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ADVANCES IN THE CHEMISTRY OF AROMATIC DIAZONIUM COMPOUNDS

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INTRODUCTION

The diazotisation reaction, the centenary of whose discovery by Griess was celebrated in 1958,[1-3] is extraordinarily versatile. The complexity of the process, the ease with which diazonium compounds undergo change, and the peculiarities of their conversion into other substances have given rise to numerous controversies concerning the structure, the reaction mechanisms, and the reactions of diazonium compounds. Unfortunately, the theories which have been put forward are far from perfect, and right up to the present time diazotisation and the reactions of diazonium compounds have provided a continuous stimulus to creative chemical research.

Diazonium compounds are very sensitive to the slightest changes in conditions, and this sensitivity is linked with the variety of forms in which they can exist. The scheme of tautomeric changes of diazonium accepted up to the present time, which was worked out by Hantzsch and based on the hypothesis of stereoisomeric changes, has recently been subjected to a fundamental revision. A detailed analysis of the new ideas has been given by Porai-Koshits[4].

The present review discusses the main lines of advance in the chemistry of diazonium compounds during the five years including the first half of 1961. Progress in the practice of diazotisation, the state of ideas on the kinetics and mechanism of diazotisation, and also the changes undergone by diazonium compounds, other than azo-coupling, are covered in the review.

1. CONDITIONS OF DIAZOTISATION AND PROPERTIES OF DIAZONIUM COMPOUNDS

The introduction of new electrometric methods for controlling chemical reactions has enabled continuous methods of diazotisation[5,6] to be applied in practice. German chemists, who have patented a continuous process for the diazotisation of amines[7], suggest the precise regulation of the addition of reagents at a few points in the path of a turbulent flow of the reaction liquor, from which the reaction products are continuously removed. The supply of the diazotising agent is regulated in conformity with the change in redox potential measured with a platinum–calomel electrode system, while the acidity of the medium is controlled by a pH-sensitive system. Diazotisation proceeds smoothly and quantitatively with all the usual amines, for which it is necessary merely to choose the optimum redox potentials.

In the diazotisation of *p*-amino-*p'*-methoxydiphenylamine, for example, the amounts of nitrite added were such that the potential between the electrodes was ~520–580 mV. Later this method was extended to the diazotisation of feebly basic amines [8].

Conditions have been worked out [9] for the conversion of weakly basic amines (for example, 4-amino-2,5-dimethoxy--4'-nitroazobenzene) into a finely dispersed paste of particle size up to 3 μ by dispersion with a condensation product of formaldehyde and a naphthalenesulphonic acid. Subsequent diazotisation in acetic acid (pH 2.9–3.5) with nitrite takes place quantitatively. Good results are obtained by using a mixture of diacetone alcohol (4-hydroxy-4-methylpentan-2-one) with a non-ionogenic dispersing agent [10]. The use of dilute tetrahydrofuran has been suggested [11] for the diazotisation of amines which are insoluble in mineral acids and in glacial acetic acid (for example, 4-amino-3-bromo--4'-nitrobiphenyl). These procedures enable several difficultly diazotisable amines to be diazotised in good yields [12,13].

Various additives have been recommended for accelerating diazotisation; for example, it has been proposed [14] to diazotise amines in sulphuric acid in the presence of soluble metal chlorides. Addition of up to 40%, with respect to the weight of the amine, of sodium xylenesulphonate or naphthalene-1-sulphonate is claimed [15] to increase the yield of diazonium compounds [19], and the diazotisation of 4-amino--3-hydroxynaphthalene-1-sulphonic acid is best carried out in the presence of salts of heavy metals with the addition of non-ionogenic surface-active agents such as esters of fatty acids and polyoxyethylenes, in amounts of 10–20% based on the original amine [16].

Considerable difficulty is encountered in the diazotisation of aminoanthraquinones. Lukin [17] suggests that 1-aminoanthraquinone should be diazotised as the free base in dilute sulphuric or hydrochloric acid, when the yield of products reaches 85–95%. Kozlov and Belov have established the possibility of diazotising aminoanthraquinones in good yields with a nitrite in acetic acid without the use of mineral acids [18].

Examination of the variation in redox potential of the system at the end of diazotisation has enabled it to be used as an end-point indicator in the potentiometric titration of aromatic amines with a nitrite solution. A detailed study of this process and a check of earlier suggested procedures [19] revealed the optimum conditions for titrations [20]: 25 ml of a 0.25 M solution of the aromatic amine is titrated with 2.5 *N* nitrite solution in the presence of 8 g of hydrochloric acid at 19° using a smooth platinum electrode and a saturated calomel electrode. Under these conditions the potential at the end-point is 0.585 V, the error involved in the titration not exceeding 0.2%.

Butt and Stagg [21] established the possibility of applying the usual potentiometric method to the automatic titration of primary aromatic amines with a nitrite solution with satisfactory accuracy.

The behaviour of an already formed diazonium compound towards an electric current is extremely complicated. Attempts to establish a relation between the half-wave potential and the nature of a nuclear substituent in a diazonium compound were unsuccessful, but Budevska [22] established that, in the reduction of 4-diazo-3-hydroxynaphthalene-1-sulphonic acid and its 7-nitro-derivative at pH 4.7 and 9.0 at a dropping mercury electrode, the height of the main wave is proportional to the concentration of the diazonium compound, and she recommended this method for the analytical determination of these acids. Matrka and Sàgner [23], who studied the potentiometric titration of *o*- and *p*-phenylenediamines and of naphthalene-1,4-diamine, consider that 1 mole of nitrite is used up. It is impossible to titrate the *meta*-isomer under such conditions. They recommend that 1,4-diaminoanthraquinone should be titrated in a mixture of 10% sulphuric and 5 *N* hydrochloric acids with sodium *m*-xylenesulphonate.

Recently the production and application of diazotised polymers have been achieved. Natural macromolecular substances have been used, containing primary amino--groups and capable of conversion with nitrous acid into diazonium compounds. It is considered [24] that, when wool is treated with nitrous acid, the tyrosine is diazotised. The presence of the diazonium group is indicated [25] by a comparison of the ultraviolet absorption spectra of such a diazotised fibre with those of diazonium compounds.

The preparation of synthetic polymers and macromolecules capable of diazotisation with nitrous acid is of great interest. The diazotisation of an emulsion of a *p*-aminostyrene–acrylonitrile copolymer has been accomplished [26] in the heterogeneous system; coloured films can be obtained by coupling with well-known azo-components. Use of an ion-exchange resin of high molecular weight and containing sulpho-groups provides an interesting method of stabilising diazonium cations; such diazonium resins are recommended for the quantitative separation of phenols [27]. Mixing with cation-exchange resins is advised [28] for diminishing the water solubility of a diazonium compound. The use of long-chain amines makes it possible to prepare diazonium compounds having several new properties. Diazotised *p*-n-octylaniline couples with naphthionic acid to form a surface-active azo-dye [29]. The 4-mono- and 2,5-di-decyloxybenzenediazonium chlorides, which are moderately soluble in hot benzene and couple with 2-naphthol in the presence of pyridine, have been described [30].

The relative stability and poor water solubility of diazonium phosphates enables them to be isolated from solution in a stable form [31,32]. Several carboxylic acids confer great stability on diazonium salts: excess of oxalic acid enables crystalline diazonium salts, of general formula $Ar-N=N-Ar'-N_2Cl.H_2C_2O_4$ and stable up to 45°, [33] to be isolated from aminoazo derivatives. In the neutralisation of the diazonium solutions for cold dyeing, the use is recommended [34] of the sodium salts of ethylenediaminetetraacetic and nitrilotriacetic acids, which are able, in addition to complex formation and stabilisation of the solution, to shift the pH from weakly acid to neutral and weakly alkaline. The solid diazonium salts formed with perhalogenated carboxylic acids are characterised [35] by good stability. The crystalline products which are isolated show good solubility in polar solvents, are stable in the solid state, and melt at definite temperatures. The diazonium salts obtained from *p*-toluidine and CF_3COOH, C_3F_7COOH, and CCl_3COOH, for example, have melting points of 70°–72°, 50°–53°, and 88° respectively. The comparative stability of double diazonium salts formed with metal chlorides depends to a considerable extent on the nature of the cation. It has been established [36] that the stability of double diazonium salts increases in the sequence of metals

$$Fe^{III} < Sb^{III} < Bi < Hg^{II} < Sn^{IV} \simeq Zn < Cd,$$

and coincides with the order in which their electronegativity decreases.

Le Fèvre[37] and then Wetsel *et al.*[38], who were the first to study the infra-red absorption spectra of double diazonium salts, established that the N≡N group is characterised by a band within the range 2100–2350 cm^{-1}, the displacement of the bands being practically independent of the anionic portion of the molecule. A similar situation was found by Kazitsyna *et al.*[39], who were unable to derive a direct relation between the shifts in the absorption bands in this region and the nature or position of the anion in the molecule of the diazonium salt. Subsequently these workers showed, in the case of the double diazonium salts with bismuth trichloride and antimony pentachloride, that the position of the peak due to the N≡N triple bond in the infra-red spectrum depends on the composition of the double salt and the valency of the metal[40]. Gremillion *et al.*[36] consider, in view of the constancy of the infra-red absorption spectra of a series of double diazonium salts with the chlorides of various metals, that the metal atom interacts with the whole π system of the diazonium salt; an increase in electronegativity of the metal and the presence of vacant *d* orbitals in it strengthen the tendency for electrons to be repelled from the π system towards the metal. In their opinion, the metal ions are situated above the benzene ring, and do not show any preference for either of the nitrogen atoms of the diazonium group. On the other hand Kazitsyna *et al.*[41], in a study of the infra-red and ultra-violet spectra of double diazonium salts with the chlorides of cobalt and of copper, detected in them an absorption corresponding to the band of copper and cobalt complexes containing nitrogen atoms in the complex. This fact led these workers to suggest that a chemical bond was present between the metal atom and the terminal nitrogen of the arenediazonium group.

2. DIRECT INTRODUCTION OF THE DIAZONIUM GROUP INTO AN AROMATIC NUCLEUS

Attention has recently been paid to the direct formation of the diazonium group in the aromatic nucleus. Nemodruk, who extended this process to salicylic acid, noted[42] that it reacts with nitrous acid to form *o*-diazophenol with the simultaneous evolution of CO_2 owing to elimination of the carboxyl group. By using several salts of salicylic acid, which were more reactive in this respect (the Al, Cr, Zn, and Be salicylates), he was able to obtain in acid medium containing five moles of nitrous acid up to 90–93% of 5-diazosalicylic acid[43] with clear evidence of the intermediate formation of 5-nitrososalicylic acid.

The direct introduction of the diazonium group has been the subject of detailed study by the English chemists Tedder and Theaker, who found it to be a general reaction applicable to almost all classes of aromatic compounds: hydrocarbons, phenols, tertiary amines, carboxylic acids, etc.[44] Direct introduction of the diazonium group into the pyrrole and pyrazole rings yielded the very stable diazopyrrole and diazopyrazole, which coupled slowly with 2-naphthol in organic solvents[45,46]. The reaction takes place in the presence of an excess of nitrous acid or of a nitrosyl derivative *via* a nitrosation stage.

Phenols and tertiary amines are smoothly nitrosated with sodium nitrite or ethyl nitrite in alcohol in the presence of HCl, giving with excess of the nitrosating agent 55–80% yields of the diazonium salts; stable intermediate quinone monoximes can be isolated[44].

The success of the reaction is greatly dependent on the first stage, that of nitrosation. Unreactive substances require more acid, active nitrosating agents than nitrous acid, the following being recommended by Tedder: NOCl, $NOHSO_4$, $NOClO_4$, $NOOCOCF_3$,[47] and the complex $N_2O_3BF_3$.[48]

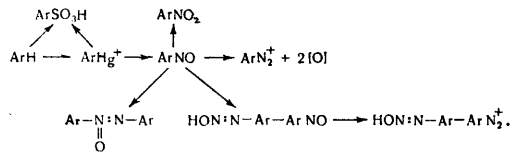
A system which is especially reactive with aromatic hydrocarbons consists of nitrosylsulphuric acid and an inert solvent (nitrobenzene); it is characterised by high acidity and is not readily oxidised by an excess of the nitrosating agent. The method of activation by mercuration has been suggested[44] for the diazotisation of unreactive derivatives of benzene and other hydrocarbons.

The mechanism of the process can be expressed as follows:

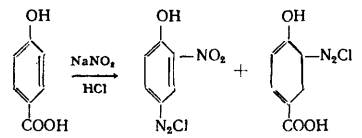
$$ArH + Hg^{2+} \longrightarrow ArHg^{+} + H^{+},$$
$$ArHg^{+} + NO^{+} \longrightarrow ArNO + Hg^{2+},$$
$$ArNO + NO^{+} \longrightarrow ArN_2^{+} + 2[O].$$

The mercury ion is regenerated, and acts as a catalyst for the process.

The introduction of a diazonium group into aromatic derivatives is not a simple process; side-reactions are possible, such as nitration, sulphonation, decarboxylation, alkylation, and also decomposition and coupling of the diazonium derivatives. This is reflected in the following mechanism[44] for the diazotisation of benzene with nitrosylsulphuric acid in the presence of mercuric oxide:



The action of nitrous acid on salicylic, hydroxybenzoic, and hydroxynaphthoic acids in buffer solutions[49] is accompanied by decarboxylation and nitration of the ring. Belikov[50] established that under these conditions direct diazotisation of *p*-hydroxybenzoic acid takes place as follows:

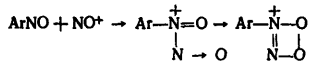


He explained the formation of the 4-hydroxy-3-nitrobenzenediazonium salt by nitration of the starting material *meta* to the carboxyl, replacement of the latter by a nitroso-group, and its subsequent conversion into a diazonium group.

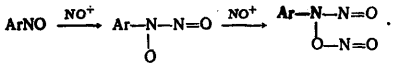
In the reaction of *m*-cresol with ethyl nitrite in alcoholic hydrogen chloride solution it has been found[51] that alkylation of the hydroxy-group occurs in addition to entry of the diazonium group.

Tedder and Theaker established[52] that: (a) the reaction must pass through a stage involving a nitroso-derivative, for, if it is carried out in the presence of Cu^{2+} ions or of sulphamic acid, the formation of diazonium salts is completely suppressed and the process stops at the nitrosation stage with conversion of the nitroso-compound into a copper complex; (b) direct introduction of the diazonium group into the nucleus requires at least three molecules of nitrous

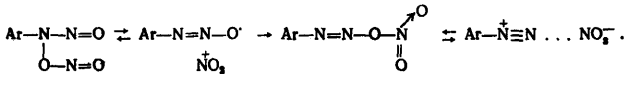
acid per molecule of the aromatic compound. In a strongly acid medium a brownish-red coloration is observed, due to complex ions of the nitroso-compounds with the nitrosyl cation:



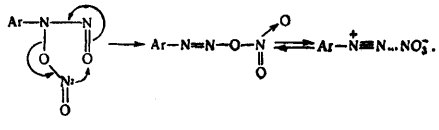
or



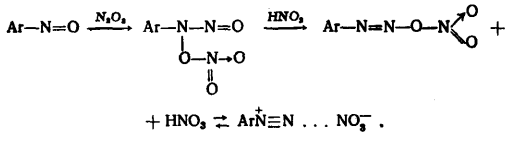
The resulting complexes are converted into diazonium salts on treatment with water, as a result of cleavage and further reactions:



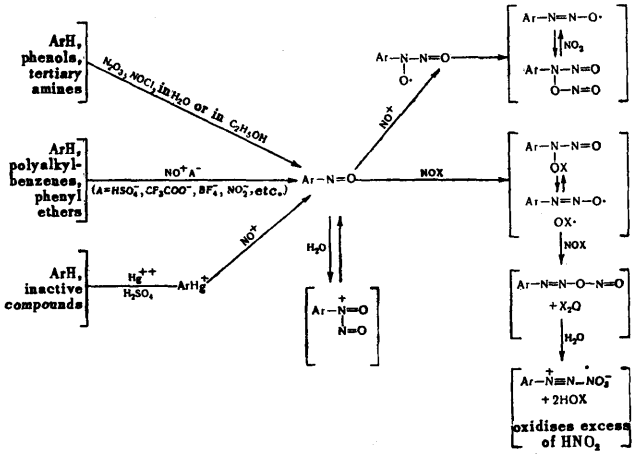
Intramolecular rearrangement is also quite possible:



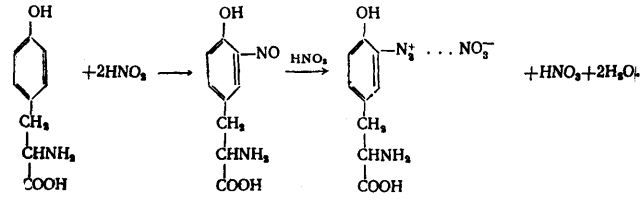
In dilute acids the reaction probably proceeds as follows:



All pathways for the direct entry of the diazonium group into an aromatic nucleus can be represented by the general scheme:



The above considerations on the direct entry of the diazonium group into derivatives of aromatic hydrocarbons have enabled a fresh interpretation to be given of the mechanisms of several reactions, in particular the diazotisation of the proteins of wool and silk. Thus Rodionov and Shleer[53] suggest that the diazotisation of the tyrosine in the keratin of fur involves the intermediate formation of a nitroso--compound:



The absorption spectra of azo-dyes from diazotised pure tyrosine and fur tyrosine are absolutely identical. The suggested interpretation of the process is supported also by the similarity of the ultra-violet absorption spectra of diazotised wool and of 4-diazo-3-hydroxynaphthalene-1-sulphonic acid[25]: *i.e.* the presence of the diazonium group *ortho* to a hydroxy-group is confirmed.

3. KINETICS AND MECHANISM OF DIAZOTISATION

The mechanism of diazotisation is extremely complicated, and has not yet been completely elucidated. The absence of a single interpretation of the mechanism is due primarily to the inaccuracy of and sometimes contradictions in the kinetic measurements, made by a number of investigators from 1899 onwards. In our opinion there are two main reasons for this situation: (a) the lack of sufficiently exact methods for following analytically the process of diazotisation and for the analysis of diazonium compounds; and (b) the neglect by investigators of the effects on the reaction velocity of individual components of the medium in which diazotisation is taking place.

The absence of accurate and convenient direct methods for the analysis of diazonium compounds, with the exception of the azotometric method, which is somewhat clumsy, led to the utilisation of the most diverse indirect methods, a brief account of which has been given in a review by Matrka[54].

The colorimetric analysis of diazonium compounds which yield coloured products on coupling with certain compounds has proved extremely fruitful and valuable. This method is quite widely employed both for exact kinetic determinations and also for technical purposes. Repeated checks of the method[55] have confirmed its accuracy and convenience. Furthermore, the colorimetric method has found wide application in the analysis of organic compounds of various classes and from different sources.

The use of spectrophotometric methods of investigation in the visible and ultra-violet regions of the spectrum[56] opens up still greater prospects for research workers. Dilute solutions of diazonium compounds obey the Beer–Lambert law[57], and can be successfully used for both qualitative and quantitative analyses of diazonium compounds, amines, and nitrite[58,59]. In view of the instability of diazonium compounds in solution to the action of light, the technique of spectrophotometric measurements is somewhat difficult, and may be a source of error. To avoid this, it is advisable for each measurement to be made on a fresh solution of the diazonium compound[60]. Good results are obtained by the use of self-recording instruments and a special oscillographic attachment, on the screen of which the spectrum is outlined after 1–2 min. Differences in nature and concentration of acids, amines, and diazotising

agent have been the cause of discrepancies in the results and in their interpretation. The first investigators of the kinetics of diazotisation worked with dilute (0.002 M) hydrochloric acid, and found the reaction to follow a second-order equation[61]:

$$v = K\,[\overset{+}{\mathrm{ArNH_3}}]\,[\mathrm{HNO_2}]\ . \qquad (1)$$

This finding completely explained the mechanism of diazotisation according to which reaction takes place between the arylammonium ion and undissociated nitrous acid with formation of an unstable adduct, which is stabilised as the diazonium ion. When higher acid concentrations (0.2 M) were used, it was found that in sulphuric and nitric acids the reaction is of third order, its rate being directly proportional to the concentration of free amine and to the square of the concentration of nitrous acid. This has been expressed in a number of mathematical relations[62].

Several workers regarded the third reaction order under these conditions as only apparent, but a careful check of the equations forced chemists to revise their views on the mechanism of diazotisation. It was accepted that the base, not a salt of the amine, undergoes diazotisation. In such a case diazotisation can be represented, in conformity with Bamberger's early work, as an initial nitrosation of the primary amine with subsequent conversion of the aryl-*N*--nitrosamine into a diazonium salt by the action of acid:

$$\mathrm{ArNH_2} \xrightarrow{\mathrm{HNO_2}} \mathrm{Ar\overset{+}{N}H_2NO_2} \longrightarrow \mathrm{ArNHNO} \longrightarrow \mathrm{ArN:N{\cdot}OH} \rightleftarrows \mathrm{ArN_2^+}\ldots\mathrm{OH^-}.$$

Examination of the infra-red spectra of solutions of aromatic amines in several acids confirmed the presence in them of a definite quantity of free base[63]. Hence there is now no doubt that a free base can be diazotised.

According to Ingold[64] the first step consists of attack by the nitrosating agent, which may be the nitrosyl cation NO^+ or its carrier NOX, on the lone pair of electrons of the amine nitrogen with subsequent protolytic conversion into the aryl-*N*-nitrosamine:

$$\mathrm{ArNH_2} \xrightarrow{\text{slow}} \mathrm{ArNH_2\overset{+}{N}O} \xrightarrow{\text{rapid}} \mathrm{ArNHNO}.$$

The slowest step during these stages is the attack by the nitrosating agent on the unshared electron pair of the amine nitrogen atom, and it is obviously this which determines the rate of diazotisation, since all subsequent steps take place rapidly, and exert no influence on the overall rate of diazotisation.

Several views have been expressed concerning the "apparent" third-order kinetics of diazotisation, among which the most soundly based is that of Hammett[65], subsequently adopted by other workers, who assumed that in strongly acid media the diazotisation is effected by nitrogen trioxide:

$$2\mathrm{HNO_2} \rightleftarrows \mathrm{N_2O_3} + \mathrm{H_2O}.$$

Turney[66] made a spectroscopic and chemical study of this equilibrium in $HClO_4$ solutions of less than 46% concentration, and found the equilibrium constant at 20° to be $K_a = 0.20 \pm 0.05$.

In hydrochloric acid medium N_2O_3 and nitrosyl chloride act as diazotising agents:

$$\mathrm{HNO_2} + \mathrm{H_3O^+} + \mathrm{Cl^-} \rightleftarrows \mathrm{NOCl} + 2\mathrm{H_2O}.$$

Subsequent reaction of N_2O_3 and NOCl with the amine involves intermediate formation of the *N*-nitrosamine and results in the diazonium compound.

Investigations of the kinetics and the mechanism of diazotisation which have recently been made by the Ingold school have led to definite progress on this matter. As a result of the measurements[67], it was recognised that, depending on the conditions, more than one kinetic equation was applicable to diazotisation. According to Ingold, the active nitrosating agents fall in the following sequence of diminishing electrophilic reactivity: NO^+, $H_2NO_2^+$, NOX, $NONO_3$, $NONO_2$, NOOAc, and NOOH. Each of the kinetic equations is linked with the use of definite nitrosating agents, which can be formed under the given conditions.

A. Uncatalysed Diazotisation

Determination of the kinetics of the diazotisation of aniline in concentrated (0.05 M) and dilute (0.002 M) perchloric acid by Ingold *et al.*[68] shows the reactions to be of third and second orders respectively, represented by the following kinetic equations:

$$v = K_3''\,[\mathrm{ArNH_2}]\,[\mathrm{HNO_2}]^2, \qquad (2)$$

$$v = K_2''\,[\mathrm{HNO_2}]^2. \qquad (3)$$

In Ingold's opinion, N_2O_3 is the nitrosating agent in both cases. In concentrated solutions the formation of nitrogen trioxide does not restrict the reaction, and therefore the rate of the process is linked with the stage of attack by the N_2O_3 on the primary amine, and depends on the concentration of the latter. In very dilute acid the slowest reaction is the formation of the nitrogen trioxide, which determines the kinetics of the process. Each molecule of N_2O_3 formed reacts immediately with the amine:

$$\mathrm{HNO_2} \overset{\text{rapid}}{\rightleftarrows} \mathrm{H^+} + \mathrm{NO_2^-},$$

$$\mathrm{H^+} + \mathrm{HNO_2} \overset{\text{rapid}}{\rightleftarrows} \mathrm{H_2NO_2^+},$$

$$\mathrm{NO_2^-} + \mathrm{NO{\cdot}OH_2^+} \overset{\text{slow}}{\rightleftarrows} \mathrm{O_2N{\cdot}NO} + \mathrm{H_2O}.$$

It is improbable that N_2O_3 is formed as a result of interaction of NO^+ and NO_2^- ions, since the presence of NO^+ in a weakly acid solution is extremely problematic. The distinction between NO^+ and $NO.OH_2^+$ may seem difficult because one is the hydrate of the other, but it can be settled by experiments based on oxygen exchange[69].† In the absence of an amine in the solution nitrogen trioxide can be readily hydrolysed to nitrous acid. The velocity of this reaction has been studied[70] by means of water labelled with oxygen-18. The rate of transfer of oxygen is consistent with the rate of diazotisation and especially with Eqn. (3) This shows that oxygen transfer and diazotisation have identical intermediate complexes, formed from two molecules of nitrous acid, and that the process involves rupture of an N–O bond. The presence of N_2O_3 under these conditions has been shown also from the absorption spectra of solutions of $NaNO_2$ in perchloric acid[71].

B. Catalysed Diazotisation

Diazotisation catalysed by the carboxylate ion. A study of the rate of diazotisation of several amines in the presence of sodium acetate and phthalate in perchloric acid (pH 5.0) showed that these salts to some extent accelerate the reaction[72], although they do not affect its order. The general kinetic equation for this case is

$$v = K^{\mathrm{OAcyl^-}}\,[\mathrm{HNO_2}]^2\,[\mathrm{OAcyl^-}]. \qquad (4)$$

† The above sentence has been modified according to Ref. 69.

It is seen from this equation that the rate-determining stage of diazotisation is in this case [as also with Eqns. (2) and (3)] the formation of nitrogen trioxide. Most likely it is this stage which is catalysed by the carboxylate ion. Two mechanisms are possible for the formation of N_2O_3 with the participation of $OAcyl^-$:

$$\begin{aligned} &NO_2^- + NO.OH_2^+ \xrightleftharpoons{\text{rapid}} NO_2.NO + H_2O, \\ &AcylO^- + NO.NO_2 \xrightleftharpoons{\text{slow}} AcylONO + NO_2^-, \end{aligned} \qquad (A)$$

and

$$\begin{aligned} &AcylO^- + NO.OH_2^+ \xrightleftharpoons{\text{rapid}} AcylONO + H_2O, \\ &NO_2^- + NO.OAcyl \xrightleftharpoons{\text{slow}} NO.NO_2 + OAcyl^-. \end{aligned} \qquad (B)$$

Mechanism (A) is improbable[73], and its first stage contradicts that given in the previous subsection and the kinetic equation (4). Mechanism (B) can be regarded as more correct, and it is fully consistent with the kinetic equations (3) and (4). The catalytic effect of different carboxylate ions is shown to different extents: the phthalate ion is more active in accelerating the reaction than is the acetate ion [the respective values of K^{OAcyl^-} in Eqn. (4) are 160 and 38 litre^2 mole^{-2} sec^{-1}].

Diazotisation catalysed by the hydrogen ion. Rate constants determined by Ingold[74] for the diazotisation of feebly basic amines at low HNO_2 concentrations in acid solution proved to be greater than in the cases described earlier. As an example, the velocity of the reaction of 0.002–0.06 mole of *o*-chloroaniline with 0.0001 mole of nitrous acid in the presence of 0.005–0.02 mole of H^+ exceeded the second-order reaction velocity by a factor of 12. The kinetic measurements show that the reaction is of first order with respect to the amine, the nitrous acid, and the hydrogen ion:

$$v = K_3^{H^+}[ArNH_3][H^+][HNO_2]. \qquad (5)$$

Such a marked acceleration of the reaction is due, in the opinion of these workers, to the catalytic action of the proton, which adds on to the HNO_2 molecule and thereby activates the nitrosating agent:

$$H^+ + HNO_2 \xrightleftharpoons{\text{rapid}} H_2NO_2^+.$$

This step in the process occurs rapidly, and does not affect the overall reaction velocity; hence the rate-determining stage will be the attack on the amine by the active nitrosating agent.

These workers assume the possibility under certain conditions of further heterolytic charge transfer and elimination of the nitrosyl cation from the protonated form of nitrous acid:

$$ON-OH_2^+ \xrightleftharpoons{\text{slow}} NO^+ + H_2O.$$

The slowness of this process would undoubtedly influence the whole kinetics of the reaction and yield the following kinetic equation:

$$v = K_2^{H^+}[H^+][HNO_2]. \qquad (6)$$

However, neither the kinetic measurements nor the regularities in the reaction order permit unreserved acceptance of the presence of the nitrosyl cation in the solution. A quantitative examination of the behaviour of nitrous acid in 46% perchloric acid solution showed that the protonated form of nitrous acid is converted into the NO^+ cation only to the extent of 3%.[75,76]

Diazotisation catalysed by ions of strong acids. Recent kinetic measurements[77] on the diazotisation of aniline and *o*-chloroaniline in dilute perchloric acid in the presence of various anions have shown that the reaction velocity is unaffected by ClO_4^-, NO_3^-, or F^-. The appreciable catalytic action of the Cl^- and Br^- ions is characterised by a reaction of first order with respect to the concentration of the hydrogen ion, the amine, nitrous acid, and the halide ion:

$$v = K_4^{Hal}[ArNH_2][H^+][HNO_2][Hal^-]. \qquad (7)$$

A different kinetic equation is possible for the iodide ion:

$$v = K_3^{Hal}[H^+][HNO_2][Hal^-]. \qquad (8)$$

These findings were explained in terms of the already known facts of the formation of nitrosyl halides, which are extremely active diazotising and nitrosating agents. These substances can be formed by interaction of the nitrosyl cation or of protonated nitrous acid with the halide ion:

$$NO^+ + X^- \xrightarrow{\text{rapid}} NOX,$$

$$H_2NO_2^+ + X^- \xrightarrow{\text{rapid}} NOX + H_2O.$$

Schmid and Fouad[78] explain the high rate of diazotisation in the presence of hydrobromic acid by the greater polarisation of the NOBr molecule compared with that of the nitrosyl chloride molecule.

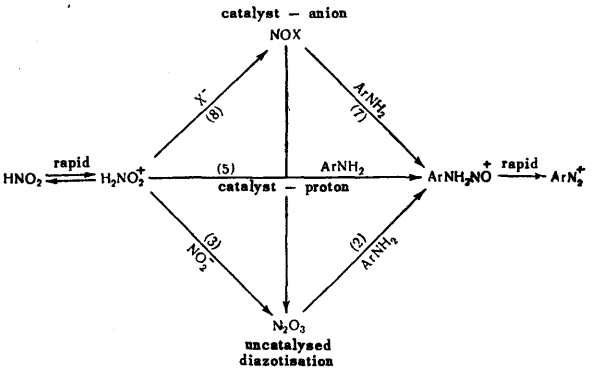
Schmid and Essler [79] regard diazotisation in the presence of the chloride ion as analogous to a process of acid–base catalysis, in which the nitrosyl cation NO^+ plays the part of the proton, while the anion is Cl^-.

The iodide ion acting as the catalyst shows greater difficulty in reacting with the protonated form of nitrous acid, so that this stage of the process proves to be rate-determining and is represented by the kinetic equation (8):

$$H^+ + HNO_2 \xrightleftharpoons{\text{rapid}} H_2NO_2^+,$$

$$X^- + H_2NO_2^+ \xrightleftharpoons{\text{slow}} NOX + H_2O.$$

Ingold suggested the following general mechanism for the diazotisation of amines in aqueous solutions of acids[73]:



It is evident that not all possible diazotising agents are utilised in this mechanism. Thus N_2O_4, NO.OAcyl, and HNO_2 are absent. The low efficiency of nitrous acid in diazotisation naturally excludes the undissociated form HNO_2 from such a mechanism. A necessary intermediate product in diazotisation and nitrosation is the protonated form of nitrous acid, which is able in subsequent stages to change into various other forms of diazotising agent.

C. Diazotisation in Very Concentrated Acids

The diazotisation of amines in concentrated acids is distinguished by its great rapidity and by the reactivity of the diazotising agent. The nitrosyl cation[80], formed by the reaction of HNO_2 with concentrated sulphuric acid,

$$O{=}N{-}OH + 2H_2SO_4 \rightleftarrows [O{\equiv}N]^+ + H_3O^+ + 2SO_4H^-,$$

is, owing to its strongly electrophilic character and its coordination unsaturation, a more active diazotising agent than are $H_2NO_2^+$, N_2O_3, and NOX. The presence of reactive nitrosyl cations in concentrated sulphuric acid is supported also by the ultra-violet absorption spectra of these solutions[81,82].

Study of the kinetic laws of the diazotisation of amines in perchloric acid[83,84], and also of the ultra-violet absorption spectra of solutions of a nitrite in concentrated $HClO_4$,[85] shows that the chief diazotising agent in these cases is NO^+ formed by the ionisation of nitrosyl perchlorate.

Nitrosyl salts can be formed even with weak acids, such as glacial acetic acid, and therefore nitrosyl acylates can be formed by interaction of the nucleophilic nitrite ion with the reactive carbonyl centre of acetic acid or acetic anhydride[86]:

$$HNO_2 + AcOH \rightleftarrows AcO{\cdot}NO + H_2O,$$

$$AcO{\cdot}NO \rightleftarrows AcO^- + [N{\equiv}O]^+.$$

Kozlov and Belov exploited the high nitrosating and diazotising activity of the nitrosyl acylates to show the possibility of smoothly diazotising amines in concentrated carboxylic acids[87,88]. The greatest diazotising effect is associated with high electrolytic dissociation constants of these acids. Weak acids (for example propionic acid) greatly complicate diazotisation by forming diazoamino--compounds.

Schmid found the rate of diazotisation of aniline and the isomeric chloroanilines to increase in the sequence

aniline < *p*-chloroaniline < *m*-chloroaniline < *o*-chloroaniline.

The diazotisation rate constant is higher, the lower the basic dissociation constant of the amine[89].

Introduction of electrophilic substituents into the amine molecule diminishes its basic strength and thereby hinders the attack of the diazotising agent on the lone pair of electrons on the amino nitrogen; introduction of a nucleophilic substituent has the opposite effect. The second stage, stabilisation of the intermediate product as a diazonium cation, is favoured by increasing mobility of the hydrogen atoms attached to the nitrogen, and this mobility is in turn linked with the electronegativity of the nucleus and depends on the nature of the substituent.

Since the slowest stage in diazotisation is the first (formation of the amine nitrite), the influence of substituents in the amine will obviously operate in only one way: if they increase the basic strength of the amine, they will increase its reactivity; if they diminish the basic strength, they will decrease the reaction velocity. These generalisations were later confirmed by determining the rates of diazotisation of substituted anilines by an electrometric method[90].

The rate of diazotisation of aniline in hydrochloric acid depends[91] on the ionic concentration of the solutions, being doubled by an increase from 4 M to 8 M Na_2SO_4 at constant concentrations of HNO_2, $ArNH_2$, Cl^-, and H^+. These observations and kinetic measurements have enabled the general formula for the rate of diazotisation of aniline in nitric and perchloric acids to be corrected for the molecular and ionic activities of the reactants[92]:

$$v = \frac{k_1 [\mathrm{ArNH_3^+}] [HNO_2]^3}{k_2 [H^+] + [\mathrm{ArNH_3^+}] + X [\mathrm{ArNH_3^+}] [HNO_2]\, m^3 \frac{a^2}{aH_2O}},$$

where m and a represent the polarity and the activity coefficient of the nitric or perchloric acid, and aH_2O is the activity coefficient of water.

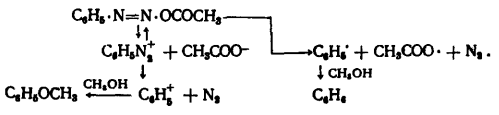
4. CONVERSION OF DIAZONIUM COMPOUNDS INTO OTHER COMPOUNDS

A. Action of Reducing Agents

Diazonium compounds react in two ways with reducing agents: the weaker reductants split off the diazonium group and convert diazonium compounds into hydrocarbons; stronger reducing agents reduce diazonium compounds to the corresponding arylhydrazines.

Alcohols form extremely convenient mild reducing agents. The way in which they react with diazonium compounds depends on several conditions, such as the nature of the substituents in the diazonium compound, the nature of the alcohol, the additives present, and the pH of the medium. Unsubstituted benzenediazonium salts and their homologues are converted mainly into phenyl ethers. The presence of negative substituents in the diazonium compound increase the yield of hydrocarbon.

The pH is especially important. In acidified methanol a diazonium salt breaks down to form mainly (up to 93%) phenyl ether[78], but in the presence of an acetate buffer the chief product (60%) is benzene. In the latter case the reaction is accompanied by the formation of several by-products, such as anisole, azobenzene, and biphenyl. The observed phenomena suggest that reaction takes place by an ionic mechanism in acid medium, and by a radical mechanism in the acetate buffer:



Decomposition by a radical mechanism can be represented in greater detail[93] as follows:

$$C_6H_5N_2^+ + CH_3O^- \rightleftarrows C_6H_5N{=}N{-}OCH_3,$$
$$C_6H_5N_2^+ + AcO^- \rightleftarrows C_6H_5{-}N{=}N{-}OAc,$$
$$C_6H_5N{=}N{-}OCH_3 \rightarrow C_6H_5\cdot + N_2 + CH_3O\cdot,$$
$$C_6H_5N{=}N{-}OAc \rightarrow C_6H_5\cdot + N_2 + AcO\cdot,$$
$$CH_3O\cdot + CH_3OH \rightarrow CH_3OH + CH_2OH\cdot,$$
$$C_6H_5\cdot + CH_3OH \rightarrow C_6H_6 + CH_2OH\cdot,$$
$$CH_2OH + C_6H_5N_2^+ \rightarrow CH_2OH^+ + N_2 + C_6H_5\cdot,$$
$$C_6H_5\cdot + C_6H_5\cdot \rightarrow C_6H_5{-}C_6H_5,$$
$$C_6H_5\cdot + \cdot CH_2OH \rightarrow C_6H_5CH_2OH,$$
$$C_6H_5N_2^+ + CH_3OH \rightarrow C_6H_5OCH_3 + N_2 + H^+.$$

The fact that addition of benzene to the reaction mixture does not increase the yield of biphenyl excluded the possibility of formation of the latter by the reaction

$$C_6H_5\cdot + C_6H_6 \rightarrow C_6H_5{-}C_6H_5 + H\cdot .$$

Further investigation of this reaction showed[94] it to be dependent on the presence of oxygen. In a vacuum two processes take place simultaneously, a radical reaction and a slower ionic process; the reaction velocity is little affected by the total concentration of the CH_3COO^- ion, but is considerably increased by the addition of copper sulphate. In solutions saturated with air[95] the initial reaction velocity is considerably diminished, and the overall rate is represented, not by a first-order equation, but by

$$\frac{d[ArN_2^+]}{dt} = k_1[ArN_2^+] + k_{1/2}[ArN_2^+]^{1/2}.$$

An explanation of this phenomenon in terms of the preferential formation of peroxide radicals by the reaction of $C_6H_5^\cdot$ and $CH_2OH^\cdot$ with O_2 was later formulated on the basis of three modes of decomposition of diazonium salts in methanol[96]: (1) an ionic process resulting in the formation of ethers; (2) a chain radical process resulting in reduction, which is suppressed by oxygen; and (3) a non-chain radical process, consisting in transfer of a hydride ion: $Ar^+ + CH_3OH \rightarrow ArH + CH_2OH^+$.

Mel'nikov found that the reaction of thiophosphates with arenediazonium salts in strongly acid medium does not result in the formation of mixed esters of thiophosphoric acid but leads to replacement of the diazonium group by hydrogen and the separation of a disulphide[97]:

$$2(RO)_2{-}P(=S){-}SH + ArN_2X \longrightarrow (RO)_2{-}P(=S){-}S{-}S{-}P(=S){-}(OR)_2 + ArH + HX + N_2.$$

The diazonium group is replaced smoothly by hydrogen also as a result of the action of sodium borohydride[98], dioxane, tetrahydrofuran, 1,3-dioxolane, and tertiary aliphatic amines in the presence of sodium acetate in aqueous medium[99].

Fokin showed that, when substances such as alcohols, dioxane, glucose, formic acid, and formaldehyde are used as reducing agents, reaction takes place by a chain mechanism, as is confirmed by the considerable acceleration of the process in the presence of $FeSO_4$ and $K_2Cr_2O_7$.[100] He distinguishes two stages, chain initiation and chain growth. The first depends to a decisive extent on the addition of an initiator (an oxidising agent or a reducing agent), and consists in the transfer of electrons to the arenediazonium ion with conversion of the latter into a free radical:

$$ArN_2^+ \xrightarrow{e} ArN_2^\cdot + Fe^{3+},$$

$$ArN_2^\cdot \longrightarrow Ar\cdot + N_2,$$

$$Ar\cdot + R{-}CH_2OH \longrightarrow ArH + R{-}CHOH.$$

The resulting free radicals ensure growth of the chains:

$$ArN_2^+ + RCHOH \longrightarrow Ar\cdot + R{-}\overset{+}{C}HOH + N_2$$

$$R{-}\overset{+}{C}HOH \longrightarrow R{-}C(=O){-}H + H^+ .$$

Diazonium compounds react quite differently with powerful reducing agents, the diazonium group being converted either into an arylhydrazine or into an aryl azide.

The reduction of diazonium salts to arylhydrazines with sulphites obeys a second-order kinetic equation, the reaction velocity being considerably increased by increasing the ionic strength of the system, for example by adding common salt[101]. On this basis, the following mechanism has been suggested for the ionic reaction mechanism:

$$C_6H_5N{=}N{-}SO_3^- + SO_3^{2-} \longrightarrow C_6H_5N(SO_3^-)N^-\cdot SO_3^- , \quad 1)$$

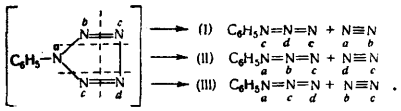
$$C_6H_5N(SO_3^-)N^-SO_3^- + H_2O \longrightarrow C_6H_5N(SO_3^-)NHSO_3^- + OH^- , \quad 2)$$

$$C_6H_5N(SO_3^-)NHSO_3^- + H_2O \longrightarrow C_6H_5NH\cdot NHSO_3^- + HSO_4^- , \quad 3)$$

$$C_6H_5NHNHSO_3^- + H_2O + 2HCl \longrightarrow C_6H_5NH\cdot NH_2\cdot HCl + H_2SO_4 + Cl^- . \quad 4)$$

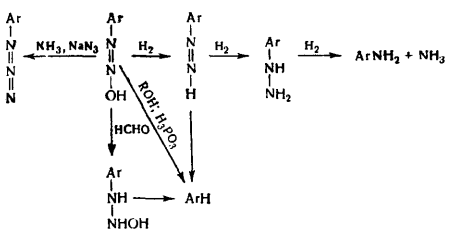
Lewis and Suhr established that the *syn*-diazosulphonate is formed here, but this can pass into the *anti*-form; both isomers are further reduced to the hydrazine derivative, but at different rates[102].

Diazonium compounds can be reduced to arylhydrazines also by an electrochemical method[103]. In the reaction of diazonium compounds with azides the intermediate product in the formation of aryl azides is an unstable pentazole, which can break down in three ways:



In fact, the aryl azide (I) is not formed at all, the isomers (II) and (III) being obtained in the ratio 85 : 15; nucleophilic substituents in the diazonium compound diminish, and electrophilic substituents raise, the yield of the isomer (III).[104] Aryl azides are highly sensitive to light, and are therefore recommended as the main components of light-sensitive layers for offset printing[105].

The overall mechanism of reductive changes undergone by diazonium compounds can be represented as follows:



B. Replacement of the Diazonium Group by Other Substituents

Replacement of the diazonium group by the hydroxyl, resulting in the formation of various phenols, which is important for preparative purposes, is best carried out by boiling solutions of diazonium salts in dilute sulphuric acid.

Phillips suggested that synthetic guaiacol could be obtained by diazotising *o*-anisidine at elevated temperatures

with simultaneous decomposition of the diazonium salt and distillation of the product in superheated steam [106].

The main products of the decomposition of dilute solutions of diazonium salts in 0.005–0.05 M H_2SO_4 were found to be phenols, the rate of the process obeying a first-order equation and being independent of the acid concentration, the nature of the anion forming the salt, and the presence of $CuSO_4$. [107] With diazotised isomeric naphthylamines, formation of naphthols was accompanied by azo-coupling, the quantity of azo-compounds formed increasing with diminution in the acid concentration and fall in temperature.

Consideration of all the changes possible in the reaction, and the fact that the rate obeys a first-order equation, suggested a heterolytic mechanism involving the diazonium cation [108].

A different situation is observed in the decomposition of concentrated (15–17%) solutions of diazonium sulphates. In this case a series of side-products — *p*-hydroxybiphenyl, phenyl ether, *p*-hydroxyazobenzene, and diphenyl sulphate — are formed together with the phenol. The process is often complicated by resin formation, which supports the view that the diazonium compound undergoes homolytic breakdown into free radicals, which react in various combinations to yield the side-products:

$$Ar{-}N{=}N{-}OH \longrightarrow Ar\cdot + N_2 + \cdot OH.$$

Thermal decomposition of naphthalene-1,2(and 2,1)-diazonium oxides yields a substance $C_{20}H_{12}O_2$, the structure of which corresponds to 2′-indenylidene-1,2-naphtho-1′,3′-dioxole [109].

The thermal decomposition of *p*-diazonium oxides (for example 3,5-dibromobenzene-1,4-diazonium oxide) at 70° and above results in the evolution of nitrogen and bromine and the formation of substituted poly(phenyl oxides) having molecular weights of 1600–3600. [110]

Measurement of the magnetic susceptibility of 10% dimethylaminobenzenediazonium chloride solution showed the formation of free radicals under the influence of ultra-violet radiation [111].

Boiling diazonium compounds in acetic acid, or better in acetic anhydride, results in the formation of acetic esters of the corresponding phenols.

Bogatskaya showed that a series of acetylated products (for example aspirin) could be obtained by diazotising amines in acetic acid with subsequent decomposition of the diazonium compounds [112]. Kozlov and Belov established the possibility of smoothly replacing the diazonium group in the acetate salts of isomeric diazotised aminoanthraquinones by the acetoxy-group [113].

Views on the mechanism of the replacement of the diazonium group by chlorine have been fundamentally revised. A comparatively recent investigation [114] of the Sandmeyer reaction indicates that it has a free-radical mechanism. The metal ion (copper) acts as a chain-terminator in the decomposition:

$$Ar\cdot + MCl_n^q \longrightarrow ArCl + MCl_{n-1}^q.$$

This process obviously involves interaction of the radicals with complex ions of metals accompanied either by the formation of a covalent bond or by electron transfer [115].

Kochi [114] denies the cyclic nature of the Sandmeyer decomposition of diazonium compounds, and considers the reaction to take place in two stages:

$$ArN_2^+ CuCl_2^- \longrightarrow Ar\cdot + CuCl_2 + N_2,$$

$$Ar\cdot + CuCl_2 \longrightarrow ArCl + Cu^{I}Cl.$$

The production of free radicals under these conditions is confirmed by the formation of *p*-iodonitrobenzene from *p*-$NO_2C_6H_4N_2Cl$ in the presence of iodine, and of *p*-nitrophenol (up to 46%) on treatment of *p*-$NO_2C_6H_4N_2HSO_4$ with cuprous chloride in the presence of oxygen and a limited quantity of Cl^- ions in aqueous acetone. In aqueous media the aryl radical can react in three ways: (a) dimerisation to a biaryl; (b) interaction with the diazonium ion and the cuprous salt to form azo-compounds; and (c) interaction with $CuCl_2$ to form the main product, the halogeno-derivative.

Clusius and Endtinger [116] prepared toluene-*p*-diazonium chloride labelled with ^{15}N [Ar–N≡^{15}N]$^+$, and converted it by the Sandmeyer reaction into the main product (ArX) and a secondary product (Ar–N=N–Ar). The resulting azo-compound contained the same quantity of the nitrogen isotope as did the original diazonium compound. This fact, in the opinion of these workers, again confirms a radical mechanism for the Sandmeyer reaction:

$$\left[Ar{-}N{\equiv}\overset{15}{N}\right]^+ + Cu^+ \longrightarrow Ar\cdot + N{\equiv}\overset{15}{N} + Cu^{2+},$$

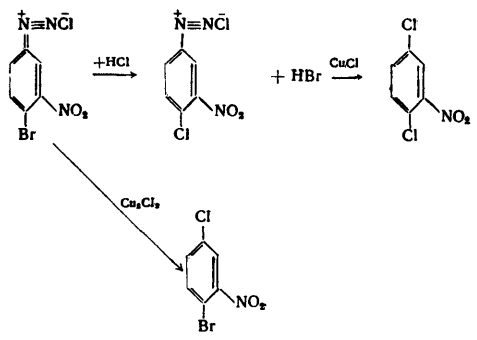
$$Ar\cdot + Cl^- + Cu^{2+} \longrightarrow ArCl + Cu^+,$$

$$Ar\cdot + \left[Ar{-}N{\equiv}\overset{15}{N}{\leftarrow}CuCl\right]^+ \longrightarrow Ar{-}N{=}\overset{15}{N}{-}Ar + (CuCl)^+.$$

The side reactions are considerably affected by the solvent: water diminishes the yield of the main product and directs the reaction towards the formation of the unsaturated hydrocarbon. An aqueous acetone solution lowers the yield of halogeno-derivative to a less extent, by forming the more stable acetonyl radical:

$$Ar\cdot + CH_3COCH_3 \longrightarrow ArH + CH_3\dot{C}OCH_2.$$

This radical readily dimerises or reacts with $CuCl_2$, forming chloroacetone and reducing Cu^{II} to Cu^{I}. [117] Apart from the main free-radical decomposition of diazonium salts in the Sandmeyer reaction, secondary reactions occasionally take place. Lamm [118] describes the interchange of halogen in the decomposition of diazonium compounds in the presence of an excess of hydrochloric acid and cuprous chloride:



Study of the decomposition of diazonium salts in acid solutions of bromides and iodides has shown the simultaneous occurrence in these solutions of two reactions, of first and second order.

Carey isolated toluene-*o*-diazonium triiodide dihydrate (yield 15–20%, decomposes at 54°) by the action of KI solution on *o*-$CH_3C_6H_4N_2^+$ in sulphuric acid solution at 5°; this compound breaks down at 40° into iodotoluene, N_2, and I_2.[119] The ease of formation of ArI was explained by a definite proportion of the diazonium ions oxidising I^- to I_2 with the formation of the strongly polarised complex anion I_3^-, which is able to displace nitrogen in ArN_2^+. These reactions can be represented by a unimolecular and bimolecular mechanism:

$$ArN_2^+ \longrightarrow Ar^+ + N_2,$$
$$Ar^+ + I_3^- \longrightarrow ArI + I_2,$$
$$ArN_2^+ + I_3^- \longrightarrow ArI + I_2 + N_2,$$
$$I_2 + I^- \longrightarrow I_3^-.$$

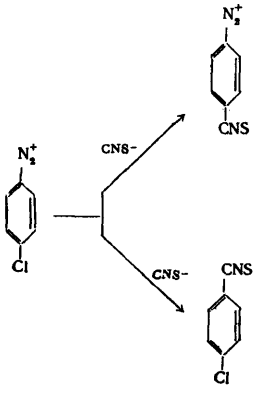
The diazonium group can be replaced by fluorine by decomposing diazonium fluoroborates in solution or in the solid state at elevated temperatures[120].

Brunton and Suschitzky[121] showed that the reaction is simpler, and the yield of fluorinated derivatives not diminished, when a mixture of diazonium fluoroborates (instead of the individual substances) is decomposed. Replacement of the diazonium group by fluorine is sometimes accompanied by secondary reactions. In the thermal decomposition of dry diazonium fluoroborates isolated from hydrochloric acid solutions chlorinated products are formed together with the fluorinated arenes[122].

Treatment of diazonium chlorides and acetates with alkali-metal selenides and polyselenides results in the smooth formation of diaryl selenides and of diaryl diselenides[123].

When $CH_3SC_6H_4X$ and $CH_3SeC_6H_4X$ (X = H, OCH_3, CH_3, Hal) react with 2,4-dinitrobenzenediazonium chloride, N_2 is evolved, the CH_3S and CH_3Se groups are demethylated, and sulphides or selenides of general formula $XC_6H_4-Y-C_6H_3(NO_2)_2$, where Y = S or Se, are formed[124]. The process probably involves the intermediate formation of an unstable diarylmethylsulphonium or diarylmethylselenonium ion.

Lewis and Suhr[125] studied the rate of reaction of a ^{14}C-labelled thiocyanate with *o*- and *p*-halogenated benzenediazonium ions, and found that in this case two reactions, replacement of halogen by thiocyanate and decomposition of the diazonium ion, take place in parallel:



The overall constants were calculated, their values depending on the dielectric constant of the medium and the reactivity of the halogen: F < Cl < Br < I.

Aromatic selenocyanates can be prepared by the action of potassium selenocyanate on diazonium salts[126]. The 4-, 5-, and 8-nitronaphth-1-yl and 1-nitronaphth-2-yl selenocyanates obtained in this way[127] were oxidised to the corresponding nitronaphthaleneseleninic acids, which are characterised by a certain sensitivity to light[128]. Nesmeyanov *et al.* obtained 35–40% yields of diaryl selenides by the decomposition of arenediazonium fluoroborates in the presence of zinc dust and $SeCl_4$.[129]

Diazonium compounds react in a peculiar fashion with sulphur dioxide, various products being obtainable depending on the conditions. Meerwein *et al.* prepared arenesulphonyl chlorides in good yields by the decomposition with cupric chloride dihydrate of concentrated solutions of diazonium chlorides in a saturated (30%) solution of sulphur dioxide in glacial acetic acid. During the reaction the copper salt is partly reduced to cuprous chloride by the sulphurous acid[130]. In the case of diazonium compounds containing electronegative groups, sulphonyl chlorides can be formed even in the absence of a catalyst, the reaction then taking place by an ionic mechanism:

$$Ar-\dot{N}\equiv\bar{N} \rightleftarrows Ar-\bar{N}=\dot{N} + :\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}} \longrightarrow Ar-\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S^+}} + N_2,$$

$$Ar-\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S^+}} + \bar{Cl} \longrightarrow ArSO_2Cl.$$

The catalytic action of copper is explained on the basis of Waters' well-known views on the function of cuprous ions as electron-donors and the breakdown of the diazonium compound with the formation of free radicals.

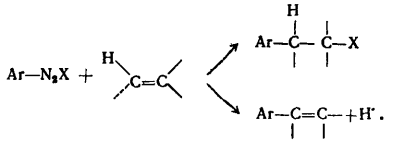
Substitution of a cyano-group for a diazonium group in an aromatic nucleus is effected in the presence of cuprous cyanide by a process analogous to the Sandmeyer reaction. The medium is usually sodium cyanide solution, and therefore the reactants undergo several initial changes: the diazonium compounds form the corresponding *syn*-diazocyanides with the CN^- ions, and with an excess of hydrocyanic acid these are able to form complexes of the type Ar–N=N–Cn·HCN.[131]

Treatment of diazonium salts with an excess of a nitrite in the presence of cuprous and cupric salts results in a smooth exchange of the diazonium for the nitro-group even in the cold. The acid diazotised solution can conveniently be added to a mixture containing an excess of nitrite, sodium carbonate, and an anti-foaming agent[132]. This method has been used to prepare *o*- and *p*-dinitrobenzenes (yield 90%), 1,4-dinitronaphthalene (92–96%), and 5,6,8-trinitrotetralin (49%). Little work has been done on the mechanism and kinetics of this substitution, although there are indications in the literature that this reaction follows a second-order equation and is of the nucleophilic substitution type[133].

C. Replacement of the Diazonium Group by Groups Containing Carbon

This type of substitution includes numerous reactions involving elimination of nitrogen and formation of a new

C–C bond. The most important reaction of this type is that discovered by Meerwein between diazonium compounds and $\alpha\beta$-unsaturated carbonyl compounds. Nitrogen is evolved in the reaction, and either replacement of hydrogen by the aryl radical or else addition of halogen and the aromatic radical at the multiple bond takes place, depending on the nature of the unsaturated compound:



This reaction takes place in a peculiar way with cinnamic and some other unsaturated acids: in this case elimination of nitrogen and hydrogen halide is accompanied by that of CO_2 owing to decarboxylation, and the corresponding stilbene derivatives are formed:

$$ArN_2X+Ar_1-CH=CH-COOH \rightarrow Ar-CH=CH-Ar_1+N_2+HX+CO_2.$$

The Meerwein reaction can be successfully accomplished in the presence of sodium acetate and cupric chloride as catalyst in aqueous acetone solution. The yields of the final products fluctuate within wide limits depending on the nature of the unsaturated compound, the nuclear substituent in the diazonium compound, and the anion of the diazonium salt. The presence of electronegative groups in the *para*-position in diazonium chlorides and bromides ensures that a good yield of a pure product will be obtained. The range of unsaturated substances which can undergo the Meerwein reaction has been considerably extended recently.

Dombrovskii and Bondarchuk[134] obtained a good yield of triphenylethylene by the reaction of 1,1-diphenylethylene with ArN_2Cl under the conditions of the Meerwein reaction. With butadiene and its homologues, it was found that in all cases the chloroarylation of the unsaturated system takes place in the 1,4-position[135].

$\alpha\beta$-Unsaturated aldehydes (acrolein and its aryl derivatives)[136] and ketones (methyl vinyl ketone)[137] condense with diazonium chlorides in the presence of HCl and $CuCl_2$ in aqueous acetone solution to form derivatives of 2-chloro-3-phenylpropionaldehyde and 3-chloro-4-phenylbutan-2-one respectively.

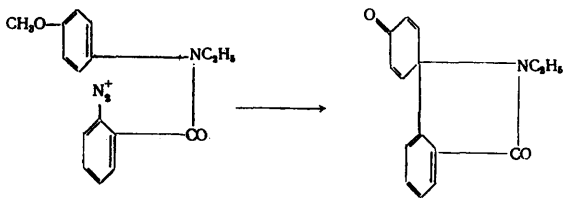
Unsaturated acids are, perhaps, most reactive in the Meerwein reaction, undergoing arylation with or without simultaneous decarboxylation, and also halogenoarylation, depending on the conditions. Arylation together with decarboxylation is most often observed: sorbic acid[138] reacts with diazonium chlorides to form 1-arylpenta-1,3-dienes. *p'*-Nitrostilbene-*p*-sulphonic acid has been obtained from *p*-$NO_2C_6H_4N_2Cl$ and *p*-sulphocinnamic acid in aqueous medium. An elevated temperature, a catalyst ($CuCl_2$), and the presence of chlorine *ortho* and *para* to the diazonium group increase the yield of the main reaction product[139].

Arylation by means of diazonium compounds has been extended to several other compounds. Diazonium salts act on *p*-benzoquinone[140] and on toluquinone[141] in the presence of sodium acetate in aqueous solution to yield monoarylquinones. Further reaction of the monoarylquinones with the diazonium compounds gives diarylquinones as mixtures of isomers[142].

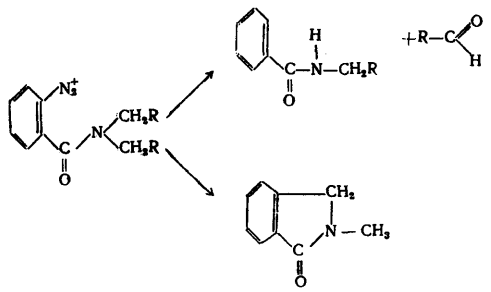
Anthracene, 9-phenylanthracene, and anthrone-9-carboxylic acid are arylated by diazonium chlorides to 9-mono- and 9,10-di-arylanthracenes respectively[143].

Puchkov was the first to succeed in substituting a phenyl radical for the diazonium group in anthraquinone-1-diazonium acetate[144] and in its derivatives substituted with chlorine and the benzamido-group in the other benzene ring[145]. Good yields (55–70%) are obtained in an emulsified mixture of benzene and sodium carbonate solution. Reaction can occur in this way only in alkaline medium (pH 8–9): according to Kozlov and Belov's experiments[113], decomposition of solid anthraquinone-1-diazonium acetate in benzene results in the formation of anthraquinon-1-yl acetate. The arylation of pyridine *N*-oxides by means of diazonium compounds has been described[146].

Several diazonium salts have been found not to undergo Pschorr internal cyclisation on thermal decomposition; for example, the diazonium sulphate from *o*-amino-*N*-ethyl-*p'*-methoxybenzanilide does not yield 10-ethyl-3-methoxyphenanthridone[147], but forms instead a spiro-dienone[148]:



In the decomposition of diazonium sulphates, cyclisation is probably a subsidiary process, while formation of the corresponding *N*-substituted benzamides is the main reaction, for example:



side-product[149]

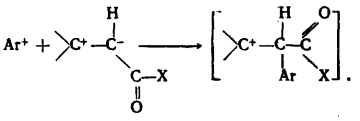
Heterocyclic compounds, for example pyridine[150] and isoquinoline[151] derivatives, can be obtained by intramolecular cyclisation *via* diazonium salts.

The arylation of both $\alpha\beta$-unsaturated and other compounds is usually accompanied by the formation of several secondary products, such as aryl halides, aromatic hydrocarbons, biaryls and polyarenes, and resins. Conditions can be selected under which the subsidiary reaction proves to be the main reaction. The possibility of obtaining symmetrical biaryls and polyarenes from diazonium salts is extremely important, and is utilised for the synthesis of polyphenyl hydrocarbons[152]. Symmetrical polyarenes are formed from diazonium compounds, with the creation of a C–C bond at the site of the diazonium group, when diazonium salts are decomposed in a solvent (alcohol, acetic acid) in the presence of copper powder.

The mechanism of the Meerwein reaction and of the arylation of aromatic compounds with diazonium compounds has formed the subject of serious discussion, which has

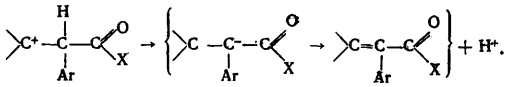
revolved mainly around two points: (a) the type of cleavage of the C–N bond (homolytic or heterolytic), and (b) the role of bivalent copper and the specificity of the solvent (acetone). Meerwein suggested an ionic reaction mechanism, in which the arenediazonium salt, in the ionic form, breaks down into nitrogen and an aryl cation.

The aryl cation adds on to the polar double bond, which carries a partial negative charge due to the conjugated multiple bond with the carbonyl group:

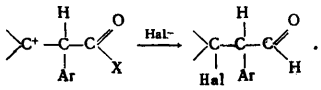


This cation can be stabilised in various ways [153].

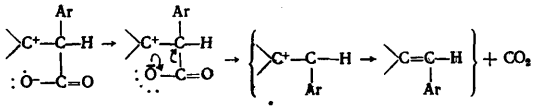
(1) With elimination of a proton and subsequent reformation of the double bond:



(2) By the addition of Hal^-:



(3) By intramolecular saturation (in the case of $\alpha\beta$-unsaturated acids) involving formation of unstable β-lactones from the carboxylate ion. These substances break down with the elimination of CO_2 and formation of an unsaturated hydrocarbon:



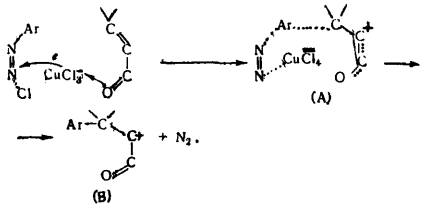
Meerwein supports an ionic mechanism by observations indicating that the reactions are favoured by the presence in the diazonium compounds of nuclear substituents having a large electronegative effect and by a readily polarisable anion. The favourable influence of the polarising action of carbonyl compounds, of polar solvents (water, pyridine, acetone), and of the addition of salts (CH_3COONa) also supports an ionic mechanism.

On the other hand, several features of the reaction — addition of the aryl radical to the β-carbon atom of $\alpha\beta$-unsaturated acids, the catalytic action of the Cu^{2+} ion, the formation of side-products — are not explained by such mechanism.

Kochi [154], who studied the role of copper in the Meerwein reaction, established that the actual catalyst here is the Cu^+ ion formed by the reduction of Cu^{2+} by the acetone:

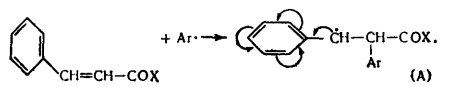
$$2CuCl_2+CH_3COCH_3 \longrightarrow 2CuCl+CH_3COCH_2Cl+HCl.$$

In his opinion [155] this fact shows that the Sandmeyer and Meerwein reactions have similar mechanisms. In the presence of an olefine the aromatic radicals formed by the decomposition of ArN_2X under the influence of CuCl add on to the double bond, and this is followed by addition of a chlorine atom to the newly formed radical, or by oxidation of the latter to a carbonium ion, which is supported by the formation of a mixture of 1-chloro-p'-nitro-1,2-diphenylethane and p-nitrostilbene by the reaction of p-$NO_2C_6H_4^{\cdot}$ with styrene. From the fact that decomposition of p-$NO_2C_6H_4N_2.HSO_4$ in aqueous acetone solution containing styrene and CuCl (*i.e.* with a limited content of Cl^-) yields 21% of p-nitrostilbene, whereas with an excess of Cl^- only 9% is formed, Kochi concludes that the direct transfer of halogen involves a more highly chlorinated complex ion of the metal than does the reaction with electron transfer [156]. A roughly similar view is held by other investigators [157], who postulate also that peroxide radicals may be formed (when the reaction is carried out in the air). Still other views are held concerning the role of bivalent copper. It is assumed that $CuCl_2$ helps to effect the transfer of electrons from activating groups in the unsaturated compounds, which are comparatively rich in electrons, to the diazonium nitrogen with the formation of a radical–cation (A). The diazonium radical, which after elimination of nitrogen is converted into an aryl radical, combines with (A), after which the resulting cation (B) loses a proton or adds on Cl^-: [158]

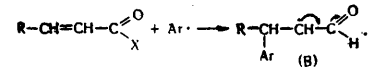


This mechanism of the arylation of unsaturated compounds does not explain the peculiarities of the process in aqueous or in pyridine medium, where it is difficult to postulate the reduction of Cu^{2+} and Cu^+. Perhaps the most plausible hypothesis in this connection is that of Dombrovskii and Terent'ev, according to which a copper complex is formed in this case, the presence of which is supported by their polarographic and spectrophotometric studies of the interaction of arenediazonium salts with $CuCl_2$. [159,160]

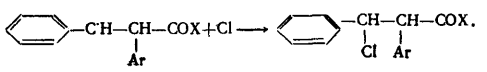
Dombrovskii gives an expanded treatment of the process [161], which reduces in essence to the following: (1) the diazonium salt is converted from an ionic form into a covalent molecular form, the change being favoured by the reaction conditions (pH, organic solvent, etc.); (2) $CuCl_2$ strongly catalyses the breakdown of the molecular form of the diazonium compound into free radicals, perhaps through the formation of copper complexes; (3) the reactive aryl radical immediately interacts with the multiple bond of the unsaturated molecule, the point where addition occurs being determined by the nature of the substance. In the case of aliphatic–aromatic unsaturated compounds the aryl radical adds on to the α-carbon atom, forming a stable radical (A) with a minimum energy content:



Aliphatic $\alpha\beta$-unsaturated carbonyl compounds direct the aryl radical to the β-carbon atom, with formation of the radical (B):



The radicals (A) and (B) then add on a halogen atom, for example:



On the basis of a radical mechanism, it is not difficult to imagine the formation of side-products by the combination of free radicals entering the reaction system:

$$Cl\cdot + CH_3COCH_3 \longrightarrow CH_3COCH_2Cl + H\cdot,$$
$$Ar\cdot + Cl\cdot \longrightarrow ArCl,$$

$$Ar\cdot + CH_3COCH_3 \rightarrow ArH + CH_3COCH_2\cdot \rightarrow \text{resin formation.}$$

It has recently been found that arenediazonium fluoroborates behave peculiarly during arylation. When they undergo decomposition in esters of $\alpha\beta$-unsaturated acids, for example, the aryl adds on to the α-carbon atom [162,163]. This fact allows a heterolytic mechanism to be postulated for the decomposition of the arenediazonium fluoroborates.

A radical mechanism has also been attributed to the arylation of aromatic hydrocarbons by means of diazonium salts in non-polar solvents. Important evidence for the formation of free radicals is the fact that the aryl enters predominantly *para* or *ortho* to an existing substituent independently of the nature of the latter, whereas it enters the α- or β-position of naphthalene depending on the electrophilic character of the substituents [164]. Moreover, the inert solvent plays an extremely important part, for it can act as a source of free radicals: Ushenko [165], for example, obtained 2-methylthio-6-phenylbenzothiazole from 6-amino-2-methylthiobenzothiazole by decomposition of the diazonium compound in benzene. In general, benzene is a good medium for the formation of free radicals; for example, stable diazonium salts which are soluble in benzene (*p*-n-decyloxybenzenediazonium chloride) exhibit a very great tendency to break down with the formation of free radicals [166]. If carbon tetrachloride or chloroform is used as solvent, chlorobenzene and other chlorinated products are formed, which also supports a radical mechanism for the reaction [167,168]. Decomposition of a diazonium acetate in benzene yields biphenyl, nitrogen, and acetic acid with the evolution of carbon dioxide, a typical cleavage product of the acetoxy radical:

$$C_6H_5N{=}NOCOCH_3 \longrightarrow C_6H_5\cdot + N_2 + \cdot OCOCH_3 \longrightarrow CO_2 + CH_3\cdot.$$

There is no doubt that the reaction has a radical mechanism, but in some cases it does not entirely correspond in detail to the mechanisms described above. Addition of metals definitely catalyses the process, the role of the metal being, just as in the Sandmeyer reaction, the transfer of electrons:

$$ArN_2X + Hg \longrightarrow Ar\cdot + N_2 + Hg^+ + X^-.$$

Furthermore, metals accumulate on their surfaces the less energy-rich acetate anion instead of the acetoxy-radical, which also favours this type of reaction.

The Nesmeyanov school has shown that, in contrast to other diazonium salts, benzenediazonium fluoroborates and fluorosilicates break down heterolytically with formation of the phenyl cation $C_6H_5^+$. When $C_6H_5N_2.BF_4$ breaks down in acetophenone [169], in benzoic esters [170], and in nitrobenzene [171], the phenyl is oriented exclusively *meta* to an existing substituent. Similar results have been observed in the decomposition of benzenediazonium fluorosilicate [172].

Heterolytic breakdown of $C_6H_5N_2.BF_4$ in chlorobenzene and in bromobenzene yields diphenylchloronium fluoroborate $(C_6H_5)_2Cl^+.BF_4^-$ [173] and diphenylbromonium fluoroborate $(C_6H_5)_2Br^+.BF_4^-$ [174] respectively, from which salts of the onium compounds with various anions are obtained by double decomposition.

The arylation of ferrocene by diazonium compounds probably goes by a free-radical mechanism, as is supported by the isolation of *pp'*-azoanisole in the preparation of *p*-methoxyphenylferrocene [175]. Introduction of acetyl and *p*-nitrophenyl groups into the ferrocene nucleus sharply diminishes the ability of the hydrogen atoms in the latter to undergo aromatic substitution. For example, reaction between diacetylferrocene and diazonium compounds results, not in the expected arylation [176], but in destruction of the ferrocene nucleus with formation of an arylazoacetylcyclopentadiene [177,178]. In Weinmayr's opinion [179], ferrocene reacts with diazonium compounds in strongly acid medium as the oxidised form, the ferricinium cation, forming mono- and poly-arylferrocenes, probably as a mixture of isomers.

The above examples of the peculiar course of the reaction under discussion show how necessary it is to proceed with caution in formulating its mechanism and how far the structure of the compound and the reaction conditions influence the mechanism of the process.

D. Formation of Organometalloid Compounds by the Decomposition of Diazonium Salts

Methods involving the use of diazonium compounds occupy an important position among the numerous procedures for obtaining organometalloid compounds.

Mel'nikov *et al.* obtained by the diazonium method moderate yields of several mixed esters of dithiophosphoric [180], thiophosphoric [181], and mono- and di-thiophosphonic acids [182] possessing a definite insecticidal action. The reaction takes place in the presence of copper, and according to these workers is homolytic in character, since it proved possible during the process of separation to isolate an intermediate dialkyl arenediazonium dithiophosphate [183]:

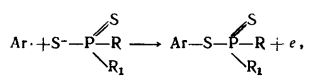
$$ArN_2Cl + (RO)_2PSSH \longrightarrow HCl + ArN_2SPS(OR)_2 \longrightarrow N_2 + ArSPS(OR)_2.$$

The amount of copper salt present plays an important part in this decomposition. Depending on the proportions of reactants and copper salts, three interlinked reactions [184] can take place at once between nitrobenzenediazonium fluoroborates and phosphorus trichloride: (1) formation of a phosphonic group, (2) reduction of the nitro-group, and (3) chlorination.

The role of copper in this process is in essence to transfer an electron to the diazonium ion:

$$Cu^+ - e \rightarrow Cu^{+2},$$

$$Ar{-}N_2^+ + e \longrightarrow Ar\cdot + N_2,$$



$$Cu^{+2} + e \longrightarrow Cu^+.$$

The diazonium method has considerable advantages for the preparation of arsinic and arsonic acids by the reaction of solid diazonium salts with $AsCl_3$, a difficultly separable

mixture of arylarsonic and diarylarsinic acids being formed. Reutov and Bundel'[185] established that Nesmeyanov decomposition of double diazonium salts goes successfully in acetone in the cold, in the presence of iron powder and $AsCl_3$ or phenyldichloroarsine, and yields a mixture of mono-, di-, and tri-substituted products. They showed that, by varying the proportions of the reactants, the reaction can be controlled so that a particular substance is formed predominantly.

The mechanism of such a decomposition can be represented as follows:

$$(ArN_2Cl)_2 \cdot ZnCl_2 + 2AsCl_3 \rightleftarrows 2ArN_2Cl \cdot AsCl_3 + ZnCl_2, \quad (a)$$

$$ArN_2Cl \cdot AsCl_3 + Fe \longrightarrow ArAsCl_2 + N_2 + FeCl_2. \quad (b)$$

Excess of $ZnCl_2$ sharply lowers the reaction velocity. This indicates the considerable ease of decomposition of the double salt $ArN_2Cl.AsCl_3$ compared with double salts containing iron and zinc chlorides.

Nesmeyanov's reaction has proved extremely valuable for the synthesis of organic compounds of tin, the importance of which has greatly increased during recent years[186]. Great advances have been made in the synthesis of organoantimony compounds, which can be obtained by the arylation with diazonium compounds of derivatives of the types $ArSbX_2$ and Ar_2SbX, yielding products of the types $ArAr'SbX_3$ and $Ar_2Ar'SbX_2$.[187] The Nesmeyanov reaction has been employed in the synthesis of organometallic compounds of lead, bismuth, and thallium, although in low yields. The best results are obtained by using arenediazonium fluoroborates.

Interaction of arenediazonium fluoroborates with zinc dust in acetone in the presence of $GeCl_4$ between -8° and +5° for 2 days, followed by treatment of the mass with 20% NaOH, yields aromatic compounds of germanium of the type $(p\text{-}RC_6H_4GeO)_2O$.[188] Decomposition of $ArN_2.BF_4$ with metallic Mg in tetrahydrofuran, dioxane, ether, etc. results in organomagnesium compounds, which form ArCOOH on carboxylation[189]. The double diazonium salts formed with $ZnCl_2$ and $FeCl_3$ proved extremely convenient for the synthesis of mixed organoarsenic compounds of the types $ArAr'AsX$ and $ArAr'_2As$.[190]

The efforts of chemists of the Nesmeyanov school have led to the development of a series of methods for the preparation of organometallic compounds of elements of Group V of the Periodic System[191].

Decomposition of the double diazonium salts formed with metal chlorides is usually accompanied by the formation of side-products, hydrocarbons and chlorination products of the solvents. This phenomenon has served as a basis for regarding the mechanism of the Nesmeyanov reaction as a homolytic process involving the formation of free radicals. It is supposed that reduction of the double diazonium salt during the reaction yields the free metal, which reacts with the arenediazonium halide by a radical mechanism, for example:

$$ArN_2Cl \cdot HgCl_2 + 2Cu \rightarrow ArN_2Cl + Hg + CuCl_2,$$

$$Ar - N_2 - Cl + \cdot Hg \cdot \rightarrow ArHgCl + N_2.$$

However, several discrepancies occur here. Firstly, homolytic breakdown is a side-reaction, since double diazonium salts are able, under the conditions of the Nesmeyanov reaction, to dissociate with formation of the free arenediazonium chloride[192]:

$$ArN_2Cl \cdot MCl_n \rightleftarrows ArN_2Cl + MCl_n$$

Decomposition of an arenediazonium chloride with a metal powder yields free radicals which react with the solvent.

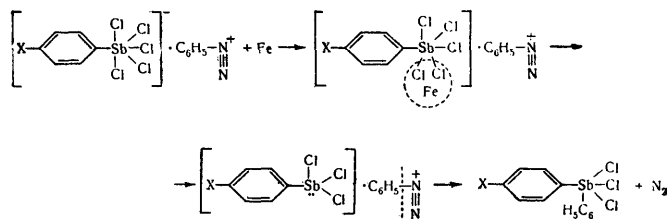
Reutov *et al.*[193] investigated the dependence of the reaction velocity of

$$p\text{-}XC_6H_4SbCl_4 \cdot C_6H_5N_2Cl + Fe \rightarrow XC_6H_4(C_6H_5)SbCl_3 + N_2 + FeCl_2$$

on the nature of X, and found that substituents increase the rate of reaction in the order in which their electron-donor properties increase, *i.e.* in the sequence

$$O_2N < Cl < H < CH_3 < C_2H_5O.$$

The observed relation gives grounds for supposing that the decomposition of the double salts with iron powder is heterolytic[194]:



It is quite clear that the addition of $C_6H_5^+$ at the free electron pair of the antimony atom should be facilitated by substituents which direct *ortho–para* and hindered by those which direct *meta*.

A heterolytic mechanism for the Nesmeyanov reaction is supported also by the facts of the varying stability of salts of the type $ArSbCl_2.Ar'N_2Cl$ depending on the nature of Ar and Ar'.[195] Substituents which direct *ortho–para* lower the stability of the double salts when they are present in the radical of the organoantimony component, and improve it when present in that of the diazonium component. Substituents which direct *meta* have the opposite effect.

The heterolytic mechanism of the Nesmeyanov reaction is confirmed also by the possibility of obtaining good yields of organomercury compounds in aqueous medium. It is interesting that antimony derivatives are not formed under these conditions, owing to the ease of hydrolysis of their double salts with diazonium compounds. All this convincingly demonstrates the heterolytic nature of the Nesmeyanov reaction, in contrast to the homolytic mechanism of the Waters reaction, involving the intermediate formation of double diazonium salts with metal chlorides[196].

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PHENOL–DIENONE REARRANGEMENT IN THE REACTIONS OF PHENOLS

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1. INTRODUCTION

Study of the chemistry of phenols is of great practical value, apart from its relevance to theoretical aspects of organic chemistry. The use of phenols and their derivatives in the production of various plastics, dyes, effective bactericides, insecticides, herbicides, etc. is well known. Phenols are successfully employed as oxidation inhibitors in motor fuels, oils, and edible fats. Finally, as Emanuel' *et al.* have shown[1-3], phenolic inhibitors can be utilised in experimental oncology and in other types of biological research. However, the literature contains too few general accounts of the chemical properties of phenols. It is only recently that a number of review papers have been published, dealing with individual properties of phenols[4-9].

The present paper discusses reactions of phenols involving disruption of the aromatic bond system of the phenol and leading to the formation of cyclohexadienones. The formation of such substances is very often postulated also as an intermediate stage in many reactions of phenols. Cyclohexadienone compounds are in some cases stable, and can be isolated in the free form, whereas in other cases their existence can be assessed only by spectroscopic methods. The conversion of a phenolic structure into a cyclohexadienone structure has been termed a phenol–dienone rearrangement. It must be remembered that such a change does not correspond to the usual concept of a rearrangement in organic chemistry, since it occurs during the reaction of the phenol with some reagent and results in the formation of a compound containing a new substituent in the carbon ring. This rearrangement is essentially a rearrangement of the aromatic bond system of the phenol. The reverse process, the conversion of *gem*-substituted cyclohexadienones into phenols, which is a typical rearrangement and is usually accompanied by a migration of substituents within the ring, is called a dienone–phenol rearrangement. In view of its fundamental difference and intrinsic significance, the latter rearrangement will not be considered here.

Phenols usually undergo the phenol-dienone rearrangement when acted on by reagents of electrophilic or radical type. In this respect the halogenation of phenols has been most fully studied, and to a less extent their nitration, some alkylation reactions, and several radical reactions of phenols. Below we shall examine only those aspects of these well-known reactions that have a direct bearing on the phenol–dienone rearrangement of monohydric monocyclic phenols and that lead to the formation of compounds having a "quinolide" structure. We apply the term "quinolide", in contrast to "quinonoid", to the structure of cyclohexadienones in which a carbon atom *ortho* or *para* to the carbonyl is linked by single bonds (not by a double bond) to two atoms or groups of atoms.

2. EFFECT OF STRUCTURE OF PHENOL ON EASE OF FORMATION OF DIENONE COMPOUNDS

The formation of cyclohexadienone structures might be most simply explained by a tautomeric change in the phenols. However, tautomerism has not been detected in monohydric monocyclic phenols containing no other functional group[10]. In several simple phenols cyclohexadienone structures are formed only at the instant of reaction with electrophilic and radical reagents. If, on the other hand, the existence of tautomerism is postulated in the phenol–dienone system,