is replaced by a " Lewis " base, *e.g.*,

$$ArN_2^+ + Cl^- \longrightarrow ArCl + N_2$$

In the second, the substitution involves an overall reduction, so that two electrons must be provided by the permanent oxidation of the catalyst or some other added reducing agent, *e.g.*,

$$\begin{aligned} ArN_2^+ + ArN_2^+ + 2e &\longrightarrow Ar{\cdot}N{:}N{\cdot}Ar + N_2 \\ ArN_2^+ + ArN_2^+ + 2e &\longrightarrow Ar{\cdot}Ar + 2N_2 \\ ArN_2^+ + H^+ + 2e &\longrightarrow ArH + N_2 \\ ArN_2^+ + C_2H_5{\cdot}OH &\longrightarrow ArH + CH_3{\cdot}CHO + N_2 + H^+ \end{aligned}$$

(A) Replacement Reactions without Reduction

(1) Formation of a C–Halogen Link.—The uncatalysed replacement of the diazonium group by halogen was discussed by Griess [1] as early as 1866 ; it proceeds readily with the iodides, but only in special instances (*e.g.*, the chloride replacement of 2-ethoxyquinoline-4-diazonium chloride)[1a] are good yields recorded for the chlorides or bromides. Not until 1884 did Sandmeyer [2] discover the remarkable power of cuprous salts for bringing about chloride and bromide substitutions. In trying to prepare phenylacetylene from cuprous acetylide and benzenediazonium chloride, he identified the reaction product as chlorobenzene contaminated with azobenzene. He established the irrelevance of the acetylene, and demonstrated the general nature of the valuable new synthetic reaction.

In his original work, Sandmeyer added the diazonium solution to the boiling cuprohalide solution, but the reaction can be carried out satisfactorily at much lower temperatures ; *e.g.*, Fry and Grote,[3] using 10 mols. of acid, 1 mol. of amine (converted into diazonium salt), and 1 mol. of

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[1] *Annalen*, 1866, **137**, 89 ; *Ber.*, 1868, **1**, 190 ; 1885, **18**, 961.

[1a] Buchmann and Hamilton, *J. Amer. Chem. Soc.*, 1942, **64**, 1359.

[2] *Ber.*, 1884, **17**, 1633, 2650.

[3] *J. Amer. Chem. Soc.*, 1926, **48**, 710.

cuprous halide, have shown that with a number of nitro- and halogeno-amines the yield is almost unchanged from 0° to 100°. Recent kinetic measurements have demonstrated that the reaction is still quite fast at 0°, even with the less reactive amines. In this respect the Sandmeyer reaction differs from the Griess replacement, where gentle warming to, say, 30—70° is usually necessary: it seems likely that the Griess reaction involves a different mechanism. There is a claim by Kuhn and Eichenberger [4] that high concentrations of very soluble salts (calcium chloride, zinc ammonium chloride) can give reasonable yields of chloride even from the less reactive compounds such as toluene-*o*-diazonium chloride. By contrast, high halide concentrations actually reduce the rate of the Sandmeyer reaction.[5] The function of the cuprous ion is purely catalytic, and quantities as little as 0·1 mole per mole of diazonium compound can be used, with almost complete conversion.

Aryl fluorides or iodides are not prepared by Sandmeyer reactions, in the former case because cuprous fluoride disproportionates to copper and cupric fluoride at room temperature, and in the latter because cuprous iodide will not dissolve in excess of iodide (it is generally accepted that the Sandmeyer reaction is a homogeneous aqueous-phase process).

Some six years after Sandmeyer's discovery, Gattermann [6] found that finely divided copper was an effective catalyst for halide replacements. This, again, was an accidental discovery, for the intention was to prepare diphenyl from benzenediazonium chloride. At the time of its discovery, the method was claimed to give higher yields than the Sandmeyer reaction because it operated at lower temperatures: this claim, however, can hardly be upheld today. As mentioned on p. 376, it now seems very doubtful whether there is any fundamental distinction between the mechanism of the two reactions.

There is an extensive literature on replacements by other metallic halides. Contardi and Mor [7] and Hodgson and his co-workers [8, 9] have demonstrated that better yields can be obtained with cupric than with cuprous chloride in the case of diazonium ions bearing a negative substituent such as nitro-. By contrast, much higher yields can be obtained with cuprous than with cupric chloride where there is an *o*- or *m*-methyl group. Fry and Grote [3] mention a borderline case (*m*-halogenodiazonium ion) where cuprous chloride is the better for chloride replacement, and cupric bromide better for bromide. These apparent conflicts are readily resolved. Cuprous halides (*a*) can cause reductive side reactions and (*b*) react at lower temperatures. Provided that the diazonium ion is reasonably stable at temperatures where the cupric halide replacement occurs, (*b*) offers no advantage, and the absence of the side reactions (*a*) makes cupric ion the better-yielding catalyst. If, however, the diazonium ion is not stable under these conditions,

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[4] D.R.-P. 541,255.

[5] Cowdrey and Davies, *J.*, 1949, S48.

[6] *Ber.*, 1890, **23**, 1218.

[7] *Rend. Ist. Lombardo*, 1924, **57**, 646 (*Chem. Abs.*, 1925, **19**, 827).

[8] Hodgson, Birtwell, and Walker, *J.*, 1944, 18.

[9] Hodgson and Sibbald, *J.*, 1944, 393.

cuprous halide can be used with advantage, for it can operate at a lower temperature where the suppression of decomposition to phenol more than offsets the waste due to the formation of diaryls or azo-compounds.

Hodgson, Birtwell, and Walker [8] have also shown that iron and cobaltous chlorides are good catalysts for the easier Sandmeyer replacements. Sometimes, too, the thermal decomposition (dry, or in organic solvents) of diazonium salts with complex anions (*e.g.*, $PtCl_6^{=}$) gives reasonable results, and Schwechten [10] showed that dichloro- and dibromo-diphenyl can be obtained in higher yield by heating the dry diazonium mercuric halide with sodium halide, than by the Sandmeyer reaction. Newman and Wise [11] used this reaction for making 2-bromonaphthalene. Oda, Nakano, and Isoda [12] recommended heating the diazonium halide and zinc chloride in aqueous suspension.

For general synthetic work, however, the decomposition of dry diazonium complexes has little to commend it if the simpler solution methods are applicable. It is only in the preparation of fluorides, where the decomposition of dry diazonium borofluorides [13] has been the only general method available, that the reaction is much used. The borofluorides are sometimes soluble, and separate in poor yields, and the subsequent decomposition may be difficult or hazardous. A method now claimed to be more convenient and to lead sometimes to higher yields has been described by Ferm and Van der Werf.[14] Here, the amine is diazotised by sodium nitrite in liquid hydrogen fluoride, and the resulting diazonium fluoride refluxed in hydrogen fluoride until decomposed.

Electrolytic techniques for halogen replacements have been described,[15] and it is quite clear that these involve the Sandmeyer reaction. In the conversion of diazotised aniline into chlorobenzene, electrolysis in a solution containing cupric chloride, with copper electrodes, can give a 71% yield. With iron electrodes and iron salts, the yield is only 3%. *o*- and *p*-Chlorotoluene have been made in this way, and in the former case the diazonium–cuprous complexes familiar in Sandmeyer reactions are observed to separate. There appears to be no economic advantage in this procedure.

(2) **Formation of a C–O or C–S Link.**—The use of metals or their compounds as catalysts for this class of reaction is not very common. The well-known decomposition of diazonium ions to phenols does not always proceed in good yield, and the addition of copper sulphate has been claimed to assist the conversion of diazotised *o*-anisidine into guaiacol.[16] The corresponding conversion of diazonium compounds into diaryl ethers has been carried out by reaction of the zinc chloride complexes with phenol.[17]

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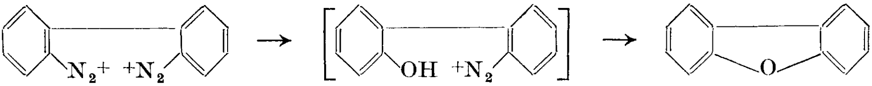
[10] *Ber.*, 1932, **65,** 1605.
[11] *J. Amer. Chem. Soc.*, 1941, **63,** 2847.
[12] *Chem. Abs.*, 1951, **45,** 7037.
[13] Balz and Schiemann, *Ber.*, 1927, **60,** 1186.
[14] Abst. 114th Meeting A.C.S., 1948, 60L.
[15] Votoček and Zenišek, *Z. Elektrochem.*, 1899, **5,** 458 ; Veseley, *Ber.*, 1905, **38,** 136.
[16] Gilliard, Monnet, and Cartier, D.R.-P. 167,211 (1904).
[17] Hodgson and Foster, *J.*, 1942, 581.

The reaction mixture obtained from the benzenediazonium complex contained 40—50% of chlorobenzene, 10—20% of diphenyl oxide, and 25—40% of 4-hydroxydiphenyl. The formation of dibenzofuran from tetrazotised 2 : 2′-diaminodiphenyl (which occurs on boiling in aqueous solution) [10] can be carried out cold by the addition of copper powder ; [18] this, although it increases the rate, does not raise the yield : [19]



The sulphur-containing compounds that can be made from diazonium ion with formation of a C–S bond include the thioacetates ($RS{\cdot}CH_2{\cdot}CO_2{\cdot}H$), the xanthates ($RS{\cdot}CS{\cdot}OEt$),[20] the thiols, the thiocyanates,[21, 22] and the sulphinic acids.[23] The first three of these syntheses do not involve the use of metallic compounds as catalysts, possibly because the normally active metals form strong bonds to sulphur and may be sequestered by reactants or products. The thiocyanates have been prepared from diazonium compounds and potassium thiocyanate, but the reaction is catalysed by a variety of metallic compounds [such as $MnSO_4$, $Cr_2(SO_4)_3$, and WCl_6] and also by Gattermann's copper. Cupric thiocyanate (which decomposes in water to cuprous thiocyanate) has also been employed.

Sulphinic acids can be made from diazonium compounds, sulphur dioxide, and copper powder. This involves an overall reduction, and it was shown that the copper and not the sulphur dioxide served as the reducing agent :

$$Ar{\cdot}N_2^+ + SO_2 + Cu \longrightarrow Ar{\cdot}SO_2^- + N_2 + Cu^{++}$$

This reaction is useful for making sulphonic acids which are inaccessible by sulphonation.

(3) Formation of C–N, C–As, C–Sb, **and** C–Bi **Linkages.**—As with halogen replacements, it is possible to displace diazonium groups directly with nitro-groups by treatment with solutions of nitrites, although this form of replacement seems limited to those compounds with electron-attracting groups in the nucleus such as 2 : 4 : 6-tribromobenzenediazonium sulphate,[24] 2 : 6-dibromo-4-nitrobenzenediazonium nitrate,[25] and the nitrobenzenediazonium halides.[26]

In seeking to extend his halogen replacement reaction to anions of acids which do not form stable cuprous salts, Sandmeyer [27] discovered that the diazonium group was readily replaced by the nitro-group on treatment

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[18] Niementowski, *Ber.*, 1901, **34,** 3325.

[19] Friedländer, *Ber.*, 1906, **39,** 1060.

[20] Leukardt, *J. pr. Chem.*, 1890, **41,** 179.

[21] Gattermann and Haussknecht, *Ber.*, 1890, **23,** 738.

[22] Kaufmann and Küchler, *Ber.*, 1934, **67,** 944 ; Korczynski, *Bull. Soc. chim.*, 1921, **29,** 283 ; *Compt. rend.*, 1920, **171,** 182.

[23] Gattermann, *Ber.*, 1899, **32,** 1136.

[24] Orton, *J.*, 1903, **83,** 806.

[25] Körner and Contardi, *Atti R. Accad. Lincei*, 1913, **22,** 625.

[26] Bücherer and Frohlich, *J. pr. Chem.*, 1931, **132,** 104.

[27] *Ber.*, 1887, **20,** 1494.

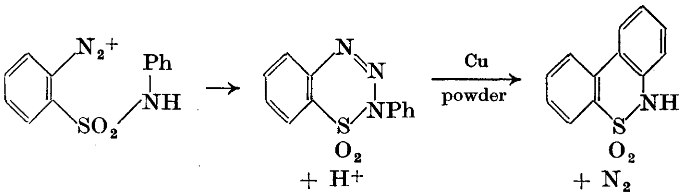
with sodium nitrite, cuprous oxide or hydroxide being used as catalyst. Other catalysts have since been reported ; Hantzsch and Blagden [28] showed that red cupro-cupric sulphite obtained from copper carbonate or oxide with aqueous sulphur dioxide was effective Hodgson; *et al.*[29] have claimed to obtain an even more active material by treating copper sulphate with sulphur dioxide, and Vesely and Dvořak [30] successfully employed finely divided copper. Contardi and his co-workers [31] have also explored the use of cupric ions, which, as for halogen replacements, succeeds well in compounds carrying electron-attracting substituents.

The nitro-replacement reaction using double salts of diazonium compounds has also been investigated. Hantzsch [28] studied the reaction with diazonium sulphite–mercurous nitrite complexes, with the object of establishing that the replacing group does not come from the radical associated with the diazonium compound but from the copper salt ; they showed that on treatment with copper or cuprous salts the diazonium compounds gave good yields of nitro-compounds, and in certain difficult replacements, *e.g.*, for preparing 2-nitronaphthalene, this method was more efficient than the orthodox Sandmeyer process. Hodgson and his co-workers [32, 33] studied the copper-catalysed reaction of aryldiazonium cobaltinitrites, and claimed improved conversions into nitro-compounds, and Starkey [34] reports high yields from the borofluorides of diazonium compounds with nuclear electron-attracting substituents.

Reactions of diazonium ions with secondary amines according to the equation

$$ArN_2^+ + R_2NH \longrightarrow ArNR_2 + N_2 + H^+$$

are known, but are not common. The 1-diazonium group in the anthraquinone nucleus has been replaced in this way (in rather complex reactions) : [35] copper and zinc compounds are mentioned as catalysts. A ring-formation reaction, involving copper catalysis, has also been reported,[36] *viz.*,



A remarkable reaction leading to a C–N linkage has been described by

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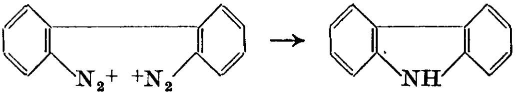
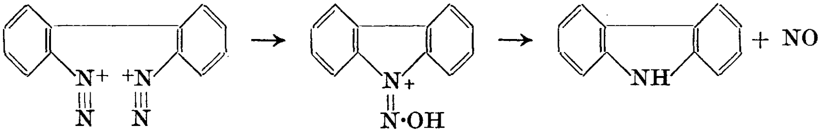
[28] *Ber.*, 1900, **33**, 2544.
[29] Hodgson, Mahadevan, and Ward, *J.*, 1947, 1392.
[30] *Bull. Soc. chim.*, 1922, **31**, 421.
[31] *Ann. Chim. appl.*, 1922, **7**, 13.
[32] Hodgson and Marsden, *J.*, 1944, 22.
[33] Hodgson and Ward, *J.*, 1947, 127.
[34] *J. Amer. Chem. Soc.*, 1937, **59**, 1479.
[35] I.G., B.P. 331,217 (1929).
[36] Ullmann and Gross, *Ber.*, 1910, **43**, 2694.

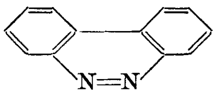
Niementowski[37] and by Dobbie, Fox, and Gauge.[38] This is the conversion of tetrazotised 2 : 2′-diaminodiphenyl into carbazole :



Niementowski used potassium hydrogen sulphide to bring about this reaction : complex sulphur-containing intermediates are then involved. Dobbie, Fox, and Gauge used cuprous chloride or bromide at 90—100°, and reported that nitric oxide was evolved. This strongly suggests that there is effective reversal of the diazotisation reaction in one of the groups, *e.g.*,



No attempt is made here to specify the role of the copper catalyst, but such an interpretation seems more likely than those previously advanced which involve hydrazine intermediates. It may be mentioned that 3 : 4 benzocinnoline is also formed and that this product predominates if cold cuprous halides are used. If the diaminodiphenyl is diazotised in presence of cuprous bromide some 2 : 2′-dibromodiphenyl is obtained.



Gattermann and Cantzler's reaction[39] has been used to give aryl *iso*cyanates :

$$ArN_2^+ + CNO^- \xrightarrow[\text{powder}]{\text{Cu}} Ar{\cdot}NCO + N_2$$

but yields are poor and this synthesis is hardly ever used.

No corresponding reactions are described for forming C–P linkages, but Bart's reaction[40] for the formation of aromatic arsonic acids $Ar{\cdot}AsO(OH)_2$ and the corresponding Schmidt modification for the stibonic acids $Ar{\cdot}SbO(OH)_2$ are formally analogous to the nitro-replacement, with the difference that the ortho-acids $R(OH)_3$ are the stable forms with arsenic and antimony whilst the meta-form is the stable nitrogen acid. Arsenious and antimonous acids are much weaker ($pK \sim 10$) than nitrous acid ($pK \sim 4$), and because the anionic forms of the acids are required for reaction with incipient carbonium ions from the diazonium compounds, the formation of the arsonic and stibonic acids requires more alkaline conditions. This requirement carries with it its own complications ; at more alkaline pH's the diazonium salts are converted into diazoates and *iso*diazoates, and furthermore, decomposition with loss of nitrogen at intermediate pH's becomes quite appreciable. The reaction is consequently very sensitive to con-

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[37] *Ber.*, 1901, **34,** 3325.

[38] *J.*, 1911, **99,** 1615.

[39] *Ber.*, 1890, **23,** 1225.

[40] B.P. 568 (1911) ; *Annalen*, 1922, **429,** 55.

ditions, so that the precise mode of mixing the alkaline arsenites with the diazonium salts and the pH of the resultant solution are of considerable importance.[41] Sodium carbonate has been recommended by Blas [42] as a buffer for making phenylarsonic acid, but the optimum pH depends considerably on the nature of the diazonium compound, and for *p*-nitrobenzene- and 2 : 4-dinitrobenzene-diazonium halides it even lies slightly on the acid side.[43]

As with the nitro-replacement, the Bart reaction can be carried out in absence of catalysts, but copper salts, finely divided copper, and other substances such as silver, nickel, cobalt, and their salts have all been reported to lead to improved performances.[44] An interesting modification of the Bart reaction is due to Scheller,[45] who prepared the mixed diazonium salt–arsenic trichloride compound in absence of water, and then treated it with water in presence of cuprous salts to bring about the diazo-replacement reaction. Starkey's technique of using the borofluoride [46] is claimed to have advantages with certain diazonium compounds.

An attempt has been made by Hamilton and Morgan [47] to correlate the yields from Bart reactions with the structure of the diazonium compound; little regularity is observed beyond the apparently hampering effects of certain *m*-substituents (*e.g.*, NO_2 and OH). The data, however, relate to yields obtained with insufficiently rigid standardisation of experimental conditions to warrant any theoretical conclusions from them.

Finally, the formation of C–Bi links has been little investigated. Gilman and his co-workers [48] have shown that the double diazonium halide–$BiCl_3$ salts can be reduced in solvents with copper or copper bronze to yield $Ar{\cdot}BiCl_2$, Ar_2BiCl, and Ar_3Bi.

(4) Non-reductive Formation of a C–C **Link.**—This type of reaction includes the very well-known reaction of diazonium compounds with cuprocyanide solutions, discovered at the same time as the halide substitutions by Sandmeyer [49] in 1884. The original method for the reaction (gradual addition of diazonium solution to hot cuprocyanide) is still widely used, although various alternative techniques have been described. Ahrens [50] improved the conversion of diazotised *o*-aminophenol into salicylonitrile by isolating the diazonium compound (a diazo-oxide) and adding the solid to cuprocyanide. Read and Clarke [51] mixed diazonium solution and cuprocyanide at 0° and obtained a light yellow precipitate which decomposed to nitrile after some minutes' delay: yields of 60—70% were obtained. Gattermann and Ehrhardt [52] also brought about cyanide replacements in

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[41] Heyden, B.P. 16350 (1912).

[42] *Chem. Abs.*, 1940, **34**, 2342.

[43] Schmidt, *Annalen*, 1920, **421**, 159.

[44] *E.g.*, Bart, D.R.-PP. 254,092, 268,172.

[45] B.P. 261,026 (1926).

[46] *J. Amer. Chem. Soc.*, 1942, **64**, 828.

[47] "Organic Reactions," John Wiley, Vol. II, 420.

[48] *J. Amer. Chem. Soc.*, 1939, **61**, 3586; 1941, **63**, 949.

[49] *Ber.*, 1884, **17**, 2650.

[50] *Ber.*, 1887, **20**, 2952.

[51] *J. Amer. Chem. Soc.*, 1924, **46**, 1001.

[52] *Ber.*, 1890, **23**, 1226.

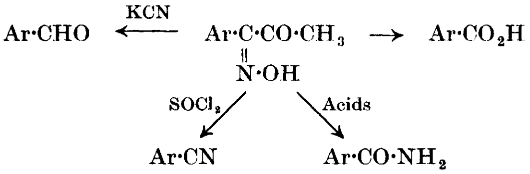
the cold by mixing diazonium solution and cyanide (obtaining, presumably, Hantzsch's *syn*-diazocyanide) and then adding copper powder. Korczynski and Fandrich [53] discovered that nickel cyanide (but not cobalt cyanide) could be used, and this method has given 4 : 4′-dicyanodiphenyl in 66% yield, and α-naphthonitrile in 58—65% yield.

A less commonly used but apparently more versatile reaction of this class involves the condensation of diazonium compounds with oximino-compounds :

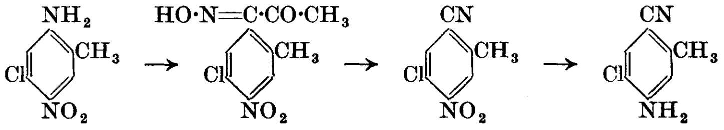
$$ArN_2^+ + R{\cdot}CH{:}N{\cdot}OH \longrightarrow Ar{\cdot}CR{:}N{\cdot}OH + N_2 + H^+$$

The reaction, which occurs under mild conditions (10—20°), requires a cupric catalyst and careful pH control. It was first used by Borsche [54] for the preparation of 1-aryl-1-oximinopropan-2-ones from ω-oximinoacetone (R = COMe). The yield from benzenediazonium chloride was 33% (20—25% from toluene- and methoxybenzene-diazonium chlorides). Oximinoacetophenone [55] (R = Ph·CO) and oximinoacetanilide [56] (R = CO·NHPh) could also be used.

Various methods have been worked out for converting the oximes into aldehydes, nitriles, amides, or acids :



Yields of 89% were claimed in a particular case (the Fast Red 3G Base of I.G.) :



Some work was also carried out on the use of formaldoxime (R = H), and yields of about 50% were obtained.

An important process in this class, which has come to be known as the Meerwein reaction, involves the elimination of nitrogen between a diazonium compound and a C=C double bond, with either addition or substitution, as shown on p. 366.

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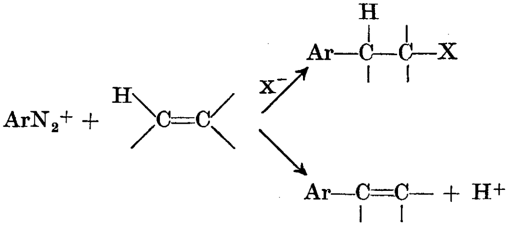
[53] *Compt. rend.*, 1926, **183**, 421 ; see also de Milt and Sartor, *J. Amer. Chem. Soc.*, 1940, **62**, 1954.

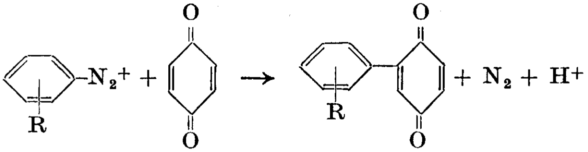
[54] *Ber.*, 1907, **40**, 737.

[55] Borsche and Fritsche, *Ber.*, 1926, **59**, 272.

[56] B.I.O.S. Microfilm FD/2729/46 (B.I.O.S. DOCS 1156/1121, pp. 31—56).



It was first observed in the case of quinones [57a]



(R = NO_2 or $SO_2{\cdot}NH_2$)

In acetic acid, yields of 20—30% can be obtained without a catalyst, and up to 50% with the addition of copper powder.

Subsequently, it has been found possible to arylate coumarin, acrylonitrile, cinnamic acid and its derivatives, crotonic acid and esters, cinnamylideneacetic ester, and even ethylene, acetylene, and butadiene. The reaction is usually carried out with a cupric catalyst in aqueous acetone, and yields up to 75% are recorded. It is not possible here to enumerate all the applications, but a few are given below:

$$\begin{tikzcd} ArN_2^+ + CH_2{:}CH{\cdot}CH{:}CH_2 \arrow[r, "Cl^-"] & ArCH_2{\cdot}CH{:}CH{\cdot}CH_2Cl \arrow[d] \\ & ArCH{:}CH{\cdot}CH{:}CH_2 \end{tikzcd}$$

$$ArN_2^+ + CH_2{:}CH{\cdot}CN \xrightarrow{Cl^-} Ar{\cdot}CH_2{\cdot}CHCl{\cdot}CN$$

$$ArN_2^+ + CH_2{:}CH_2 \xrightarrow{Cl^-} ArCH_2{\cdot}CH_2Cl$$

$$ArN_2^+ + ClCH{:}CCl_2 \xrightarrow{Cl^-} ArCHCl{\cdot}CCl_3$$

$$ArN_2^+ + CH{\vdots}CH \xrightarrow{Cl^-} ArCH{:}CHCl$$

(Ar = *p*-nitrophenyl [57e])

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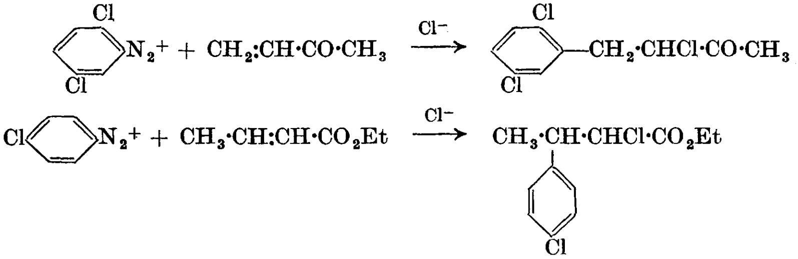
[57] (*a*) I.G., D.R.-P. 508,395 (1924); Kvalnes, *J. Amer. Chem. Soc.*, 1934, **56,** 2478; Marsini-Bettolo and Rossi, *Gazzetta*, 1942, **72,** 208; Fieser *et al.*, *J. Amer. Chem. Soc.*, 1948, **70,** 3203; (*b*) Meerwein, Buchner, and van Emster, *J. pr. Chem.*, 1939, **152,** 237; (*c*) Koelsch, *J. Amer. Chem. Soc.*, 1943, **65,** 57; Koelsch and Boekelheide, *ibid.*, 1944, **66,** 412; (*d*) Bergmann and Weinberg, *J. Org. Chem.*, 1941, **6,** 134; Bergmann, Weizman, and Schapiro, *ibid.*, 1944, **9,** 408; Bergmann and Schapiro, *ibid.*, 1947, **12,** 57; Bergmann, Dimant, and Japhe, *J. Amer. Chem. Soc.*, 1948, **70,** 1618; (*e*) Müller, *Angew. Chem.*, 1949, **61,** 179; (*f*) l'Ecuyer *et al.*, *Canadian J. Res.*, 1947, **25,** *B*, 689; 1948, **26,** *B*, 78; 1949, **27,** *B*, 575.

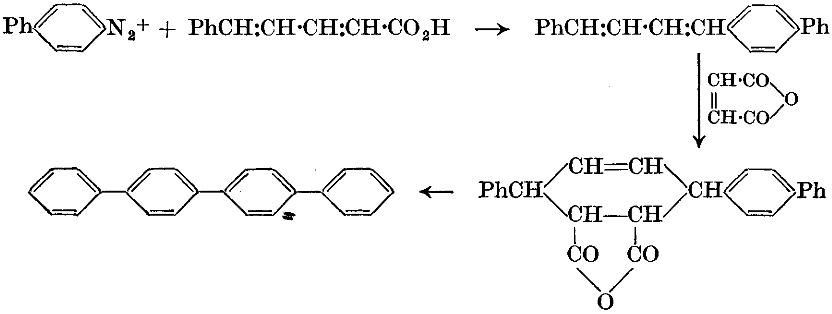
(The ethylene and acetylene reactions require an autoclave and give yields of less than 20%.)



With cinnamic acid, it is carbon dioxide which is eliminated, and stilbenes are formed:

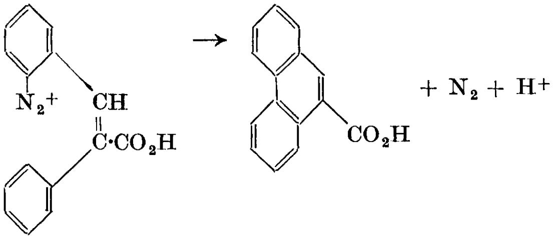
$$ArN_2^+ + PhCH:CH\cdot CO_2H \longrightarrow PhCH:CHAr + CO_2 + N_2 + H^+$$

this reaction has been used in a synthesis of quaterphenyl:[57d]



The mechanism of the Meerwein reaction is discussed on p. 377.

Internal arylation reactions, leading to ring compounds, are also of importance. Pschorr's phenanthrene synthesis [58] merely involves shaking the appropriate diazonium compound with copper powder:



(93% yield)

The use of the stilbenecarboxylic acid in this reaction (rather than the stilbene itself) gives better yields: this is because the stable form of the carboxylic acid has the CO_2H and $C_6H_4\cdot N_2^+$ groups *trans* to one another,[59]

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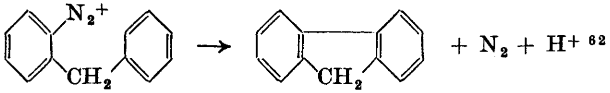
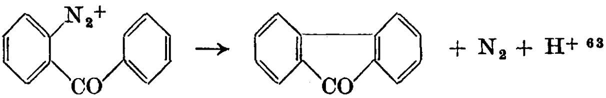
[58] *Ber.*, 1896, **29,** 496; 1900, **33,** 1826, 1829; 1904, **37,** 1926; *Annalen*, 1910, **373,** 75.

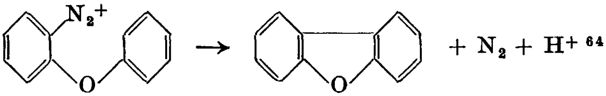
[59] Ruggli and Staub, *Helv. Chim. Acta*, 1936, **19,** 1288; Taylor and Hobson, *J.*, 1936, 181.

so that the two aromatic nuclei are held in a position more favourable for condensation. Phenanthrene can be made by the Pschorr reaction on the diazotised aminostilbene itself,[60] provided that the isomer in which the aryl groups are *cis* is first isolated. 1 : 2-Benzanthracenes [61] have been made by this reaction.

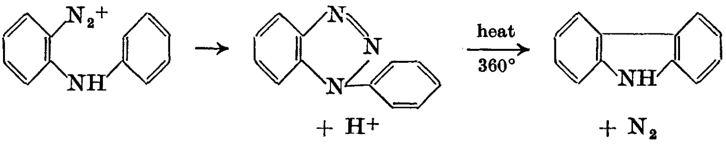
Fluorenes, fluorenones, and dibenzofurans may be prepared without catalyst, simply by boiling diazonium compounds; the phenol ordinarily occurs as a by-product:



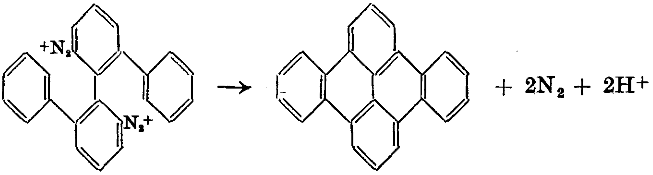




Diazotisation of *o*-aminodiphenylamines is followed by internal coupling to give triazoles, and these can be converted into carbazoles by heating to 360°:[65]



Various complex ring systems have been made, including a dibenzopyrene whose formation involves a double arylation: [66]



Finally, it has been found possible to make fluorenes from diazotised 2-amino-2′-methyldiphenyl.[67]

There appears to be no other case of arylation of alkyl C–H bonds, and it would be of interest to investigate the possibility of this reaction in

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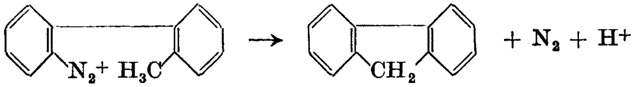
[60] Ruggli and Staub, *Helv. Chim. Acta*, 1937, **20**, 37.
[61] Cook, *J.*, 1931, 2524.
[62] Fischer and Schmidt, *Ber.*, 1894, **27**, 2787.
[63] Graebe and Ullmann, *ibid.*, p. 3484.
[64] *Idem*, *Ber.*, 1896, **29**, 1876.
[65] *Idem*, *Annalen*, 1896, **291**, 16.
[66] Sako, *Bull. Chem. Soc. Japan*, 1934, **9**, 55 (*Chem. Abs.*, 1934, **28**, 3730).
[67] Mascarelli and Gatti, *Chem. Abs.*, 1935, **29**, 4351.

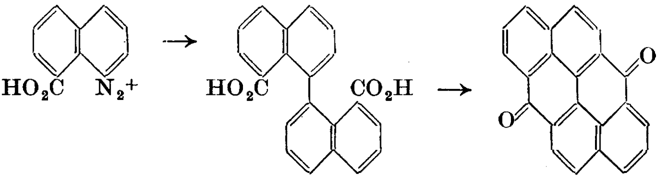


simpler systems. No examination has been made of the effects of copper or other catalysts for these processes.

(B) Reductive Reactions

There are four main types of reaction in this class : formation of a symmetrical azo-compound, of a symmetrical diaryl, of a hydrocarbon, or of an organometallic compound.

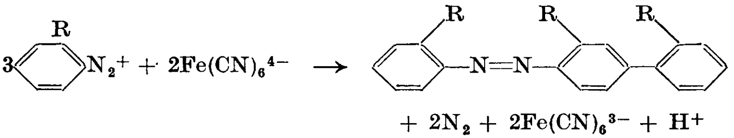
The first three of these processes and possibly also the fourth occur as side reactions in halogen Sandmeyer reactions. By a suitable adjustment of the conditions (rapid addition to the diazo-solution of a high concentration of cuprous chloride dissolved in the minimal amount of chloride) quite good yields of azo-compound can be achieved ($> 50\%$).[68] It emerges very clearly from papers by Ullman and Frentzel [68] and Vorländer and Meyer [69] (who used ammoniacal cuprous oxide) that this type of reaction leads mainly to azo-compound when electron-repelling or weakly electron-attracting substituents are present (alkoxy, hydroxy, alkyl, H, halogen), and to the symmetrical diaryl when the nucleus is strongly deactivated by electron-attracting substituents, such as NO_2. Carboxyl is a borderline case : diazotised *p*-aminobenzoic acid and ester give mainly azo-compound, but anthranilic acid gives 2 : 2′-diphenic acid. The conversion of 1-naphthylamine-8-carboxylic acid into 1 : 1′-dinaphthyl-8 : 8′-dicarboxylic acid is a stage in the commercial synthesis of anthanthrone : [70]



Finely divided copper can be used to make diaryls from diazonium ions where cuprous compounds give mainly the azo-compound.[71]

It is, of course, essential in all these reactions to ensure that at least one equivalent of reducing agent is present per mole of diazonium compound.

Possibly the most surprising process in this class is the interaction between diazonium compounds and potassium ferrocyanide to give arylazodiaryls :



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[68] *Ber.*, 1905, **38,** 725 ; see also Bogolovskii, *J. Gen. Chem. Russia,* 1946, **16,** 193.

[69] *Annalen,* 1901, **320,** 122 ; see also Atkinson *et al., J. Amer. Chem. Soc.,* 1940, **62,** 1704 ; 1941, **63,** 730.

[70] B.P. 278,100.

[71] Knoevenagel, *Ber.,* 1895, **28,** 2049 ; Atkinson *et al., J. Amer. Chem. Soc.,* 1943, **65,** 476.

Griess discovered this in 1876,[72] and subsequent work has been carried out by Locher,[73a] by Ehrenpreis, [73b] and by Ford, Waters, and Young.[74] Yields up to 20% can be attained with benzene- or toluene-diazonium salts, but very little of this type of product is obtained with nitro- or methoxy-substituents : pH values of 4—5 are best (at neutrality, tars result). Azo-compounds were obtained as by-products.

The replacement of NH_2 by H is, of course, usually brought about by diazotisation in alcohol. This reaction is catalysed by finely divided metals or cuprous oxide.[75, 76] Hypophosphites have been used for this reaction.[77]

Organometallic compounds have been prepared from diazonium ions by Waters [78a] and Nesmejanov.[78b] The former examined a wide range of reactions between the elements and diazonium ions in acetone solution. B, Ce, Tl, C, Si, Ti, Ge, Zr, Th, and Pt were without action ; Ag, Au, Zn, Cd, Al, Pb, Sb, Mo, Mn, Fe, Co, and Ni were attacked, and in most cases small yields of diaryl or aryl chloride were obtained. Mercury gave HgPhCl, tin $SnPh_2Cl_2$, arsenic $Ph_3As(OPh)(OH)$, antimony $SbPh_3Cl_2$ and other antimony chloro-aryls, Te gave Ph_2TeCl_2, and sulphur and selenium Ph_2S and Ph_2Se. (There also occurred in these decompositions a reaction with acetone : $ArN_2Cl + CH_3{\cdot}CO{\cdot}CH_3 \longrightarrow ArH + N_2 + CH_2Cl{\cdot}CO{\cdot}CH_3$.[78])

Perhaps the most interesting case of a replacement of the diazonium group by a metal is the preparation of the copper aryls themselves. They are formed by the action of copper powder on diazonium borofluorides at about 80°, and isolated as substituted pyridine complexes, $ArCu(py)_4$.[79] It is possible that such compounds appear in the Sandmeyer reaction. Cowdrey and Davies [4] found that the carbon balance on the Sandmeyer reaction of toluene-*o*-diazonium salts was always short by 7—10%, although the whole of the weight of the oily layer was accounted for. Evidence of the presence of organic matter other than cresol in the aqueous phase was obtained, but attempts at isolation failed.

The Mechanism of the Action of Catalysts

(1) Copper in the Sandmeyer Reaction.—From the beginning of its use in preparative chemistry, the mechanism of the Sandmeyer reaction has aroused curiosity. The first fact noted (by Sandmeyer himself) was that cuprous complexes appeared to be formed, since there were changes in the colour and also some precipitation of solid from the solution when diazonium salt and cuprous halide were brought into contact. Lellman and Rémy,[80]

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[72] *Ber.*, 1876, **9**, 132.

[73] (*a*) *Ber.*, 1888, **21**, 911 ; (*b*) *Zentr.*, 1907, **78**, 1789.

[74] *J.*, 1950, 833.

[75] Tobias, *Ber.*, 1890, **23**, 628.

[76] Hodgson and Turner, *J.*, 1942, 748.

[77] *Ber.*, 1902, **35**, 162.

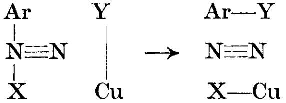
[78] (*a*) *J.*, 1939, 864 ; (*b*) *e.g.*, *J. Gen. Chem. Russia*, 1936, **6**, 167,172.

[79] Bolth, Whaley, and Starkey, *J. Amer. Chem. Soc.*, 1943, **65**, 1456.

[80] *Ber.*, 1886, **19**, 810.

Hantzsch,[81] and Waentig and Thomas [82] were all able to isolate a compound at low temperatures which contained copper and decomposed, on warming, to give nitrogen and the aryl halide. These complexes were too unstable to be characterised, but were regarded as essential intermediates in the reaction.

In a paper which subsequently attracted much attention, Hantzsch and Blagden [28] sought to find out whether the halogen atom which was ultimately attached to the aryl nucleus originated in the cuprous halide molecule or as the anion associated with the diazonium ion. Their method was to mix equimolar amounts of cuprous chloride and *p*-bromobenzenediazonium bromide, either in aqueous suspension or in dimethyl sulphide solution, isolate the resulting dihalogenobenzene, and subject it to thermal analysis. In other experiments, cuprous bromide was treated with the diazonium chloride. In aqueous suspension, mixtures of the two possible products were obtained; in dimethyl sulphide, the cuprous bromide experiment gave almost entirely dibromobenzene, and the cuprous chloride experiment mainly bromochlorobenzene. The experimental details were not given. Mesitylene- or ψ-cumene-diazonium iodides with cuprous chloride gave mixed products. From this work, the inference was drawn that the reaction took the course $\mathrm{ArN_2X + CuY \rightarrow ArY + N_2 + CuX}$, and in detail could be written



$$\begin{array}{ccccc} \mathrm{Ar} & & \mathrm{Y} & & \mathrm{Ar{-}Y} \\ | & & | & & \\ \mathrm{N{\equiv}N} & & | & \longrightarrow & \mathrm{N{\equiv}N} \\ | & & | & & \\ \mathrm{X} & & \mathrm{Cu} & & \mathrm{X{-}Cu} \end{array}$$

In 1913, Waentig and Thomas [82] followed up some earlier work of Heller and Tischner [83] and carried out an excellent kinetic study of the reaction, by following the nitrogen evolution. The reaction proved to be of first order with respect to diazonium ion, and negatively catalysed by hydrogen chloride. The effect of changing the cuprous chloride concentration was somewhat complex. The temperature coefficient for benzenediazonium chloride was found: from their results a good Arrhenius plot may be obtained with an apparent activation energy of 9·8 kcal./mol. They regarded the reaction as a two-stage process, the initial and rate-determining reaction being the formation of a diazonium–cuprous halide complex, followed by the rapid breakdown of this to aryl halide, with nitrogen evolution. They adopted Hantzsch and Blagden's mechanism, postulating an intermediate complex $\mathrm{ArN_2Cl,Cu_2Cl_2}$.

The matter provoked no more investigations until 1941, when Hodgson, Birtwell, and Walker [84] challenged Hantzsch and Blagden's mechanism, pointing out that cuprous chloride will dissolve in a solution of bromide ions to give complex cuprohalide anions containing both halogens: the bromide would be expected to be the more reactive, but either aryl halide could in principle be formed. Experimentally, they found that *p*-nitrobenzenediazonium ion with cuprous bromide dissolved in concentrated

[81] *Ber.*, 1895, **28,** 1751.

[82] *Ber.*, 1913, **46,** 3923.

[83] *Ber.*, 1911, **44,** 250.

[84] *J.*, 1941, 770.

hydrochloric acid gave an aryl chloride : bromide ratio of 60 : 40. Reaction with cuprous chloride dissolved in concentrated hydrobromic acid gave a ratio of 4 : 96. The overall reaction, therefore, should be written

$$\mathrm{ArN_2^+ + CuX_2Y_2^{3-}} \longrightarrow \begin{cases} \mathrm{ArX + N_2 + CuXY_2^=} \\ \mathrm{ArY + N_2 + CuX_2Y^=} \end{cases}$$

These authors, however, set aside the earlier suggestions that a complex diazonium–cuprous halide intermediate involving a covalent N–Cu link was formed, and considered that the sole function of the cuprous halide was to render the halide ion more strongly nucleophilic and so assist a straightforward S_N2 replacement of N_2 by halide ion, and Hodgson later suggested that the compounds sometimes observed during the reaction were salts such as $(ArN_2^+)_3CuCl_4^{3-}$. The side reaction leading to diaryls, he suggested, was due to an entirely different type of process in which the cuprous halide functioned as a reducing agent and gave an aryl radical : these radicals then gave diaryl by dimerisation.

Since there is no special reason why cuprous chloride should be alone among metallic halides in enhancing the nucleophilic reactivity of an attached halide ion, Hodgson examined a number of other halides and showed that the conversion of *p*-nitrobenzenediazonium ion into *p*-chloronitrobenzene could be catalysed by $CoCl_2$, $FeCl_3$, and $CuCl_2$. The catalysis by the last chloride had been demonstrated earlier by Contardi,[7] and Hodgson further claimed that the reaction did not involve transient reduction to cuprous chloride.[85]

Further experiments on the cupric- and ferric-catalysed Sandmeyer reactions were carried out by Pfeil and Velten.[86] These showed clearly that it was only in the presence of negative substituents that good yields of aryl halide could be obtained : the nitroanilines gave over 90%, *p*-chloroaniline 34%, and *p*-toluidine and aniline only about 20%. Moreover, the yield dropped from over 90% to $< 50\%$ in the case of *p*-nitroaniline when the amount of cupric chloride was reduced. Addition of urea, sulphamic acid, the undiazotised amine, or sulphuric acid improved the aryl chloride yield.

Waters,[87] meanwhile, suggested that the reducing properties of cuprous chloride play a part not only in the side reactions accompanying the Sandmeyer process, but also in the halide replacement itself. Strong reducing agents such as stannous salts convert diazonium ions into the hydrazine : weak reducing agents such as bivalent Mn, Ni, Co, or Fe are without action, while Cu^+, he suggests, has the correct potential for bringing about the reaction $ArN_2^+ + e \longrightarrow Ar\cdot + N_2$. The aryl radical can then react with Cl^- to give ArCl, with ArN_2^+ to form the symmetrical azo-compound, or with another aryl radical to give the symmetrical diaryl :

$$\begin{aligned} \mathrm{Ar\cdot + Cl^-} &\longrightarrow \mathrm{ArCl} + e \\ \mathrm{Ar\cdot + ArN_2^+} + e &\longrightarrow \mathrm{Ar{-}N{=}N{-}Ar} \\ \mathrm{Ar\cdot + Ar\cdot} &\longrightarrow \mathrm{Ar{-}Ar} \end{aligned}$$

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[85] *J.*, 1942, 720.

[86] *Annalen*, 1949, **561,** 220 ; **562,** 163 ; **565,** 183.

[87] *J.*, 1942, 266.

Two experimental investigations, intended to discriminate between the Hodgson and the Waters mechanisms, were carried out independently in 1949. Pfeil and Velten [86] measured the influence of changes in diazonium, cuprous chloride, and chloride-ion concentrations on the yield of the main by-product (4 : 4′-azotoluene) and on the reaction rate, when pure toluene-*p*-diazonium sulphate reacted in aqueous solution with cuprous chloride dissolved in aqueous sodium chloride or hydrochloric acid. Unfortunately, the kinetics under these apparently simple conditions proved somewhat complex, possibly because of changes in acidity—*e.g.*, through phenol formation—and first-order behaviour was observed only when the CuCl : diazonium ratio was 2 : 1. It emerged, however, that the rate decreased with increasing chloride-ion concentration, and that the azo-yield increased with the cuprous chloride concentration and fell with increasing chloride-ion or diazonium-ion concentration. Pfeil and Velten therefore inferred that the catalytic species was formed by the loss of a chloride ion from the cuprochloride ions, and that it might be CuCl itself. The intermediate complex might then be $Ar[N{\equiv}N{:}CuCl]^+$, and the azo-compound might be formed by the interaction of two of these species. Some work was also done on the influence of solvent changes on the by-products : replacement of water by methanol, acetic acid, formic acid, or formamide reduced the yield of azo-compound, and the changes in rate did not parallel the changes in yield. The absence of such a correlation was thought to argue against a radical mechanism ; it was suggested that on this interpretation the concentration of radicals should be higher during a faster reaction, so that dimerisation should occur to a larger extent.

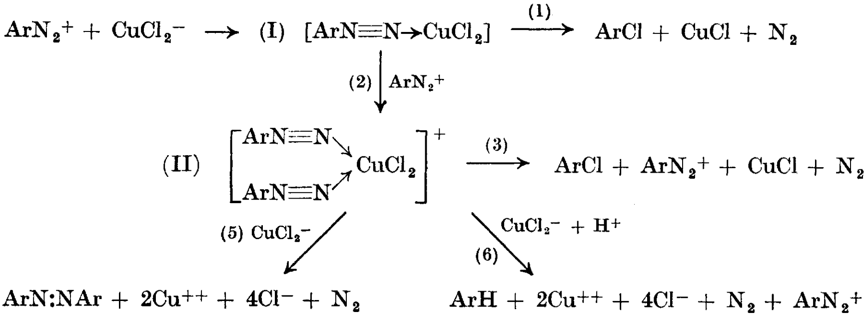
Cowdrey and Davies [5] chose a reaction system in which the pH was buffered at 1·7 and the ionic strength held constant. Under these conditions, the reaction takes a first-order course. In the case of *o*-diazotoluene, the main by-product is again the azotoluene, and the minor by-products are *o*-cresol and toluene (but no ditolyl).

The variations in rate content and azo-yield with cuprous chloride, diazonium ion, and chloride-ion concentration were found to be peculiarly simple. Qualitatively, the results were the same as those of Pfeil and Velten : quantitatively, they were accounted for in terms of the assumption that CuCl dissolves in chloride solution mainly as $CuCl_2^-$ and $CuCl_4^{3-}$ (a hypothesis which could also be used to give a satisfactory account of the variation of the solubility of CuCl with $[Cl^-]$). The kinetics then reduce to the equations

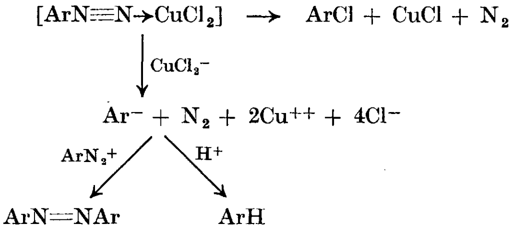
$$-\,d[\text{diazo}]/dt = k_1[ArN_2^+][CuCl_2^-]$$

$$d[\text{azo-compound}]/d[\text{chloro-compound}] = k_2[CuCl_2^-]$$

i.e., $CuCl_2^-$ is a catalyst and $CuCl_4^{3-}$ is inactive. These equations suggest a mechanism in which the primary, rate-controlling step is the union of ArN_2^+ and $CuCl_2^-$ ions to give an intermediate complex. $CuCl_4^{3-}$ ions, where the copper atom is covalently saturated, are unable to form a complex and therefore do not catalyse the reaction. The following complete scheme (p. 374) accords with the kinetics



Where ArN_2^+ is present in considerable concentration (all added at the outset), step (2) is much faster than (1), so that most of the ArCl arises from step (3). The azo-yield, therefore, depends on $[CuCl_2^-]$, the factor governing the relative parts taken by reactions (5) and (3) in provoking the decomposition of (II). (The small dependence of azo-yield on $[ArN_2^+]$ arises from the different extents of CuCl consumption during the reaction of varying amounts of $[ArN_2^+]$.) If, however, $[ArN_2^+]$ is kept very low by a gradual addition technique, then reaction (1) assumes prominence, and in consequence the azo-yield drops. This fact argues against an alternative mechanism of the following kind:



A further point in favour of the first mechanism is the observation that the azo-by-product often appeared as an unstable, solid cuprous chloride complex.

Electron-attracting substituents accelerate the reaction (*i.e.*, the rate falls in the order p-$NO_2 > p$-Cl $>$ H $> p$-Me $> p$-OMe), presumably by facilitating the approach of the terminal nitrogen of the diazonium ion and the negatively charged $CuCl_2^-$ ion.

Reinforcement of the notion that the primary, rate-controlling act involves the terminal nitrogen atom of the diazonium group follows from the close analogy between the Sandmeyer reaction and azo-coupling, studied by Conant and Peterson.[88] The two reactions are affected very similarly by substituents, *i.e.*, the log (coupling rate) varies linearly with log (Sandmeyer rate) though in neither case does the logarithmic rate vary linearly with the Hammett substituent constant σ. Further, the reactions both have a curiously low pre-exponential (A) factor in the Arrhenius equation.

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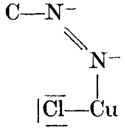
[88] *J. Amer. Chem. Soc.*, 1930, **52,** 1220.

Coupling almost certainly involves the reaction of ArN_2^+ with $Ar'O^-$: such a process is like the postulated first stage of the Sandmeyer reaction in uniting ions of opposite charge. Instead of the expected high A value (10^{13}—10^{19}), these two reactions have values of 10^6—10^8 (after due allowance has been made for pre-equilibria). Whatever the explanation for this (it has been suggested that it is due to the terminal nitrogen atom bearing a small negative charge), it is very tempting to infer that the key stage in the Sandmeyer reaction is in fact a coupling rather than a displacement reaction.

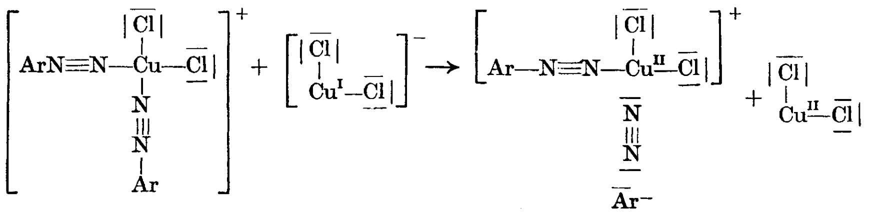
Close examination shows that this mechanism is not essentially a new departure, but that it embodies certain features of a number of the previously postulated schemes. The formation of a copper-containing intermediate was a very early idea. The experiments reveal nothing of the nature of the transition from $ArN{\equiv}N{\rightarrow}CuCl_2$ to ArCl, but it is very likely that Waters is right in suggesting that the reducing properties of the cuprous atom play a key part. For example, the complex as written would have a linear C—N≡N—Cu system. The transfer of two electrons from the copper (giving transiently the unstable Cu^{3+} state [90]) would transform this to the bent system (III) ; there would then be little difficulty in the occurrence of an internal nucleophilic displacement by halogen, as suggested by Hodgson. It would also be rash to deny that this internal transformation might involve single-electron transfers and therefore, in a sense, radical intermediates.


(III)

One is inclined to suggest that there is an important difference between the cuprous- and cupric-catalysed Sandmeyer reactions. The latter type of process is very much slower (in the case of *p*-nitrodiazobenzene, the cuprous reaction occurs too rapidly for measurement at 0°, and the cupric reaction at appreciable rates only above 70°) and cannot be carried out with the more unstable diazonium ions where decomposition to phenols, etc., occurs at temperatures below that necessary for the halide replacement. It may be that the reaction with cupric, ferric, and other chlorides is in fact a direct S_N2 replacement (*i.e.*, a case where the simple Hodgson mechanism applies). The special place occupied by cuprous copper must then depend on its ability to form complexes so that both of the reagents ArN_2^+ and Cl^- are activated, and also brought together more often.

The precise mechanism of the rearrangements involved in the reductive formation of by-products (azo-compound, hydrocarbon, or diaryl) is interesting. Several workers [89] have noticed that diaryl as opposed to azo-formation is more important in the Sandmeyer reaction of compounds bearing strongly electron-attracting groups. This suggests that all the reductive reactions involve the primary transfer of one electron from $CuCl_2^-$ to the complex $[(ArN_2)_2CuCl_2]^+$, followed by the incipient formation of an Ar^- ion (cf. p. 376).

[89] See Kleinberg, "Unfamiliar Oxidation States," Univ. of Kansas Press, 1950, p. 59.



The partly free aryl carbanion can then attack the neighbouring positively-charged diazonium cuprichloride complex either on the terminal nitrogen atom to give azo-compound, or in the nucleus (with elimination of nitrogen) to give diaryl. Presence of a nitro-group in the complex can reasonably be expected to favour the latter reaction by furnishing a larger partial positive charge on the nuclear carbon atom and so assisting the approach of Ar^-. With less electropositive nuclei, this approach will be relatively more difficult, and azo-compound will result. Little is known of the factors affecting hydrocarbon yield, but this reaction may simply be a solvolysis of Ar^-.

This reaction sequence leads to azo-compound being formed in attachment with cupric copper : a subsequent electron transfer can presumably lead to the cuprous azo-complexes referred to earlier.

In a recent article, Bunnett and Zahler [90] suggest a re-examination of the possibility, mentioned by Cowdrey and Davies [5] as kinetically acceptable but rejected as mechanistically unlikely, that the combination of diazonium ion and $CuCl_2^-$ is a pre-equilibrium rather than a primary rate-controlling step. Clearly, the development of experimental techniques for studying this point would be of decided interest. A further matter that has aroused comment is the rather remarkable charge-distribution on the diazonium–cuprochloride complex, which amongst other things violates the adjacent-charge rule. It is possible that the copper releases one or two electrons from its *d* orbitals as the complex is formed, and that the complex involves a cuprichloride group (or even Cu^{3+}) [89] rather than cuprochloride. Dewar's suggestion [91] that $CuCl_2^-$ brings about a direct nucleophilic substitution without intermediate complex formation is open to two objections : first, it does not suggest that $CuCl_4^{3-}$ should be catalytically inactive, and secondly, it offers no explanation of the source of the reductive by-products. There seems to be no good reason, either, for accepting his suggestion that facile Sandmeyer reactions occur by a nucleophilic substitution, and more difficult ones by a radical process, since they all seem to follow the same kinetic pattern.

It is difficult to decide whether the Gattermann reaction involves a surface layer of cuprous compound, or whether it is fundamentally different from the Sandmeyer reaction. As has already been mentioned, Gattermann himself considered the reaction fundamentally different, and Hantzsch and Blagden [28] quoted a single case (the decomposition of *syn*-diazocyanides) where copper powder is a much more effective catalyst than cuprous compounds. In view of the complexity of heterogeneous reactions between

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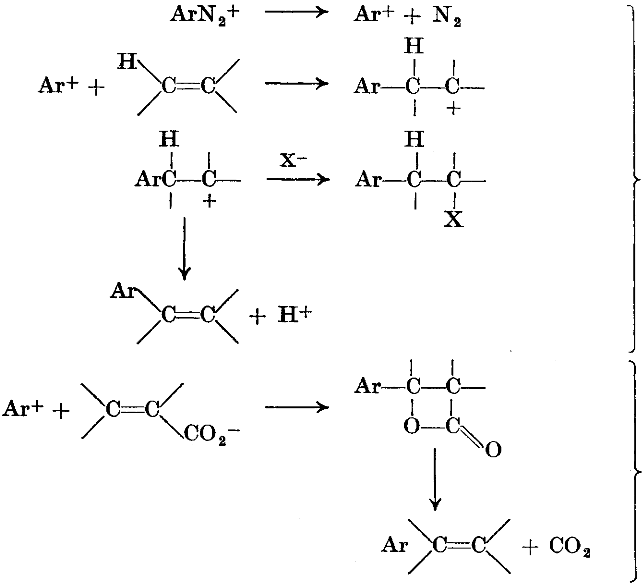
[90] *Chem. Reviews*, 1951, **49**, 273.

[91] *Research*, 1950, **3**, 154.

solids and solutions, the satisfactory solution of this problem is probably a long way off.

(2) **Other Metal Catalysts.**—There is not very much evidence in the literature about the mechanism of reactions related to the halogen Sandmeyer process. This may be partly due to experimental complexities such as Cowdrey and Davies encountered in an unsuccessful attempt to extend their kinetic study to include the cyanide Sandmeyer reaction : here, precipitation occurred when the diazonium salt was added to cyanide or cuprocyanide (owing to formation of diazocyanide or diazocuprocyanide) under a fair variety of conditions. Blumberger [92] studied the catalytic action of cupric sulphate (in combination with a variety of aromatic compounds) on the decomposition of diazobenzene. He found that a number of naphthylaminesulphonic acids (and one or two naphtholsulphonic acids) in conjunction with copper sulphate promoted the decomposition : combinations of copper sulphate with other naphtholsulphonic acids, or a variety of copper salts with amines such as aniline, α-naphthylamine, or anthranilic acid, did not. This effect only occurred in weakly acid solution, and was cancelled by increasing the acid strength. The nickel, cobalt, and manganese salts of naphthylaminesulphonic acids were not active. No detailed study of concentration dependencies was made in any particular case, so no detailed conclusions can be drawn, and more information on this particular catalysis would be most interesting.

There has been a certain amount of discussion about the mechanism of the Meerwein reaction between diazonium ions and ethylenic compounds. The authors of the first paper [57b] (which described reaction with coumarin and cinnamic acid derivatives) suggested that it was a simple ionic process :



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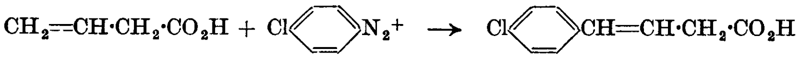
[92] *Rec. Trav. chim.*, 1930, **49**, 257, 259, 267.

This view was supported by Bergmann and Schapiro,[57d] who showed that *p*-chlorodiazobenzene with vinylacetic acid gave a 5% yield of the γ-aryl derivative:



Since the addition of hydrobromic acid to vinylacetic acid gives the γ-bromo-compound in presence of peroxide (radical attack) and the β-compound in its absence (ionic attack), the Ar group enters the same place as the H^+ ion, and this indicates that it is entering as Ar^+. Koelsch and Boekelheide,[57c] and Müller [57e] consider that a radical reaction occurs, *e.g.*,

$$\begin{aligned}
PhN_2^+ + OAc^- &\rightleftharpoons PhN{=}N{\cdot}OAc \longrightarrow Ph\cdot + N_2 + \cdot OAc \\
Ph\cdot + RCH{:}CHR' &\rightarrow PhCHR{\cdot}CHR'\cdot \\
PhCHR{\cdot}CHR'\cdot + Cu^{++} &\rightarrow Cu^+ + PhCHR{\cdot}\overset{+}{C}HR' \\
Cu^+ + \cdot OAc &\rightarrow Cu^{++} + OAc^- \\
PhCHR{\cdot}\overset{+}{C}HR' + Cl^- &\rightarrow PhCHR{\cdot}CHClR' \\
PhCHR{\cdot}C^+HR' &\rightarrow PhCR{:}CHR' + H^+
\end{aligned}$$

Two pieces of evidence are quoted in support; first, the reaction requires an acetate or similar buffer, which suggests that the formation of 4-covalent diazo-compounds (known radical precursors) is necessary, and secondly, the orientation of the adducts with cinnamic acid derivatives is said to be characteristic of radical addition.

It cannot be said that either of these mechanisms is entirely satisfactory. The copper very probably plays a part by forming complexes with either or both of the reactants and, in view of the fact that cases are now known in which high yields are possible, it may be that a system can be found where a kinetic study would give useful information.

(3) The Catalysed Decomposition of Diazonium Compounds.—The very striking difference between the effect of substituents on Sandmeyer-type reactions (where *p*-nitrodiazobenzene reacts rapidly) and diazonium decompositions (where *p*-nitrodiazobenzene reacts very slowly) must often have attracted attention. However, the decomposition reaction is peculiarly complex, and Dewar's suggestion [91] that it is simply an S_N1 process pays no attention to the complexities. For example, the diazotised anisidines decompose much more slowly than diazobenzene (and not faster, as this theory predicts). Further, diazotised *p*-toluidine is more stable, and diazotised *m*- and *o*-toluidine are much less stable, than diazobenzene.[93] It is, of course, easy to put forward special explanations for this (in terms of the influence of the N_2^+ group on the OMe group, or of the conflict between the effect of the substituent on the strength of the C–N bond on the one hand and the electron displacements necessary for the separation of N_2 on the other), but it is difficult to see how these could be examined experimentally.

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[93] Crossley, Kienle, and Benbrook, *J. Amer. Chem. Soc.*, 1940, **62**, 1400.

(4) The General Mechanism of Catalysed Diazonium Replacement Reactions.—It seems that there are three ways in which the replacement of the diazonium group can be catalysed :

(*a*) The nucleophilic species which is to be substituted by the N_2^+ group can be activated by the attachment of a suitable molecule. This corresponds to Hodgson's mechanism for the Sandmeyer reaction, and probably accounts for catalysis by cupric and ferric compounds (*e.g.*, Blumberger's work [92]).

(*b*) The aromatic system can be activated, and the splitting of aryl carbanions, carbonium ions, or radicals facilitated by the co-ordination of a suitable molecule on to the terminal nitrogen atom of the diazonium group. This may be occurring in the ferrocyanide reaction reported by Ford, Waters, and Young.[74]

(*c*) The co-ordination both of the nucleophilic reactant *and* of the diazonium ion on to a single molecule may facilitate reaction simply by bringing the reactants together. This may be the case in the Balz–Schiemann reaction, where the boron atom may serve to hold together the ArN_2^+ and F^- ions.

The catalysis is, of course, most powerful when all three effects are combined, and this seems to be just what happens in cuprous-catalysed Sandmeyer-type reactions, *e.g.*, the cyanide reaction

$$\mathrm{Ar{-}N{\equiv}N \longrightarrow Cu(N{\equiv}C)_2 \quad \longrightarrow \quad ArCN + N_2 + CuCN}$$

It does not follow that all types of complex formation lead to increased reactivity : there are many well-known cases (*e.g.*, the *anti*-diazocyanides) where the complex is more stable. Evidence has been accumulating in support of Hantzsch's view that the stereochemistry is important in determining the reactivity, but the precise electronic requirements remain difficult to define.