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QUINONE DIAZIDES AND *p*-IMINOQUINONE DIAZIDES

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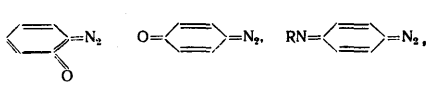
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I. INTRODUCTION

para-Substituted and *para*- and *ortho*-hydroxy-substituted diazonium salts have characteristic properties; when treated with alkaline agents they form compounds of the type:



although most diazonium salts form diazoates. The following names are used in the literature for these compounds: diazoanhydrides, diazoquinones, diazo-oxides, and quinone diazides for the oxo-derivatives, and *p*--diazoimines (*p*-diazoimides if R is an acyl group), *p*-iminodiazoquinones, and *p*-iminoquinone diazides (or *p*-imidoquinone diazides) for the imino-derivatives. We shall call these compounds quinone diazides and *p*-iminoquinone diazides (or *p*-imidoquinone diazides)†.

Because of their unusual properties, these compounds occupy a special place in the chemistry of the diazo-compounds. *p*-Iminoquinone diazides and quinone diazides are theoretically interesting, as they may be regarded as occupying an intermediate position between aliphatic diazo-compounds and aromatic diazonium salts. Moreover, these compounds are widely used industrially for the synthesis of photosensitive dyes. In the laboratory, many compounds otherwise difficult to obtain are synthesised from *p*-iminoquinone diazides and quinone diazides.

Although good reviews have been published on the structures and properties of diazonium salts [1,2] and of aliphatic diazo-compounds [3-5], there is no review on the present state of the chemistry of *p*-iminoquinone diazides and quinone diazides. Since a large number of papers has appeared, particularly in recent years, on the reactions and structures of these compounds, it seemed useful to systematise the extensive information that has accumulated. A review of the literature on the synthesis, properties, and structure of quinone diazides and *p*-iminoquinone diazides (*p*-imidoquinone diazides) is given below.

II. PREPARATION OF *o*- AND *p*-QUINONE DIAZIDES AND *p*-IMINOQUINONE DIAZIDES

A. Preparation of Quinone Diazides

Methods used for the preparation of diazo-ketones and methods for synthesising diazonium salts may both be used for the synthesis of quinone diazides.

The following are five different methods of synthesis: (1) diazotisation of aminophenols; (2) diazotisation of aromatic amines not containing hydroxyl groups, with subsequent introduction of a hydroxyl group into the diazonium salt; (3) from phenols by introduction of a diazo-group; (4) from quinones, through *p*-toluenesulphonylhydrazones; (5) by the introduction of new substituents into a quinone diazide already synthesised.

It should be mentioned that each of these methods requires an acid medium at one stage, and therefore the synthesis of quinone diazides reduces to the preparation of the corresponding hydroxyaryl-diazonium salt with subsequent elimination of a molecule of acid from this salt.

A solid quinone diazide is readily formed by elimination of a molecule of acid from the diazonium salt, if the aryl group consists of a system of condensed benzene rings [6] or has negative substituents [7,8]; the solid quinone diazide is then precipitated when the diazo-solution is diluted with water. Sometimes the solution must be strongly cooled, or it must be neutralised [9-11]. If the diazide is poorly soluble in water, it may be extracted with benzene [12]. If the diazides are very soluble in water, special methods are used for their separation. Thus, Anderson and Roedel [13] obtained *p*-benzoquinone diazide in low yield by

† The second of these alternatives is usually favoured in the Russian text but the first has been employed in the translation (Ed. of Translation).

treating the diazonium chloride with silver oxide in alcohol, and cooling the solution to -70° after the addition of ether; *o*-benzoquinone diazide was first obtained by Anderson and Le Fevre, using the same procedure [14]. Stille and coworkers used an analogous method for the preparation of some *p*-benzoquinone diazides [15]. Later, *o*-benzoquinone diazide was obtained in high yield by treating dry *o*-hydroxyphenyldiazonium chloride with anhydrous sodium carbonate, the diazide being subsequently extracted by boiling ether or hexane [11].

1. Synthesis of quinone diazides by diazotisation of *o*- or *p*-aminophenols. Difficulties are encountered in the diazotisation of aminophenols by the usual methods, because of the readiness with which these compounds are oxidised, or because of their low solubility. For this reason, the diazotisation of aminophenols is often carried out under special conditions. The diazotisation proceeds most smoothly in organic solvents. Schmidt and Glitz were the first to diazotise the simplest aminophenols with nitrogen oxides in ether [16]. Hantzsch and Davidson later used this reaction for the diazotisation of unsubstituted aminophenols [10].

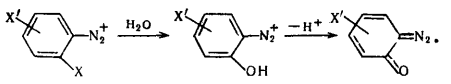
Diazotisation of aminophenols with sodium nitrite in a medium of concentrated organic acids proved to be a very convenient method, solutions of the corresponding diazonium salts being obtained in high yield [17-20]. The yield of the salt increases with the strength of the organic acid used as solvent [17,18]. In the diazotisation of some highly condensed or heterocyclic hydroxy-amines, good results are obtained with the use of dimethylformamide or glycol methyl ether as solvent [7].

When aminophenols are diazotised in the usual way with nitrite in hydrochloric acid solution, large amounts of oxidation products are obtained. Thus, diazotisation of aminonaphthols in aqueous acid gives the corresponding quinones and azo-dyes [21,22]. Aminophenols with positive substituents in the nucleus, for example, aminoresorcinol, are very strongly oxidised [23]. However, it has been shown that in dilute sulphuric acid the diazotisation of unsubstituted *o*- and *p*-aminophenols proceeds without complications [11]. Using this method, Ershov and Nikiforov [12] obtained a number of crystalline *p*-quinone diazides with alkyl substituents in positions 2 and 6.

The presence of electronegative substituents in the nucleus gives rise to a difficulty of another kind: diazotisation does not occur because of the poor solubility of these aminophenols in weakly acid solution. Although monohalo- and mononitroso-substituted aminophenols can be diazotised in the usual way [7,9,24], the introduction of additional negative substituents into the nucleus makes diazotisation impossible under ordinary conditions.

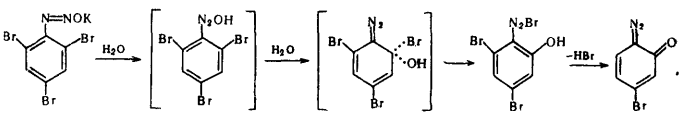
To overcome these difficulties, it has been proposed that oxidisable aminophenols should be diazotised with sodium nitrite in an aqueous solution not containing mineral acids but containing salts of heavy metals, $CuSO_4$,[6,25] $SnCl_2$,[26] etc.[1] Aminophenols with negative substituents are smoothly diazotised by nitrosylsulphuric acid in concentrated sulphuric acid [20,27]. Hodgson and Birtwell [20] showed that substituted aminophenols that cannot be diazotised by other methods because of oxidation, are readily diazotised in concentrated sulphuric acid without the addition of nitrite. In this way a diazonium salt was obtained from 1-amino-4-diazonaphth-2-ol, and the diazotisation of this amine was equally smooth in glacial acetic acid [20].

2. Synthesis from amines containing no hydroxy-groups. If the diazonium salt has a substituent in the *ortho*- or *para*-position to the diazonium group, under certain conditions (dilution of the diazo-solution with water or addition of bases) this substituent is readily exchanged for a hydroxyl group, and the hydroxyaryldiazonium salt formed is converted into the corresponding quinone diazide by the loss of a molecule of acid:



A nitro-group, halogen, sulpho-, or methoxyl group may be replaced by a hydroxyl group [1]. Orton, who was the first to make a systematic study of replacement of halogens by the hydroxyl group, found [28] that the reaction rate greatly depends on the structure of the diazonium compounds (Table 1).

The accumulation of negative substituents on the nucleus facilitates replacement. In the naphthalene series, replacement occurs much more readily than in the benzene series. Since potassium tribromophenyldiazoate is stable under the reaction conditions, Orton suggested that the diazohydroxide, and not the diazoate, takes part in the reaction [28]. According to Orton, an intermediate quinonoid transition state is formed:



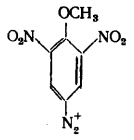
Much later, Mills noted that substitution occurs in the diazonium cation [29].

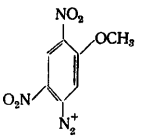
Meldola and coworkers made a detailed study of the replacement of substituents by hydroxyl groups and observed a number of special features in this exchange [30-35]. Meldola and Eyre showed that the nitro-group and halogens are eliminated as the corresponding anions [34]. For example, in the elimination of the nitro-group nitrous acid is formed in solution, and this can diazotise the starting amine [34]. This is the first description of what is called auto-diazotisation. These workers also showed that in concentrated hydrochloric acid the substituent is exchanged not for a hydroxyl group but for a chlorine atom [34]. In sulphuric or nitric acid, the acid anion is never exchanged for a substituent in the diazonium salt. Meldola and coworkers established [33,35] that two conditions are necessary for the replacement of a substituent by the hydroxyl group: the group replaced must be in the *o*- or *p*-position to the diazonium group and it must be activated by a nitro-group

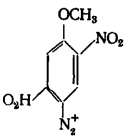
TABLE 1.

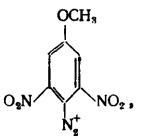
Diazo-compound from	Chlorine eliminated in 24 hours, %	Diazo-compound from	Chlorine eliminated in 24 hours, %
2,4-Dibromo-1-naphthylamine	97	2,3,4,6-Tetrabromoaniline	74
2,4,6-Tribromo-3-nitroaniline	93	2,4,6-Tribromoaniline	64
2,4-Dibromo-5-nitroaniline	80	2,4,6-Trichloroaniline	63
1-Chloro-2-naphthylamine	76	2,6-Dibromoaniline	24
		2,4-Dichloroaniline	traces

in the *ortho*-position to it[35]. Thus, of the compounds I to IV:


(I)


(II)


(III)


(IV)

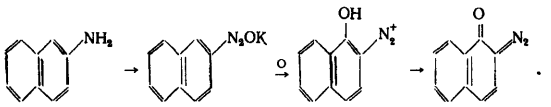
only I and III, which satisfy these conditions, are capable of exchanging a nitro-group or a methoxyl group for a hydroxyl group and undergoing conversion into quinone diazides. If the nitro-group and the alkoxyl group are in positions equally favourable for replacement, the nitro--group is replaced[35]. Continuing this work, Morgan and Evens showed that the nitro-group in the diazonium salt obtained from 2,4-dinitroaniline can also be replaced[36]. If conditions are equally favourable for the replacement of a halogen atom or an alkoxyl group by a hydroxyl group, the alkoxyl group is replaced[37]. If conditions are equally favourable for the replacement of an *o*- and a *p*-nitro-group, the *ortho*-group is preferentially replaced[36,38]. The tendency for the formation of *o*-quinone diazides is so great that in the diazotised 2,6-dichloro-4-nitroaniline molecule a chlorine atom and not a nitro-group is replaced by a hydroxyl group[39].

Hodgson and Birtwell showed[27] that if a substituted naphthylamine is diazotised in sulphuric acid containing the minimal quantity of water, the diazonium sulphates corresponding to the initial amine are formed[27]. However, if the diazo-solution is diluted, or if the diazotisation is carried out in acetic acid, or in a mixture of acetic and sulphuric acids, the corresponding substituent is replaced and diazides are formed[27]. These workers recommend that the diazotisation should be carried out with sodium nitrite in a mixture of sulphuric and acetic acids, or in glacial acetic acid, and that the diazide should be separated by diluting the solution with water or by neutralising it with ammonia or copper carbonate.

The formation of quinone diazides following the replacement of electronegative groups in the diazonium cation by a hydroxyl group is sometimes undesirable, for example, in Sandmeyer's reaction with diazonium salts obtained from 2,4-*x*-trinitro-1-naphthylamine (x = 3, 5, 7, 8)[40]. In order to avoid the formation of quinone diazide as a by-product, it has been proposed that Sandmeyer's reaction should be carried out in non-aqueous media with, for example, acetic acid saturated with hydrogen halide as solvent[41].

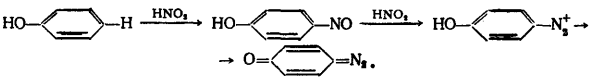
This reaction in which substituents are exchanged is of great importance in the azo-dye industry, since on coupling the hydroxyaryl-diazonium (*ortho*-isomers) salts formed are converted into hydroxyazo-dyes, which are capable of forming lakes with heavy metal cations. The synthesis of hydroxyazo-dyes incorporating a stage in which various groups are replaced by a hydroxyl group is described in many patents. The hydroxyaryldiazonium salts are then formed in solution only as intermediate products and the corresponding diazides are never separated. Detailed information on these patents is given in the monograph of Saunders[1].

The oxidation reaction, in which a hydrogen atom is replaced by a hydroxyl group, is a special case of the introduction of a hydroxyl group into the molecule of a diazonium compound. Bamberger[42-44] proposed this method of synthesising diazides; he oxidised diazoates obtained from 1- or 2-naphthylamines with potassium hexacyanoferrate(II) in alkaline solution:



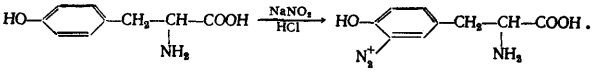
1,2- and 2,1-naphthoquinone diazides were obtained in high yield.

3. Synthesis of quinone diazides from phenols. In this method phenols or nitrosophenols are treated with nitrous acid in aqueous solution. Hydroxyaryldiazonium salts are first formed, and these are then converted to quinone diazides:



Although this method has been little studied, it is very promising, because it permits the preparation of quinone diazides directly from phenols, and it obviates the synthesis of aminophenols, which are not always accessible and are sometimes difficult to diazotise. This applies particularly to phenols with positive substituents.

The method is based on a reaction discovered by Weselsky[45], who treated phenol with nitrogen oxides and obtained hydroxyphenyldiazonium nitrate. The same salt was obtained in a similar way from nitrosophenol[46]. Morel and Sisley carried out the following reaction[47]:



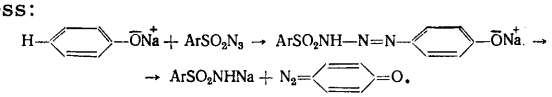
It was shown by azo-coupling that the yield of the diazo--compound is 80%. Phenols containing sulpho-groups[48] or chlorine[49] were also treated with nitrogen oxides, and the corresponding diazophenols were found in the reaction mixture. Nesmeyanov and Ioffe[50] showed that the presence of substituents of the first kind in the nitrosophenol nucleus promotes the formation of a quinone oxime structure and thereby prevents diazotisation. Nitrosonaphthols, which exist as naphthoquinone oximes, do not react with nitrogen oxides. From the results obtained it was concluded that nitroso-compounds react with nitrogen oxides in the benzenoid and not in the quinonoid form.

Nemodruk showed that when nitrous acid acts on salicylic acid carbon dioxide is liberated and diazophenol is formed in the solution in good yield[51]. If cyclic metal salts of salicylic acid are introduced into the reaction, the diazo-group enters the *para*-position to the hydroxyl group, and salts of 5-diazosalicylic acid are formed in nearly quantitative yield[52].

In recent years Tedder and Theaker developed a method for the preparation of hydroxyphenyldiazonium salts from phenols[53]. They showed that the greatest yield of diazo--compound is obtained when the reaction is carried out in aqueous solution with a molar ratio of starting materials (phenol:HCl:$NaNO_2$) of 1 : 4 : 14.5. The mixture is maintained at 0° for 20–40 h, and the yield of the diazo-compound is determined by azo-coupling. The yield largely depends on the nature of the phenol: the greater the acidity of the starting phenol, the lower the yield of the diazo-compound. It is assumed that nitrosophenols are formed as intermediates. Naphthols do not form diazo--compounds, as they are converted into quinoneoximes. If

the position *para* to the hydroxyl group is free in the phenol, the corresponding *p*-hydroxyphenyldiazonium compound is formed.

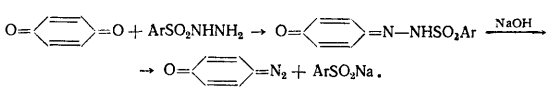
Tedder and Webster treated various phenoxides with *p*-toluenesulphonyl azide and obtained mixtures of azo--dyes [54]. They proposed the following scheme for the process:



The quinone azide couples with an excess of phenoxide to form the dye. If the diazide obtained couples slowly, it may be separated. This reaction provides a convenient method for the introduction of a diazo-group into phenols containing negative substituents which do not react with nitrogen oxides in acid solution.

The preparation of quinone diazides by treatment of compounds with nitrogen oxides has been used in industry. The preparation of 1,4-didiazo-anthra-9,10-quinone by treating anthraquinone with nitrosylsulphuric acid has been described in a patent [55].

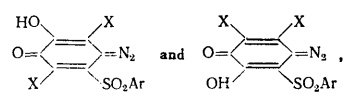
4. Synthesis of quinone diazides from quinones. Börche and Frank showed that treatment of quinones with aromatic sulphonyl hydrazides gives arylsulphonylazophenols $HO.C_6H_4N_2SO_2Ar$, which are also obtained from quinone azides and arylsulphonic acids [56-59]. When treated with mineral acids or alkalis, the arylsulphonylazophenols are decomposed into arylsulphinic acids and hydroxyphenyldiazonium salts (or the corresponding diazoates, according to Börche and Frank [56]). Later this reaction was used for the synthesis of aliphatic diazo--cations [59], and then Cava and coworkers [60] used it for the synthesis of cyclic diazo-ketones, including some quinone diazides. The reactions proceed according to the following scheme:



Using the method they had developed, Cava and coworkers [60] were the first to obtain the diazides corresponding to isatin and 9,10-phenanthraquinone; a previous attempt to obtain this compound by diazotisation of aminohydroxyphenanthrene was not successful [61].

The method of synthesising diazides from quinones became particularly valuable after Horner and Dürckheimer had proposed [62] a simple procedure for the preparation of *o*-quinones by the oxidation of aromatic diazo--compounds with chloroaniline or bromoaniline.

Reid and Dietrich made a detailed study of the synthesis of quinones through *p*-toluenesulphonyl hydrazones. They showed [63] that the hydrazones of aliphatic ketones decompose only in alkaline solutions, but quinone hydrazones decompose in both acid and alkaline solutions. The colour of the hydrazone is a rough indication of its stability: the more intense the colour, the lower the stability. It was also noted that if the oxidation potential of the quinone is sufficiently high, side-reactions occur in the preparation of the diazides. For example, compounds of the following type were obtained from halo-anils:



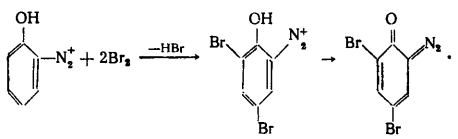
where X is a halogen atoms.

Reid and Dietrich [64] showed that the compounds obtained do not result from the secondary reaction of quinone diazides with arylsulphinic acid, but replacement of chlorine by an arylsulphinic acid residue occurs with the formation of a diazide from quinone *p*-toluenesulphonylhydrazones [64].

Horner and Dürckheimer studied [65] the reaction of various *o*-quinones of the benzene series with *p*-toluenesulphonyl hydrazide in order to determine which of the two non-equivalent quinone carbonyl groups takes part in the reaction. The results showed that in 4- or 5-substituted *o*-quinones the C=O group not conjugated with the substituent reacts with the hydrazide, but in 3- and 3,5-substituted quinones the reactive group is the carbonyl remote from the substituent in position 3. In these instances steric factors predominate over electronic factors.

The synthesis of quinone diazides has permitted the preparation of a large number of diazides with electropositive substituents [65].

5. Preparation of substituted quinone diazides. Only a few examples are known of the preparation of diazides by the introduction of new substituents into a previously synthesised diazide. In 1881 Bohmer [66] showed that when treated with bromine water, *o*- and *p*-benzoquinone diazides give 2-diazo-4,6-dibromo-*o*-benzoquinone and 4-diazo-2,6-dibromo-*p*-benzoquinone. The mechanism of these reactions has not been studied, but the author assumes that a diazonium cation takes part:



The reaction with hydroxyphenyldiazonium nitrate and hydrobromic acid proceeds in the same way; a nitrate ion formed in the first stage of the process oxidises the acid to bromine, which then brominates the diazide.

The halogen atom may replace other groups besides the hydrogen atom. Kollrepp [67] established that when bromine water acts on 3-chloro-5-diazo-2-oxocyclohexa-3,4-dienesulphonic acid, sulphurous acid is eliminated and 6-bromo-2-chlorobenzoquinone diazide [6-bromo-2--chloro-4-diazocyclohexa-2,5-dien-1-one] is formed [67].

It has been reported [68] that 6-bromo-4-sulphonaphtho--1,2-quinone 1-diazide is formed from 4-sulphonaphtho--1,2-quinone 1-diazide by the action of bromine in chlorosulphonic acid or sulphuric acid. However, in the naphthalene series this reaction sometimes leads to the oxidation of the diazide with elimination of diazoate. Thus, the action of bromine on 4-bromonaptho-1,2--quinone 2-diazide gives dibromonaphtho-1,2-quinone [69]; sometimes brominated naphthols are formed [70].

According to patent information [71-73], 1-diazo-2-naphthol--4-sulphonic acid can be nitrated and sulphonated. According to Ruggli and coworkers [68-72], the nitro-group (and probably also the sulpho-group) enters position 6 in the naphthalene ring.

All the reactions mentioned above are carried out in strongly acid solution, and there is reason to suppose that it is the diazonium, and not the diazide, form of the compounds that takes part in the replacement reaction.

Another example of substitution in the quinone-diazide ring is the conversion of diazides of the naphthalene series containing sulpho-groups; when these diazides are treated with sulphuryl chloride or chlorosulphonic acid, sulphonyl chlorides are formed, which give sulphonamides on treatment with amines [7,8,74-82].

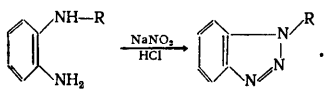
In recent years various examples of this reaction have been published in patents [74-82]. These sulphonamide derivatives of quinone diazides are of interest because they are widely used in the production of photosensitive materials.

Reid and Dietrich have succeeded in acylating a hydroxyl group in quinone diazides [64].

B. Preparation of *p*-Iminoquinone Diazides

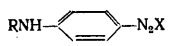
Only *para*-substituted diazonium salts form iminoquinone diazides (imidoquinone diazides). When treated with even weak alkaline agents (sodium acetate) *meta*-substituted diazonium salts lose the diazo-nitrogen and are converted into phenol derivatives, which immediately condense with another diazonium molecule [83].

In contrast to *o*-quinone diazides, *o*-iminoquinone diazides cannot be prepared, because diazotisation of *o*-phenylenediamines gives, instead of the diazonium salt, a precipitate of a colourless internal condensation product (benzotriazole derivative) [83]:

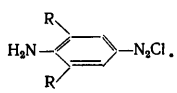


p-Iminoquinone diazides are much less stable compounds than quinone diazides, and there are therefore much fewer methods of preparing them. *p*-Iminoquinone diazides are mainly prepared by the action of alkaline agents on solutions of amino-substituted diazonium salts.

p-Iminoquinone diazides are formed only from *N*-substituted *p*-aminophenyldiazonium salts:



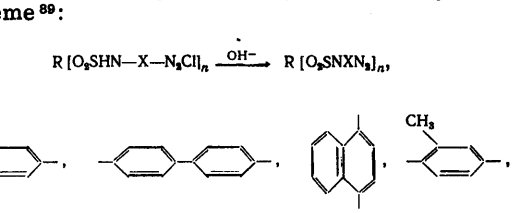
or from nuclear-substituted diazonium salts:



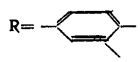
NaOH, NH_4OH, Na_2CO_3, $NaHCO_3$, or CH_3COONa may be used as the alkaline agent, according to the nature of the substituent R; sometimes the *p*-iminoquinone diazides may be separated by simply diluting the diazo-solution with water.

p-Iminoquinone diazide was first obtained by Ykuta [84], who prepared it in an impure state by treating the corresponding diazonium sulphate with ammonium hydroxide. Hantzsch investigated and described the compound [85]. Morgan and coworkers then found that *p*-iminoquinone diazides are formed by the action of a saturated solution of sodium acetate (or other alkaline agents) on diazotised *N*-substituted *p*-phenylenediamines, in which the substituent is an alkylsulphonyl [83], arylsulphonyl [86,87], or a mixed arylalkylsulphonyl group [88].

The reaction may be represented by the following general scheme [89]:

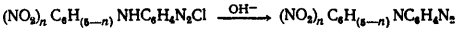


and *n* is the valency of the radical linked to the sulphonyl group; when $n = 1$, R = CH_3, C_6H_5, p-$CH_3C_6H_4$; when $n = 2$, R = $-CH_2-$, 1,3-phenylene; when $n = 3$,



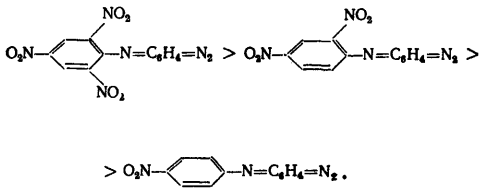
p-Iminoquinone diazides with substituents in the *ortho*- or *meta*-position to the diazo-group are formed without the addition of alkaline agents by simply diluting the diazo-solution with water [90].

p-Iminoquinone diazides are also formed fairly readily from nitro-derivatives of diazotised *p*-aminodiphenylamine [91]:



where $n = 0, 1, 2, 3$.

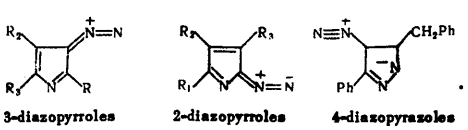
Morgan notes that the reaction rate and the stability of the *p*-iminoquinone diazide formed increase with increasing acidity of the substituent on the amino-nitrogen [91]:



Thus, trinitro-derivatives are obtained by adding sodium acetate to a hydrochloric acid solution, but the separation of a dinitro-derivative requires the addition of a more alkaline agent, such as potassium hydrogen carbonate, to the diazo-solution, and mononitro-derivatives are obtained from the diazo-solution only by adding ammonium hydroxide.

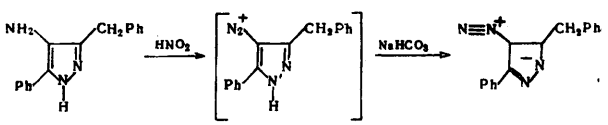
p-Iminoquinone diazides are also obtained from carbazole-3-diazonium chloride [92].

The following heterocyclic diazo-compounds may also be regarded as diazo-imines [93-95]:

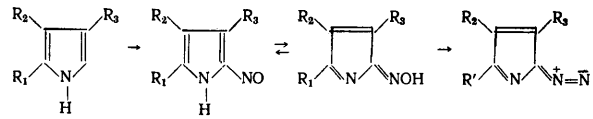


3-diazopyrroles 2-diazopyrroles 4-diazopyrazoles

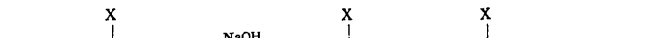
These compounds may be prepared by the usual diazotisation of the corresponding amine and neutralisation of the solution obtained [93,96]:



Tedder's method may also be used: in this the diazo-group is introduced into the ring with the aid of nitrous acid[94,95]:

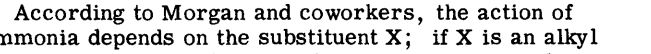


For a long time attempts to prepare *p*-iminoquinone diazides from *N*-formyl-, *N*-acetyl-, and *N*-benzoyl--amino-substituted diazonium salts were not successful. Morgan and coworkers showed that in these instances the use of ordinary alkaline agents leads to some unexpected results[97]. When the diazo-solutions of *N*-benzoyl-1,4--phenylenediamine and *N*-benzoyl-1,4-naphthylenediamine are treated with sodium acetate no precipitate is formed, but treatment with cold concentrated solutions of potassium hydrogen carbonate and sodium nitrite gives yellow crystalline precipitates, which Morgan regarded as aryldiazonium hydrogen carbonate and nitrite[97]. The action of alkali on *p*-*N*-benzoylaminophenyldiazonium chloride gives a different result: Morgan considers the main reaction product to be a diazo-oxide[98]:



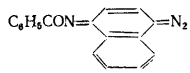
where X = H, CH_3, C_2H_5.

According to Morgan and coworkers, the action of ammonia depends on the substituent X; if X is an alkyl group, the main product is a diazoamino-compound:



if X = H, a mixture of diazo-oxide and diazoamino-compound is obtained. It has been shown that the action of a cold concentrated solution of potassium hydrogen carbonate, a cold solution of ammonium hydroxide, or a 0.1 *N* solution of sodium hydroxide on an aqueous solution of *p*-*N*-benzoylaminophenyldiazonium chloride at 0–4° leads to the formation of a yellow precipitate consisting of a mixture of diazonium chloride and the corresponding *p*-iminoquinone diazide, but the pure *p*-iminoquinone diazide *p*-$C_6H_5CONC_6H_4N_2$ could not be obtained in this way[99].

The action of alkali on the diazo-solution of *p*-*N*-benzo-amino-1,4-naphthylenediamine leads to the separation of a yellowish brown product, which Morgan regarded as the nitrosoamine $C_6H_5CONHC_{10}H_6NHNO$.[100] Later Dimrot and coworkers[101] showed that the *p*-iminoquinone diazide



is in fact formed, and not the nitrosoamine.

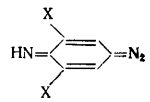
The preparation of *p*-iminoquinone diazides from *p*-*N*-acetyl and *p*-*N*-formyl-aminophenyldiazonium chlorides is still more difficult. Morgan and coworkers tried the effect of various alkaline agents ($KHCO_3$, $NaNO_2$, CH_3COONa, NH_4OH) on these diazonium chlorides[97]. No precipitate was obtained with potassium hydrogen carbonate or sodium nitrite; with sodium acetate the diazoamino--compound $R'CONHC_6H_4N_2NHC_6H_4NHCOR'$ was precipitated; and with ammonium hydroxide a compound was formed the analysis of which indicated that it was most likely a nitrosoamine.

Thus, the *p*-iminoquinone diazides $RNC_6H_4N_2$ (where R = HC(=O)–, CH_3C(=O)–, or C_6H_5C(=O)–) cannot be prepared by the usual method, that is, by the action of various alkaline agents on diazonium chlorides.

Morgan and coworkers[89,102] proposed another method of preparing *p*-iminoquinone diazides, consisting in the direct diazotisation of the amine $R'CONHC_6H_4NH_2$, where R' = H, CH_3, C_6H_5, with dinitrogen trioxide in a solution of dry acetone. The *p*-iminoquinone diazides obtained in this way are described as unstable compounds that cannot be purified, because they become more contaminated on recrystallisation; they are pale yellow, while all quinone diazides and *p*-iminoquinone diazides have a bright yellow, orange, or red colour.

Later it was shown[99] that the action of dinitrogen trioxide on *p*-*N*-acetyl- and *p*-*N*-benzoyl-*p*-phenylenediamines leads to the formation of the corresponding aryldiazonium nitrate and not to iminoquinone diazides.

The unsubstituted *p*-iminoquinone diazide $HNC_6H_4N_2$ could not be obtained at all. The ring-substituted *p*-iminoquinone diazides



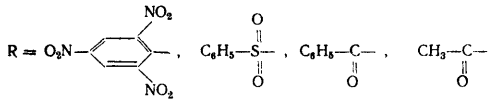
were obtained by the diazotisation of the corresponding amines with dinitrogen trioxide[102]. However, this work requires confirmation.

Thus, iminoquinone diazides (imidoquinone diazides) are only formed from *N*-substituted *p*-aminophenyldiazonium salts $RNHC_6H_4N_2^+X^-$; the reaction proceeds more readily as the electronegativity of the substituent R increases, and the ease of formation increases with the molecular weight of the *p*-iminoquinone diazide. The stability of the *p*-iminoquinone diazides increases in the same order. This explains why the *p*-iminoquinone diazides $RCON{:}C_6H_4{:}N_2$, where R = CH_3, C_6H_5, could not be obtained for a long time and why *p*-iminoquinone diazide itself

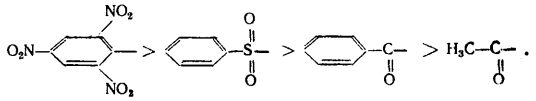


has not been prepared.

Ultraviolet and infrared spectroscopy have been used successfully to investigate the conversion of the diazonium chlorides $RNHC_6H_4N_2Cl$, where



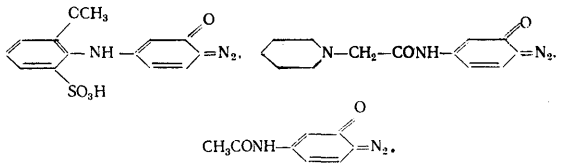
into the corresponding *p*-iminoquinone diazides in buffered solutions[99]. The two latter *p*-iminoquinone diazides decompose very rapidly in light at ordinary temperature. It has been shown that this conversion is an acid–diazo-cation dissociation. The strength of the acid $RNHC_6H_4N_2^+$ decreases in the following order according to the substituent R:



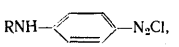
Thus, *p*-*N*-picrylaminophenyldiazonium chloride is instantly converted into the *p*-iminoquinone diazide even by dissolution in water, but an appreciable quantity of *p*-iminoquinone diazide is formed from *p*-*N*-acetylamino-phenyldiazonium chloride only in alkaline solutions of pH 9 or higher.

Para- and *ortho*-hydroxyphenyldiazonium chlorides are stronger acids, and they therefore form quinone diazides

more readily; this is due to the greater acidity of the hydroxyl group. Thus, diazonium salts with both OH- and RNH- groups in the ring form quinone azides [103,104], but not *p*-iminoquinone diazides, for example:



The special properties of hydroxy- or amino-substituted diazonium salts whereby they form quinone diazides and *p*-iminoquinone diazides when treated with alkaline agents is due, on the one hand, to the presence in the molecule of the hydroxy- or amino-group, which can eliminate a proton under certain conditions, and, on the other hand, to the presence of an extremely strong electronegative diazonium group, which confers acidity on the hydroxy- or amino-group in the *ortho*- or *para*-position. In the diazonium chloride



an electron-acceptor substituent R is also needed to ensure the elimination of a proton from the amino-group.

III. PROPERTIES OF QUINONE DIAZIDES AND *p*-IMINOQUINONE DIAZIDES

A. Physical Properties

Quinone diazides and *p*-iminoquinone diazides are coloured crystalline compounds, with colours varying from yellow to red.

Their behaviour with solvents greatly depends on their structure. Thus, *o*-quinone diazides are always more soluble than the *para*-isomers. Unsubstituted *o*- and *p*-benzoquinone diazides, their methyl and methoxy--derivatives, *p*-*N*-acet- and *p*-*N*-benziminoquinone diazides are very soluble. Arylsulphonyliminoquinone diazides are moderately or even poorly soluble in organic solvents and water. Some *p*-iminoquinone diazides are readily soluble in *p*-toluidine [86], but depression of the freezing point indicates that they form addition products with the solvent. The presence of a large number of condensed benzene rings in quinone diazides and *p*-iminoquinone diazides reduces the solubility of these compounds in water and increases the solubility in organic solvents. Thus, 1,2- and 2,1-naphthoquinone diazides are easily crystallised from aqueous solution [7,13], but are readily soluble in organic solvents. The introduction of negative substituents into quinone diazides reduces their solubility in both polar and non-polar solvents.

Some diazides contain water of crystallisation [10,24,105]. Hantzsch and Davidson studied a number of simple quinone diazides by the cryoscopic method and showed that they are not associated in solution [10].

All quinone diazides and *p*-iminoquinone diazides are sensitive to heat, and nitro-derivatives explode when heated in the dry state. The decomposition temperature largely depends on the rate of heating [106]. The thermal stability increases with the number of negative substituents in the nucleus.

Photosensitivity is a specific property of quinone diazides and *p*-iminoquinone diazides, the latter being the more sensitive to light. The use of these compounds in the printing industry is based on this property. *o*-Quinone diazides are more photosensitive than the *para*-isomers, and naphthalene derivatives are more sensitive than benzene derivatives.

A large amount of information on the use of diazides for the preparation of photosensitive compositions has been published in the patent literature [74-82] and has been reviewed by Saunders [1] and Dinaburg [107].

De Jonge and coworkers [108] determined quantum yields for the photolytic decomposition of quinone diazides irradiated in aqueous solution with light of wavelength 3500-4000 Å. They found that the quantum yield varies between 0.20 and 0.40, and they noted that, although the quantum yields are similar for all the compounds, variations in the photosensitivity of quinone diazides are due to differences in light-absorbing capacity. The more highly absorbing quinone diazides are more photosensitive. This also accounts for the higher photosensitivity of quinone diazides compared with diazonium salts; absorption curves of quinone diazides are displaced towards the long-wave side compared with the curves of diazonium salts.

The higher photosensitivity of *o*-quinone diazides compared with *para*-isomers may be explained in the same way.

Different physicochemical characteristics (spectra, dipole moments) are closely related to the structures of these compounds; for this reason, the relevant published information is considered in the section dealing with the structure of quinone diazides and iminoquinone diazides.

B. Chemical Properties

1. Diazide-diazonium acid-base equilibrium. It is characteristic of quinone diazides and *p*-iminoquinone diazides that they are converted into diazonium salts by the action of acids. Using ultraviolet spectroscopy, Kazitsyna and coworkers [99,109,110] made a detailed study of this transition as applied to unsubstituted, bromo-substituted and nitro-substituted *ortho*- and *para*--benzoquinone diazides, and the *p*-iminoquinone diazides $RNC_6H_4N_2$, where R = C_6H_5CO, CH_3CO, $C_6H_5SO_2$, or $(NO_2)_3C_6H_2$. The absorption curves obtained for *o*-benzoquinone diazides and *p*-benzenesulphonyliminoquinone diazides (Figs. 1 and 2) in various acidity regions have isobestic points, which indicates that only two forms (diazonium and diazide) occur in solution [110,111]. A similar picture is observed with substituted quinone diazides [110,112]. Therefore, the diazonium-cation-quinone diazide (*p*-iminoquinone diazide) change is an acid-base equilibrium.

Thus, quinone diazides and *p*-iminoquinone diazides are bases. These bases may differ greatly in strength. The *p*-iminoquinone diazides *p*-$CH_3CONC_6H_4N_2$ and *p*-C_6H_5·.$CONC_6H_4N_2$ are fairly strong bases; they are protonated, that is, converted into the corresponding diazonium cations, even in neutral or weakly alkaline solution [99]. Unsubstituted *para*- and *ortho*-quinone diazides and the *p*-iminoquinone diazides *p*-$C_6H_5SO_2NC_6H_4N_2$ are weak bases, and are protonated in acid solution, but within the limits of the pH acidity scale [109-111]. Bromo- and nitro-derivatives of quinone diazides, as weak bases, are only protonated in

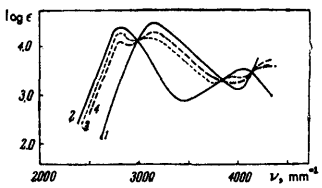


Fig. 1. Electronic absorption spectra of *p*-hydroxyphenyldiazonium chloride: 1) in 0.1 *N* HCl; 2) in water; 3) in 4×10^{-4} *N* HCl; 5) in 5×10^{-4} *N* HCl.

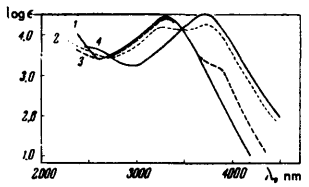
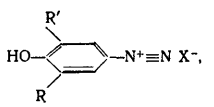


Fig. 2. Electronic absorption spectra of *p*-sulphonylaminophenyldiazonium chloride in buffer solutions. pH: 1) 1.1; 2) 3.5; 3) 2; 4) 4.8.

concentrated acids [66,110]. Ershov and Nikiforov made a spectrophotometric study of the conversion of *p*-quinone diazides with alkyl substituents in the *ortho*-position to the oxygen atom into the corresponding hydroxyphenyldiazonium salts [112]:



where R = R′ = H; R = R′ = CH_3; R = R′ = $CH(CH_3)_2$; R = = R′ = $C(CH_3)_3$; R = CH_3 and R′ = $C(CH_3)_3$, and found values for the logarithms of the equilibrium constants for this reaction. Their results show that quinone diazides with more branched alkyl substituents are weaker bases. The stability of the quinone diazide or *p*-iminoquinone diazide is inversely proportional to its basic strength.

Since diazides exist in aqueous solutions of different acidity in equilibrium with the diazonium form, it is sometimes difficult to decide whether the diazide or the diazonium form take part in the reaction. Authors of various papers on quinone diazides do not generally consider this aspect of the problem; for this reason, where possible, the form taking part in the reaction will be noted in the discussion on chemical properties.

2. Reactions in which nitrogen is retained. Both atoms are retained in many reactions of diazides and diazonium salts. Thus, with cyanides or sulphites quinone diazides form hydroxyaryl-diazocyanides or -diazosulphonates [10,43,66]. Like sulphurous acid, arylsulphonic acids react with quinone diazides to form sulphoazophenols [57,58]. As mentioned above, the same compounds are obtained by the action of arylsulphonyl hydrazides on quinones [56].

It has been reported that quinone diazides and their corresponding diazonium salts do not form perhalogen compounds [10,66].

Concentrated sulphuric acid sulphonates diazides of the naphthalene series [72], nitric acid nitrates them [72], and bromine brominates them [68]; in these reactions the substituent enters the 6-position. Diazides of the benzene series are brominated by bromine water [66].

In acid solutions of metal chlorides, quinone diazides form double salts, metal hydroxyaryldiazonium halides [10,66,113].

Hantzsch and Davidson [10], showed that, in the absence of acid, *p*-hydroxyphenyldiazonium salts form compounds of the type $HOC_6H_4N_2X.OC_6H_4N_2.MN_n$ with $CdCl_2$, CdI_2, and $HgCl_2$, but the action of cadmium iodide on quinone diazide leads to the formation of the compound $C_6H_4N_2O.CdI_2$. They put forward no hypotheses as to the structure of these compounds.

Kazitsyna and coworkers [113] made a detailed study of the reaction of *o*- and *p*-benzoquinone diazides with $ZnCl_2$, $CoCl_2$, $HgCl_2$, and $NaBF_4$. In aqueous and methanol solutions, finely crystalline, coloured compounds are formed, for which the following formula was proposed on the basis of elemental and infrared analysis:

$$[(HOC_6H_4N_2)_m\ OC_6H_4N_2]^{+m}\ [MCl_{n+m}]^{-m},$$
(II)

$m = 1$ with BF_4^-; $m = 2$ with $ZnCl_4^{2-}$, $CoCl_4^{2-}$.

The infrared spectra (ν_{CN_2} frequencies) indicates that there is some interaction between the quinone diazide molecule and the hydroxyphenyldiazonium cation.

A study of the reaction conditions showed that a weakly acid medium produced by partial hydrolysis of the salt is necessary for the formation of salts of this kind; the presence of this medium leads to quinone diazide–diazonium-cation equilibrium. Because of this property of quinone diazides, compounds of type (I) are obtained by the action of metal halides on both hydroxyphenyldiazonium salts and quinone diazides. When the acidity of the medium is increased, quinone diazides react with the metal halides to form ordinary hydroxyphenyldiazonium metal-halide salts.

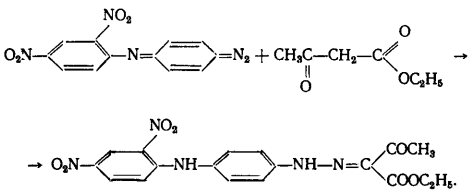
Mercury(II) chloride reacts with *o*- and *p*-benzoquinone diazides to form simple addition products of the composition $OC_6H_4N_2.HgCl_2$; Hantzsch found that mercury(II) iodide reacts in the same way.

The azo-coupling reaction of quinone diazides is of great importance, being widely used in industry for the synthesis of hydroxyazo-dyes, which form stable lakes with metal cations. Azo-coupling is also often used for the quantitative determination or identification of quinone diazides [51-54]. Diazides may be coupled in weakly acid or alkaline solution. The reaction conditions and characteristics determined with different compounds indicate that the compounds are capable of coupling in the diazide as well as in the diazonium form. The azo-coupling of diazides in acid solution is described in many patents [1]. In industry, hydroxyaryldiazonium salts are not separated in the dry state, but azo-coupling is carried out directly in solutions obtained after diazotisation, an alkaline solution of the azo-component being added.

Although no quantitative study has been made of the relation between the rate of azo-coupling and the nature of the substituent in quinone diazides, a number of rules governing the reaction may be noted. When the molecule contains a large number of condensed benzene rings, the tendency to form diazides increases, and these compounds couple less readily than simpler compounds, which are

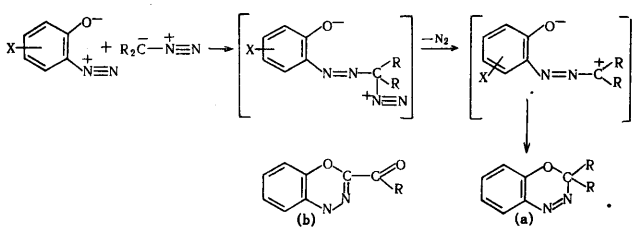
capable of being more easily converted into hydroxyaryldiazonium salts. *o*-Quinone diazides, which are formed more easily than *para*-compounds, also couple less readily than the *para*-isomers [36,38,54]. The introduction of negative substituents into the diazide nucleus leads to an increase in the positive charge on the diazo-group and significantly increases the tendency of the diazides to undergo azo-coupling [114]. Thus, Bamberger showed that unsubstituted 1,2- and 2,1-naphthoquinone diazides in alkaline solutions couple very slowly and only with active components [43,44]. Introduction of bromine or the cyano-group into the nucleus leads to more active coupling [20,68].

p-Iminoquinone diazides are also capable of undergoing the azo-coupling reaction. These compounds couple best with phenols, 2-naphthol, and resorcinol in dry pyridine [86]. Coupling occurs only with the most reactive amines: aniline and its homologues do not couple, but the reaction is quantitative with naphthylamines and toluene-2,4-diamine [86,115]. As Simonov showed [116], *p*-iminoquinone diazides couple with aliphatic and heterocyclic enols (ethyl acetoacetate, phenylmethylpyrazolone, etc.). The reaction proceeds readily at 20–30° in acetone solution:



The products are identical with those formed by the reaction of diazonium salts with enols.

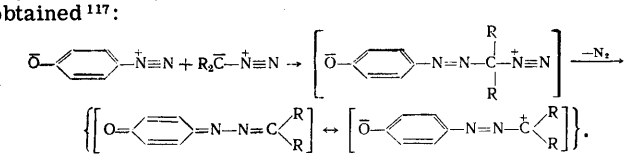
Huisgen and coworkers discovered the azo-coupling reaction of diazonium salts with aliphatic diazo-compounds [117]. These workers also coupled aliphatic diazo--compounds with quinone diazides [114]:



They noted that diazides have a much lower tendency to couple than ordinary aromatic diazonium salts; the introduction of negative substituents into diazides facilitates this reaction. The final products of coupling are derivatives of benzohydrooxadiazines (a). 1,2- and 2,1--naphthoquinone diazides do not undergo the coupling reaction.

If *o*-quinone diazides are coupled with diazo-carbonyl compounds, cyclic azoketones (b) are obtained as final products.

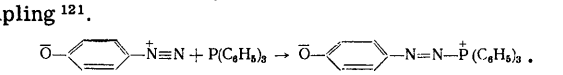
p-Quinone diazides may also react with aliphatic diazo--hydrocarbons, but substituted quinone azines are then obtained [117]:



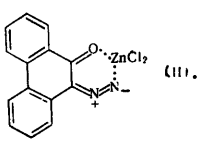
p-Quinone diazides do not react with diazo-carbonyl compounds.

Karlinskaya and Khromov-Borisov found that diazides of the pyrimidine series with a methyl group adjacent to the diazo-group are capable of intramolecular azo-coupling with the formation of indazole derivatives [118]. This reaction, of course, also occurs with diazonium compounds of the benzene series, while *o*-toluenediazonium salts form benzindazole derivatives [119].

Quinone diazides may also react with other nucleophilic compounds. Staudinger and Lüscher showed that quinone diazides, like aliphatic diazo-ketones, couple with triphenylphosphine to form quinonetriphenylphosphazines [120]. Reid and Appel made a detailed study of this reaction, and they noted that it is subject to the same rules as azo--coupling [121].



The *para*-compounds give a higher yield of phosphazines than the *ortho*-compounds, and the reaction is promoted by substituents that increase the positive charge of the diazo--group. Unsubstituted quinone diazides with condensed benzene rings undergo this reaction with difficulty. These compounds react more readily if a solution of quinone diazide and a Lewis acid are used. The authors consider that an intermediate complex of type (II) is formed, in which the Lewis acid increases the positive charge on the diazo-group:

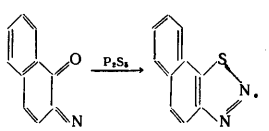


(III).

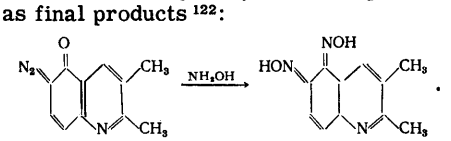
An increase in the positive charge on the diazo-group increases the tendency of quinone diazides to react with triphenylphosphine and it also increases the frequency of the stretching vibrations of the CN_2 group in the infrared absorption spectra of the diazides. It is therefore thought that the value of ν_{CN_2} may give an indication of the reactivity of a quinone diazide.

The reactions mentioned above occur with both diazides and diazonium salts, but some reactions have been described that are characteristic of diazides only.

Bamberger showed that when naphthoquinone diazide is treated with phosphorus pentasulphide, oxygen is replaced by sulphur and thiadiazole derivatives are formed by ring closure [43]:



It has been found that quinone diazides of the heterocyclic series react with hydroxylamine to give quinone dioximes as final products [122]:

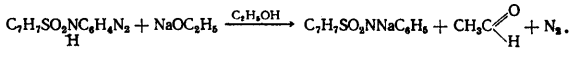


This reaction has not been further studied, but it may be supposed that it is applicable to many diazides, and might probably be a convenient method for synthesising otherwise inaccessible quinone dioximes.

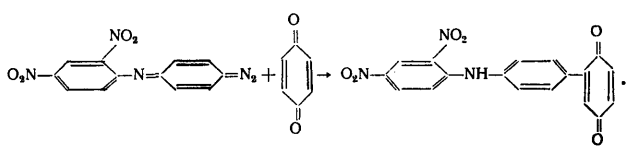
3. Reactions in which nitrogen is eliminated. In acid solutions diazides undergo all the reactions that are observed with solutions of diazonium salts

in general. Thus, in acid solutions of copper(I) chloride quinone diazides undergo the Sandmeyer reaction with the liberation of nitrogen and the formation of the corresponding chlorophenol derivative [24,34,123]. When quinone diazides are treated with potassium iodide or hydriodic acid, nitrogen is also liberated and iodophenols are formed [35,123]. When diazides are boiled in acid aqueous solution, the diazo-group is replaced by a hydroxyl group, but strong oxidation occurs and azo-dyes are also formed [43,66,124]. Reduction of the diazides with tin and hydrochloric acid gives the corresponding aminophenols with the liberation of ammonia [66]. Milder reducing agents, such as tin(I) chloride in hydrochloric or acetic acid, lead to the formation of hydroxyarylhydrazines [66,114,125]. When quinone diazides are boiled in alcoholic solution, the diazo-group is replaced by hydrogen, and the corresponding phenols are formed [30,31,126]; sometimes the reaction is carried out in the presence of alkalis or with the addition of metal powders [20,70]. This reaction was first studied in detail by Cameron [126], who established that replacement of the diazo-group by an alkoxyl group competes with replacement by hydrogen, and with alcohols higher than methanol the second reaction begins to predominate. Negative substituents in the nucleus facilitate the replacement of the diazo-group by hydrogen, and replacement occurs more readily in *ortho*- than in *para*-isomers. Hodgson and Bartwell [127] noted that negative substituents also accelerate the azo-coupling side-reaction, and the yield of reduction product therefore decreases in the order: $NO_2 < Cl < Br < I < SO_3H$. For the reduction, these workers used tin(I) chloride, or powders of aluminium, zinc, iron, or Devarda's alloy [70,126]. Horner and Dürckheimer successfully used hypophosphorous acid as a reducing agent in the presence of hydrochloric acid [65]. Replacement of the diazo-group by hydrogen is a reaction characteristic not only of quinone diazides, but also of various diazonium salts. Kornblum has published a review of the literature on this subject [128].

p-Iminoquinone diazides are reduced by sodium ethoxide, the diazo-group being replaced by hydrogen [86]:



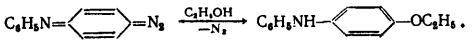
When *p*-iminoquinone diazides are heated with alkalis, resins are formed [83]. Like diazonium salts, *p*-iminoquinone diazides arylate quinones [116]:



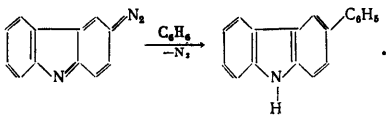
4. Photolytic and thermal decomposition of quinone diazides and *p*-iminoquinone diazides. Since many quinone diazides and *p*-iminoquinone diazides are used as photosensitive and explosive materials, the photochemical and thermal decomposition of these compounds has been intensively studied in recent years. It has long been known that hydroxydiazonium and *p*-aminophenyldiazonium compounds are more photosensitive than other diazonium salts [129]. However, the mechanism of the action of light on diazides has only been elucidated quite recently. Süs [130] and de Jonge and coworkers [131] began to study this question at the same time.

The study of the photochemical and thermal decomposition of these compounds led to the discovery of new methods of synthesising many compounds of different types that were difficult to obtain.

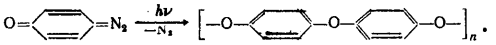
When *p*-quinone diazides and *p*-iminoquinone diazides are irradiated in alcoholic solution, monoalkyl ethers of aromatic *p*-dihydroxy-derivatives and *p*-aminophenols are obtained [8]:



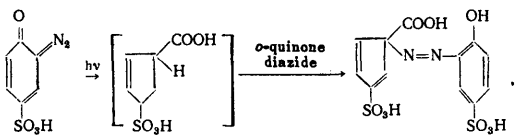
The photochemical decomposition of *p*-quinone diazides and *p*-iminoquinone diazides dissolved in aromatic hydrocarbons is used preparatively as a method of arylation and for the preparation of hydroxy- and amino-derivatives of these hydrocarbons, and also for the preparation of various heterocyclic compounds [8]:



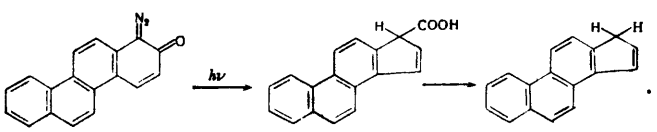
The photodecomposition or thermal decomposition of *p*-iminoquinone diazides and *p*-quinone diazides in the absence of water and polar organic solvents leads to the formation of thermostable polymers [8,132]:



Under the action of ultraviolet light the decomposition of *o*-quinone diazides proceeds quite differently. Süs who made a detailed study of this reaction, established that photolysis of *o*-quinone diazides is accompanied by ring contraction. Süs showed [130] that irradiation results in the formation of either a derivative of cyclopentadienecarboxylic acid, or the product of azo-coupling of this acid with the starting quinone diazide, the product depending on the structure of the latter:



Later, Süs and other workers studied the photolysis of *o*-quinone diazides of the naphthalene series [7,134], *o*-quinone diazides with condensed aromatic rings [7,10], and *o*-quinone diazides of the heterocyclic series [7,133,134]. In reviewing his papers on this subject, Süs [135,136] put forward some general rules governing the photolysis of *o*-quinone diazides and showed that this reaction can be used for the synthesis of new cyclic systems. For example, irradiation of chrysene-1,2-quinone 1-diazide enabled a compound with a steroid skeleton to be synthesised [7]:

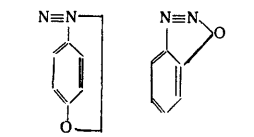


While the manuscript of this review was being prepared for the press, Dinaburg's monograph on photosensitive diazo-compounds and their applications appeared [107]; this gives a review of the literature on the photolytic decomposition of *p*- and *o*-quinone diazides and *o*-iminoquinone diazides. For this reason, we shall not consider these interesting reactions in detail here.

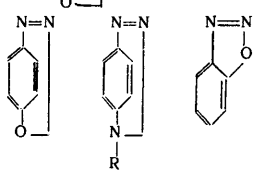
IV. STRUCTURE OF QUINONE DIAZIDES AND *p*-IMINOQUINONE DIAZIDES

The diazides are one of the classes of organic compounds the structure of which cannot be definitely established by chemical methods alone. The main conclusions as to the structure of these compounds have been drawn from the results of physicochemical investigations. We shall briefly consider this problem below and we shall analyse its present status in more detail. We shall first consider the structure of simple diazides, and then the structure of substituted diazides. We shall primarily consider material on the structure of the quinone diazides.

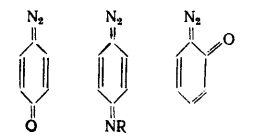
The following formulae have been proposed at different times for quinone diazides and *p*-iminoquinone diazides:



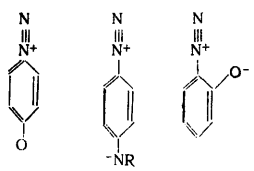
(I)



(II)



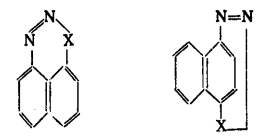
(III)



(IV)

Formula (I), containing quinquecovalent nitrogen, which was proposed by Bamberger [137], is incorrect according to modern interpretations. This formula was last used by Klemenc [124]. If Zsollinger's view [2] is accepted and the bridge bond is considered to be ionic, then this structure reduces to formula (IV).

For a long time a selection could not be made between the cyclic (II) and the quinoid (III) formulae to describe the structure of the quinone diazides and *p*-iminoquinone diazides. After the work of Morgan and coworkers [138,139], the cyclic formula (II), which had also been proposed by Bamberger [137], was considered almost up to the 1950's. Although there are now convincing proofs for the rejection of this formula, [9,13,14] some workers use it for *o*-diazides even today.[118] This is because the following facts favour the cyclic structure: (1) the yellow colour, which may be explained by the presence of the –N=N– group, as in coloured azo-compounds; (2) many properties, such as stability, azo-coupling, etc., have been associated with the presence of an easily cleaved oxydiazole ring; (3) finally, Morgan and coworkers reported (obviously in error) that diazo-oxides and diazoimides with similar properties are obtained from *peri*- and *para*-aminonaphthols and *peri*- and *para*-naphthylenediamines [138,139]. But since *peri*-derivatives cannot have a quinoid structure, both diazo-oxides and both diazoimides must have a cyclic structure:



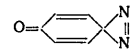
(where X = O or RN).

Using the analogy of the cyclic configuration of 1,4-diazoiminonaphthalene, Morgan proposed the cyclic formula (II) for the whole series of *p*-diazoimides, although he did not definitely reject the quinoid formula (III).

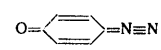
The following facts favour the quinoid structure for diazoimides and diazo-oxides: (1) colour and photosensitivity; (2) negative experiments on the preparation of *p*-diazoimides and *o*-diazo-oxides [74]; (3) differences in physical and chemical properties between *p*-diazoimides and *o*-diazoimides (the latter in fact have a cyclic structure); (4) it is difficult to suppose that the formation of *p*-diazo-oxides and *p*-diazoimides, which occurs readily (and sometimes instantaneously) in the cold, is associated with the closure of a seven-membered ring; (5) the ultraviolet and infrared spectra of the quinone diazides, which will be discussed below; (6) finally, Anderson and Roedel reported [13] that when they repeated Morgan's synthesis [140] they were unable to obtain the cyclic diazo-oxides he described from *peri*-aminonaphthol [13].

It will be seen that there is much more evidence in favour of the quinoid structure (III) and it has therefore been given preference over the others.

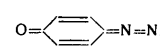
The quinoid structure, which is generally ascribed to Wolff [140], was first put forward without proofs by Bamberger [141] as one of the possible formulae of the quinone diazides; it could not be written unambiguously, because the structure of the diazonium group was not known. Later, following Wolff, this structure was accepted by Hantzsch [76,142] and other workers [9,13]. Bamberger [141] and Hantzsch [142] considered that the structure (IIIa) was the correct one. Bamberger [143] also proposed the formula (IIIb), which Angeli accepted [144]. In accordance with modern interpretations, the quinoid formula of the diazides is written in the form (IIIc):



(IIIa)

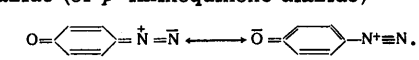


(IIIb)



(IIIc)

However, even the quinoid formula cannot exactly describe the structure of the quinone diazides and *p*-iminoquinone diazides. Recently, there has been an increasing tendency to accept the intra-ionic formula (IV), not as an independent formula, but as one of the extreme structures in a resonance hybrid describing the structure of the quinone diazide (or *p*-iminoquinone diazide)



(IV)

Sidgwick and coworkers were the first to put forward the idea of mesomerism of this type [145], and Modling and Burger represented quinone diazides in the same way [122]. Simonov [116] proposed mesomerism of ionic and quinonoid structures for iminoquinone diazides. Later, the mesomerism of these structures was used repeatedly to explain the properties of diazides [1,94,127].

It was characteristic of Hantzsch that as early as 1890 he noted that one formula alone was not sufficient to describe the properties of the diazides, and he thought that oscillation between the structures (I) and (III) was possible [10].

A. Structure and Physicochemical Properties of Quinone Diazides

As mentioned above, more precise determination of the structure of diazonium compounds became possible only with the development of physicochemical methods of investigation.

In 1945 Anderson and coworkers began the publication of papers in which they reported studies on the ultraviolet spectra and dipole moments of some quinone diazides of the benzene and naphthalene series; they compared their results with corresponding data for quinones and compounds containing triazole or thiodiazole rings [13,14]. They noted that the *o*- and *p*-quinone diazides have similar properties and their spectra are similar to the spectra of the corresponding quinones. However, the quinone diazides and cyclic thiodiazoles did not show similarities in their dipole moments and spectra. These workers concluded that the cyclic structure for quinone diazides is entirely ruled out, and they assigned a quinonoid structure to these compounds.

The results of dipole-moment measurements on six quinone diazides published by Anderson and coworkers (see Table 2) show that the *o*-quinone diazides are more "quinonoid" than the *para*-compounds [14]. The introduction of a nitro-group into the molecule increases the dipole moment.

Vaughan and Phillips studied the thermal stability of unsubstituted and nitro-substituted *o*- and *p*-quinone diazides, and showed that the *o*-quinone diazides are thermally no less stable than the *para*-isomers [106]. A nitro-group in the *ortho*- or *para*-position to the hydroxyl group stabilises the molecule, two nitro-groups have a greater effect, and a nitro-group in the *meta*-position has no effect. The results were regarded as being in agreement with the hypothesis that quinone diazides have a structure intermediate between the quinonoid and ionic structures.

TABLE 2. Dipole moments of quinone diazides

Compound	μ_H	μ_X	μ_I
3,5-Dibromobenzo-1,2-quinone 2-diazide	2.9	2.5	13.1
Naphtho-1,2-quinone 1-diazide	4.0	3.9	13.7
Naphtho-1,2-quinone 2-diazide	3.5	3.9	13.7
4-Nitronaphtho-1,2-quinone 1-diazide	4.6	2.8	16.2
1,4-Naphthoquinone diazide	4.2	1.6	27.4
p-Benzoquinone diazide	5.0	1.6	27.4

* μ_H dipole moment found experimentally; μ_X dipole moment calculated for the quinonoid form; μ_I dipole moment calculated for the ionic form.

On the bases of differences between ultraviolet absorption spectra of solutions of hydroxyphenyldiazonium sulphate in 5 *N* sulphuric acid, De Jonge and coworkers [146] concluded that the structure of *o*-benzoquinone diazides was intermediate between the quinonoid and ionic forms; they consider that in acid solutions the structure is close to that of benzene, since under these conditions, the quinonoid structure is energetically less favoured. In aqueous solutions the structure of the compound is close to the quinonoid form. These workers explain the different behaviour of *o*-hydroxyphenyldiazonium sulphate in neutral and acid aqueous solutions, and particularly the difference in ultraviolet absorption spectra and the different course of the photodecomposition reaction, by the hypotheses mentioned above. However, as mentioned above (see Section III.B.1), this is not a question of the quinonoid and benzenoid structure of *o*-benzoquinone diazide, but of the existence of an *o*-hydroxyphenyldiazonium cation in acid solutions and of *o*-benzoquinone diazide in aqueous solutions.

In recent years a large number of papers have appeared on the infrared absorption spectra of various quinone diazides. Intense absorption bands were always observed in the region of stretching vibrations of a triple bond and in the region of vibrations of the carbonyl group, which confirms the quinonoid structure, or in the opinion of a number of workers, the "mesomeric" structure of diazides. In the first paper of this type, published in 1954, the infrared spectra of seven quinone diazides were studied; the results are shown in Table 3.[147]

These results were compared with the frequency of the stretching vibrations of the CN_2(ν_{CN_2}) bond of phenyldiazonium tetrafluoroborate (ν_{CN_2} = 2296 cm^{-1}) and with the frequency of the stretching vibrations of the N–N ($\nu_{-N=N-}$) bond of benzo-1-thia-2,3-diazole ($\nu_{N=N}$ = 1542 cm^{-1}) and it was concluded that in quinone diazides the bond between the nitrogen atoms is intermediate between double and triple, and that the carbonyl group has the C=O structure.

Whetsel and coworkers [9] studied the infrared spectra of a number of diazonium salts, including diazonium compounds obtained from some aminophenols. They found the absorption bands in the region of diazo-group vibrations shown in Table 4.

To explain the lower values of ν_{CN_2} of quinone diazides compared with diazonium salts, the authors suggested that in the solid state the structure of quinone diazides is intermediate between the ionic and quinonoid forms.

TABLE 3. Infrared spectra of quinone diazides.

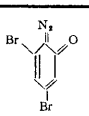
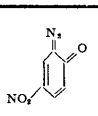
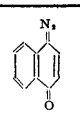
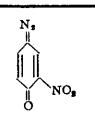
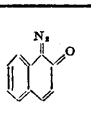
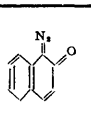
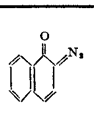
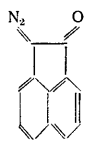
Diazide							
ν_{CN_2}, cm^{-1}	2110	2157	2014	2173	2017	2015	2148
ν_{CO}, cm^{-1}	1582	1562	1618	1618	1622	1642	1610

TABLE 4. Infrared spectra of diazo--compounds.

Diazo-compound from	ν_{CN_2}, cm^{-1}
m-Aminophenol tetrafluoroborate	2288
p-Aminophenol chloride	2237
p-Aminophenol diazide	2107
4-Nitro-2-aminophenol diazide	2183

In recent papers that contain information on the infrared spectra of quinone diazides, the authors either do not consider the relationship between spectra and structure at all[60,65,104,148,149], or they attempt to find if quinone diazide has a quinonoid, benzenoid, or mesomeric structure[150,151].

Reid and Appel[121] relate ν_{CN_2} with the reactivity of quinone diazides; they consider that the higher the value of ν_{CN_2}, the more vigorously the compound couples with triphenylphosphine. Thus, if $\nu_{CN_2} = 2125$ cm^{-1}, the compound does not undergo this reaction; if the value of ν_{CN_2} is 2125–2200 cm^{-1}, the compound couples very readily, and when $\nu_{CN_2} > 2200$ cm^{-1}, an anomalously fast reaction is observed. It is of interest that, on the basis of results obtained, these workers concluded that the quinone diazide (V) obtained from acenaphthoquinone is more an aliphatic diazoketone than a quinone diazide. This is in agreement with the conclusion based on a study of the infrared spectra of acenaphthoquinone.



(V)

All that has been said above on the structure of quinone diazides corresponding to aromatic hydrocarbons is also valid for diazides of the heterocyclic series. The spectra of these compounds show C=N̊=N̄ (or C–N̊≡N) and C=O stretching vibration bands[60,63], but the chemical properties of the compounds are the same as those of diazides of the aromatic series. Thus the similarity between the heterocyclic and aromatic diazides clearly shows that the former do not contain the oxydiazole ring[118], but have either a quinonoid structure[151], or, like uracil derivatives, the structure of a hydroxydiazonium compound[152].

Table 5 gives information on the stretching vibrations of C=N̊=N̄ and C=O bonds of diazides. Not all results are of the same value, since they were obtained under different conditions and with different degrees of precision (NaCl, LiF prisms, differences in degree of purity of the compounds, etc.). This is the reason why some frequencies given by different workers for the same compounds do not coincide. Another reason for the discordance probably resides in peculiarities in the structure of the diazides — peculiarities that have not yet been studied. Diazides obtained under different conditions may have different crystal structures, or their crystals may sometimes contain solvent molecules. The results of elemental analyses are not always given for diazides. This probably explains why the same compound may show one ν_{CN_2} band, or this band may sometimes be split into two or more components. Nevertheless, for the sake of completeness, we included a large proportion of the published results in Table 5.

The spectra of quinone diazides have a number of characteristic features. An increase in the number of condensed benzene rings in the quinone diazide molecule reduces ν_{CN_2} and increases $\nu_{C=O}$ at the same time. The value of $\nu_{C=O}$ for diazides varies within the limits 1630–1570 cm^{-1}; the results obtained by Glowiak form the only exception to this rule[150]. The values of ν_{CN_2} vary within the limits 2200–2000 cm^{-1}; higher values are observed only with carboxylic acids; these diazides containing the carboxyl or sulpho-group will be considered below. The stretching vibration band of the C=N̊=N̄ bond in *o*-diazides is nearly always split into two components, but no splitting occurs with the *para*-isomer. This interesting phenomenon has not been explained, and no research worker has even considered it. As a rule, the value of ν_{CN_2} for diazides is increased by electronegative substituents and diminished by electropositive substituents. However, this relationship, on the basis of which a number of workers have drawn conclusions about the structure and reactivity of the quinone diazides, is not very pronounced, and examples may be found in Table 5 in which substituents have the opposite effect. No such relationship is observed with regard to the effect of substituents on the

TABLE 5. Values of ν_{CN_2} and ν_{CO} for quinone diazides.

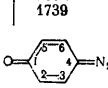
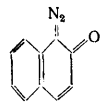
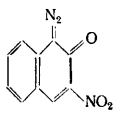
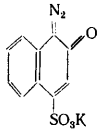
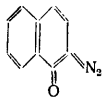
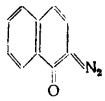
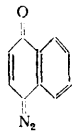
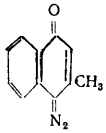
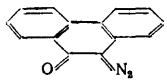
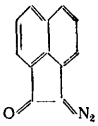
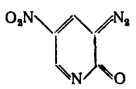
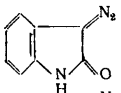
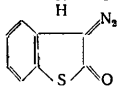
Substituents	ν_{CN_2}	ν_{CO}	References
ortho-quinone diazides 			
Unsubstituted	2175, 2140	1620	65
»	2134, 2168	1626	162
5-OCH_3	2128	1620	65
3-OCH_3, 6-OCH_3	2135, 2087	1613	65
5-$OCH_2 \cdot C_6H_5$	2150	1620	65
5-CH_3	2175, 2130	1613	65
4,5-$(CH_3)_2$	2170, 2120	1625	65
4,5-$(CH_2)_3$	2180, 2135	1637	63
4,5-$(CH_2)_6$	2150, 2100	1625	132
5-$C(CH_3)_3$	2182, 2160	1618	65
3,5-$[C(CH_3)_3]_2$	2135, 2124	1625	65
4,6-$[C(CH_3)_3]_2$	2120	1622	143
4,6-$[C(CH_3)_3]_2$	2170	1622	63
4-$CHC_6C_6H_5$	2200, 2130	1630	132
4-C_6H_5	2100	1620	143
4-$NHCOCH_3$	2200, 2150	1640, 1630	132
4-$COCH_3$	2150	1700, 1630 w.	104
4-COC_6H_5	2170	1610, 1580	104
5-Cl	2205, 2158	1613	65
6-Cl	2195, 2158	1610	65
4-Cl, 5-Cl	2160	1613	65
3-Br, 5-Br	2110	1582	147
4-Br, 6-Br	2152s.	—	162
4-COOH	2215	—	9
4-NO_2	2157	1562	147
4-NO_2	2183, 2150	—	9
4-NO_2, 6-COOH	2223	1760, 1616	150
6-NO_2, 4-COOH	2235	—	121
4,6-$(NO_2)_2$	2225	—	121
	2190	1666	150
4,6-$(NO_2)_2$-3-OH	2132	1664	150
4,6-$(NO_2)_2$, 6-COOH	2190, 2207	1739	150
para-quinone diazides 			
Unsubstituted	2109	—	9
»	2080	—	16
»	2110s.	1578	162
Unsubstituted.$4H_2O$	2080		16
Ditto	2125, 2135s.		162
2,6-$(CH_3)_2$	2090	1615	63
2,6-$(CH_3)_2$	2060	1600	159
2,6-$(CH_3)_2$	2070	—	16
2,6-$(CH_3)_2 \cdot 4H_2O$	2070	—	16
3,6-$(CH_3)_2$	2105	1610	63
2-CH_3, 6-COOH	2225	—	121
2-Cl, 6-Cl	2140	—	121
2-Br, 6-Br	2122 s., 2144 s.	—	162
2-NO_2, 6-COOH	2225	—	121
2,6-$(NO_2)_2$, 3-CH_3	2207	1653	150
5,6-Br_2	2140	1615	63
5-Cl, 6-Cl	2175	1610	63
5-F, 6-F	2190	1605	63

TABLE 5 (contd.)

Compounds	ν_{CN_2}	ν_{CO}	References
Quinone diazides of the naphthalene series			
	2132w., 2096	1621	148
ditto	2110	—	54
»	2017	1622	147
	2015	1642	147
	2089s., 2109s.	—	162
	2155w., 2114	1621	148
ditto	2090	—	54
»	2148	1610, 1618	147
	2150, 2180	—	121
	2014	1618	147
	2090	1625	63
Quinone diazides with condensed benzene nuclei			
	2066	1631	60
ditto	2100, 2125	—	121
Chrysene-5,6-quinone 6-diazide	2090	—	121
Fluoranthene-2,3-quinone diazide	2095	1635	63
	2070	1667	60
Quinone diazides of the heterocyclic series			
	2024	1716	151
	2092	1704	60
	2095	1625	63

value of $\nu_{C=O}$; the frequency varies very little and substituents of the same type may increase it or reduce it. The value of ν_{CN_2} is always higher for *ortho*-isomers than for the corresponding *para*-compounds. The integral intensity of the absorption band of the CN_2 bond in *o*-benzoquinone diazide is half that of the band for the bond in the *para*-isomers [153].

B. Structure of Substituted Quinone Diazides

The study of infrared spectra, especially in the 2000–2300 cm^{-1} region, that is, in the absorption region of $C=\overset{+}{N}=\bar{N}$ and $C-\overset{+}{N}\equiv N$ groups, is very useful in the determination of the structure of quinone diazides. But when this method is used, other physical and chemical properties of the quinone diazides and the corresponding diazonium salts must be taken into account.

In examination of the structure of the quinone diazides, it is generally assumed that diazides with high values ν_{CN_2} have a structure closer to the benzenoid form, and those with low values have a structure closer to the quinonoid form. However, examination of the data in Table 5 shows that one value of ν_{CN_2} alone is not sufficient to enable a decision to be made as to whether a compound is more or less benzenoid (or quinonoid). For example, Table 5 shows that the value of ν_{CN_2} is higher for *o*-diazides than for *p*-diazides, but chemical properties and dipole-moment measurements show that *o*-quinone diazides are more quinonoid than *p*-diazides [14]. Moreover, workers studying the structure of quinone diazides have not compared values of ν_{CN_2} obtained for quinone diazides with values for the corresponding hydroxyaryldiazonium salts (known to have a benzenoid structure), but have limited themselves to comparisons within the diazides. But experimental results show that for each quinone diazide there is a corresponding hydroxyaryldiazonium salt; the values of ν_{CN_2} in the spectra of the diazonium salts are higher than the values for the corresponding quinone diazides by 100–150 cm^{-1} (Table 6).

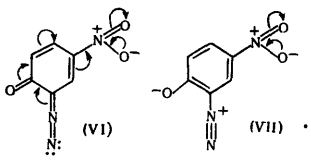
Thus, those diazides with high values of ν_{CN_2}, which are considered by many workers to exist in the benzene form, must have corresponding diazonium salts with known benzene structures and with still higher values of ν_{CN_2}. For example, ν_{CN_2} = 2190 cm^{-1} for 4,6-dinitrobenzo-1,2-quinone 2-diazide [150]. The corresponding hydroxyphenyldiazonium cation containing two nitro-groups, if it exists, must have a ν_{CN_2} of about 2300 cm^{-1}.[154] Therefore, higher values of ν_{CN_2} for substituted quinone diazides do not indicate that these compounds have a more benzenoid structure, since the corresponding benzene form (hydroxyphenyldiazonium salt) has a still higher value of ν_{CN_2} compared with these quinone diazides.

TABLE 6*.

Compound	ν_{CN_2} of quinone diazide			ν_{CN_2} of diazonium chloride*
p-Benzoquinone diazide	2107 s.	—	2278 w.	2251 m.
4,6-Dibromobenzo-1,2-quinone 2-diazide	2122 s.	2144 s.	2260 w.	2248 m.
o-Quinone diazide	2107 s.	2132 s.	2063—2169s.	2247 m.
1-Diazo-2-hydroxy naphthalene 4-sulphonic acid	2089 s. (potassium salt)	2109 s.	2230 w.t	2229 (internal salt)

* s. strong band; m. band of moderate intensity; w. weak band.

The increase in ν_{CN_2} observed when negative substituents are introduced into the quinone diazide occurs, because these substituents, acting on the diazo-group through the ring, withdraw electrons from this group, in the same way as the presence of a nitro-group in the ring of the nitrophenyldiazonium cation leads to a reduction in the electron density of the diazonium group. Although the diazo-group of the quinone diazide is somewhat similar in type to the diazonium group, the effect of substituted nitro-groups is to decrease the electron density of the oxygen of the C=O group, and not to increase it, as would be required for the intra-ionic benzene structure (VII)

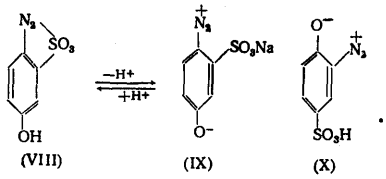


(VI) (VII)

Thus, quinone diazides with electronegative substituents, in contrast to the corresponding diazonium cations, do not have a benzenoid structure but the structure (VI), which is characteristic of unsubstituted quinone diazides; in this structure electrons are somewhat displaced towards the electronegative substituent.

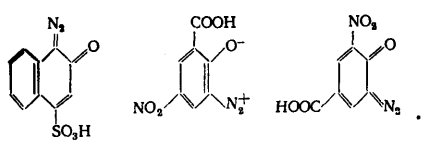
Compounds containing a carboxylic or sulphonic group occupy a special place in the hydroxyaryldiazonium series. In these compounds the diazonium group may interact with the acid group to form an internal diazosulphonate, and with the hydroxyl group to form a quinone diazide. Although the structure of these compounds has been under discussion for 50 years, the question has still not been finally cleared up.

Morgan and Tomlins [155], Battegay and Schmidt [156], and Schmidt and Maier [157] have discussed the structure of hydroxyaryldiazosulphonic acids. Some information on this question has been systematised in the book by Saunders, in which the literature up to 1949 is examined [1]. Saunders noted that in acid solutions these compounds are colourless and appear to be internal diazosulphonates (VIII), but in alkaline solutions they are yellow and probably have the structure (IX). Saunders ascribed the structure (X) to some quinone diazides that are coloured in acid solution, for example, 4-sulphobenzo-1,2-quinone 2-diazide:



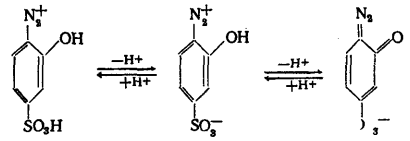
(VIII) (IX) (X)

At present a number of workers use formulae (XI)–(XIII) to represent the structure of quinone diazides containing sulpho- or carboxyl groups [121,150,158]:



(XI) (XII) (XIII)

In any examination of the structure of these compounds, it should be noted that hydroxyphenyldiazonium cations containing sulpho- or carboxyl groups are dibasic acids:



(XIV) (XV) (XVI)

The first acidity constant, corresponding to dissociation of the sulpho-group, is much greater than the second constant, corresponding to the dissociation of the hydroxyl group (it is well known that sulphonic and carboxylic acids are more acidic than phenols). Therefore, in acid solutions, in which dissociation of the hydroxyl group is suppressed, these compounds exist as the internal diazonium salt (XV). In neutral and weakly acid solutions, in which dissociation of the hydroxyl group is possible, the compound must exist as an equilibrium mixture of form (XV) and the diazide form (XVI). Finally, in alkaline solutions these compounds have the quinonoid structure (XVI). Thus, the solid compound obtained from acid solutions is the internal diazonium salt (XV). From neutral solutions that form separates which has the lowest solubility under the given conditions. Obviously, this will be form (XV), since it is known that internal diazonium salts of sulphonic acids are poorly soluble in water, but quinone diazides with an ionised sulpho-group should be much more soluble. From alkaline solutions the quinonoid form of the compounds will separate as the metallic salt of the acid, for example:

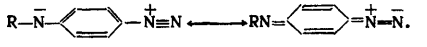
$$O{=}C_6H_3{=}N_2\ (SO_3Na)$$

(XVII).

Thus, these compounds never exist in the form of quinone diazide with an un-ionised sulphonic of carboxylic group — structures (X), (XI), and (XIII).

C. Structure of *p*-Iminoquinone Diazides (*p*-Imidoquinone Diazides)

As early as 1940, Simonov [116], who examined the chemical properties of *p*-iminoquinone diazides, rejected the cyclic formula proposed by Morgan [139] and proposed that the structure of these compounds cannot be generally represented by a single formula, but rather by the superposition of ionic and quinonoid structures:



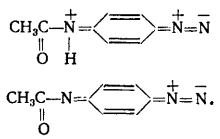
He emphasised that these structures were in a mesomeric and not a tautomeric relationship.

The state of the compound will be determined by the predominance of one structure or the other, according to the strength of the competing effects of the diazonium group and the substituent R. If the substituent is a weak electron acceptor (R = $CH_3-\overset{\overset{O}{\|}}{C}-$, $C_6H_5-\overset{\overset{O}{\|}}{C}-$, C_6H_5-), equilibrium is displaced towards the formation of the quinonoid structure, but if the substituent is a strong electron acceptor, as when R = $ArSO_2-$, $(NO_2)_3C_6H_2-$, etc., then the dipolar-ion structure predominates; in other words, the *p*-diazoimine (*p*-diazoimide) structure is regarded as the internal diazonium salt.

TABLE 7.

Substituent	Diazonium chlorides: ultraviolet spectrum λ_{max}, nm	Diazonium chlorides: ultraviolet spectrum logϵ	Diazonium chlorides: infrared spectrum ν_{CN_2}, cm^{-1}	Diazonium chlorides: colour	p-Iminoquinone diazides: pH region in which the two forms are in equilibrium in solution	p-Iminoquinone diazides: ultraviolet spectrum λ_{max}, nm	p-Iminoquinone diazides: ultraviolet spectrum logϵ	p-Iminoquinone diazides: infrared spectrum ν_{CN_2}, cm^{-1}	p-Iminoquinone diazides: colour	Literature reference
$C_6H_5SO_2NH$	327	4.41	2259	colourless	1.1—4.8	372	4.56	2181	yellow	111
CH_3CONH	335	4.49	2250	colourless	8.2—12	395	4, ...		yellow	99
C_6H_5CONH	342	4.52	2255	colourless	7.5—11.8	405	4.48	2150	yellow	99
C_6H_5NH	376	4.56	2244					2208		
			—		—	394	4.52	—	—	160
$(NO_2)_2C_6H_2NH$	—	—	2236	yellow	—	—	—	2112	red	99
								2090		

The hypotheses and conclusions of Simonov were not confirmed by studies of the physicochemical properties of *p*-iminoquinone diazides. Anderson and coworkers used ultraviolet and visible absorption spectra to establish the structure of the *p*-diazoimines [160,161]. According to their results, the ultraviolet spectra of solutions of *p*-diazoimines are identical with those of the corresponding diazonium chlorides. These workers were not surprised at this finding, because they considered that both the diazonium cation and the *p*-iminoquinone diazide have the quinonoid structure:

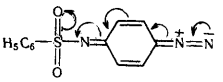


But the properties of the *p*-iminoquinone diazides differ from those of the corresponding diazonium chlorides. The former are much more photosensitive, and more strongly coloured; for these reasons, it is unlikely that these compounds have the same ultraviolet spectrum and therefore the same structure. In the analogous case of *p*-hydroxyphenyldiazonium chloride and *p*-quinone diazide, the compounds have different ultraviolet spectra and structures [109].

A recent study of the ultraviolet spectra of *p*-amino-substituted salts and of their conversion into *p*-iminoquinone diazides [99,111] showed that the latter absorb in a more longwave region of the spectrum than the corresponding *p*-amino-substituted diazonium salts (Table 7).

The ultraviolet spectra obtained by Anderson and coworkers are characteristic only of *p*-amino-substituted diazonium cations [160,161]. Anderson and coworkers did not succeed in obtaining the ultraviolet spectra of *p*-iminoquinone diazides, with the exception of the spectrum of one compound, because they did not sufficiently closely observe the conditions under which these compounds exist. When these conditions were observed (the diazo-solution was adjusted to pH 11.8 with NH_4OH), Anderson and Steedly found [160] that the spectrum of the diazonium salts *p*-$C_6H_5NHC_6H_4N_2HSO_4$ differed from that of the *p*-iminoquinone diazide *p*-$C_6H_5NC_6H_4N_2$, the latter absorbing in the more longwave region.

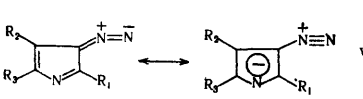
The values of ν_{CN_2} in the infrared spectra of *p*-iminoquinone diazides are close to the value for the cumulated C=N=N bond, and the values for *p*-amino-substituted diazonium salts are close to the value for the triple C–N≡N bond (see Table 7), but lower than the values for other aryldiazonium salts [99]. These results show that the structure of *p*-amino-substituted diazonium cations is close to the benzenoid form, but the structure of the *p*-iminoquinone diazides is close to the quinonoid form. But the ordinary formulae do not accurately reflect the structures of these compounds. Although the structure of *p*-iminoquinone diazides is closer to the quinonoid form in comparison with the initial *p*-amino-substituted diazo-compounds, this structure has a greater or lesser tendency to approach the benzenoid form, according to the electron-acceptor properties of the substituent:



This is reflected in an increase in the values of ν_{CN_2} in the infrared spectra and in a displacement of the ultraviolet absorption band towards the shortwave side (see Table 7).

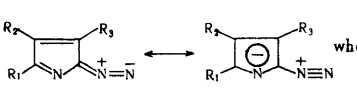
Little information has been published on the physicochemical properties and structure of *p*-iminoquinone diazides, and they have generally been much less studied than the more accessible quinone diazides. However, the study of these compounds is of undoubted practical and theoretical interest.

According to Tedder and Webster, the structure of heterocyclic diazo-imines is represented by a resonance hybrid [94,95].



where

R_1	R_2	R_3	ν_{CN_2}, cm^{-1}
Ph	NO_2	Ph	2150
Ph	H	Ph	2095
Ph	H	CH_3	2062

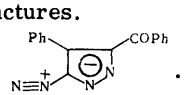


where

R_1	R_2	R_3	ν_{CN_2}, cm^{-1}
Ph	H	Ph	2138
Ph	NO_2	Ph	2172

Values of ν_{CN_2} have not been compared with those of the corresponding diazonium salts, although these salts have been separated in some instances [94].

Farnum and Yates [93] consider that the diazo-pyrazoles have structures close to the intra-ionic form, because the ν_{CN_2} values for these compounds are higher than those for the diazo-ketones, and close to those for the diazonium salts; however, they do not deny the possibility of resonance of two structures.



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BULK POLYMERISATION OF VINYL MONOMERS AT HIGH EXTENTS OF REACTION

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