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Diazotisation of Weakly Basic Aromatic and Heterocyclic Amines in Strongly Acid Media

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The review is devoted to the diazotisation of weakly basic aromatic amines. The methods of synthesis of diazonium salts based on these amines by non-traditional methods are examined. Data on the mechanism of the diazotisation reaction in strongly acid media are surveyed. Reactions of diazonium salts leading to the synthesis of new compounds are presented. The bibliography includes 75 references.

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I. INTRODUCTION

The diazotisation reaction has been known for a long time in organic chemistry. Diazotisation in weakly acid aqueous solutions has been particularly thoroughly investigated. Diazonium salts, used to synthesise a wide variety of different classes of compounds, are obtained in this way from strongly and moderately basic amines. Thus all possible azo-products, including azo-dyes, have been synthesised by a reaction without evolution of nitrogen. Reactions with evolution of nitrogen lead to functional derivatives of aromatic compounds. The reaction involving the substitution of the diazo-group by a metal has been developed by the school of Academician A.N.Nesmeyanov.

The diazotisation of weakly basic amines, which in the present review are understood as aromatic amines containing electronegative groups in the nucleus, has been much less well studied. The diazotisation of such compounds is as a rule carried out in strongly acid media. There are a number of reasons for this. The most inert amines, such as 2,4,6-trinitroaniline[1] or 6-bromo-2,4-dinitroaniline[2], are not diazotised under other conditions. Many diazonium salts containing strongly electronegative substituents, for example, 2,4,6-trinitrobenzenediazonium[3] or 3-carboxypyrazole-4-diazonium[4] sulphates are stable only in concentrated acids, decomposing on dilution with water, frequently with substitution of the diazo-group by the hydroxy-group[4]. A high acid concentration hinders, as a result of the protonation of the amino-group, the formation of 1,3-disubstituted triazenes from the diazonium salt and the initial amine in the course of the reaction[5-8].

The range of reactions of the diazonium salts obtained from weakly basic amines is limited, which we believe to be due to the inadequate attention devoted to the diazotisation of such amines.

The necessity to analyse the literature data and to describe them systematically has arisen in view of the possibility of employing weakly basic amines in the diazotisation reaction, which can lead to the synthesis of many substances of practical value which are otherwise difficult to obtain.

II. THE MECHANISM OF DIAZOTISATION IN STRONGLY ACID MEDIA

The present understanding of the diazotisation reaction of aromatic and heterocyclic amines is based on the consideration of four stages in the process[9,10]:

$$ArNH_2 + NOX \rightleftarrows ArNH_2^{\oplus}NO + X^{\ominus}, \quad (1)$$

$$ArNH_2NO^{\oplus} \underset{+H^{\oplus}}{\overset{-H^{\oplus}}{\rightleftarrows}} ArNHNO, \quad (2)$$

$$ArNHNO \rightleftarrows Ar{-}N{=}N{-}OH, \quad (3)$$

$$Ar{-}N{=}N{-}OH \begin{cases} \xrightarrow{HX} ArN_2^{\oplus}X^{\ominus} + H_2O, \\ \longrightarrow ArN_2^{\oplus}OH^{\ominus}. \end{cases} \quad (4)$$

In diazotisation in dilute acid solutions the rate-determining stage is the first—involving reaction with the nitrosating agent NOX with formation of a nitrosoammonium ion, which, being a strong acid[11], is readily deprotonated to the nitrosoamine. It is extremely probable that both stages can occur simultaneously.

In the third stage the nitrosoamine undergoes a tautomeric rearrangement to the diazohydrate†, which instantaneously gives rise to the diazonium cation [stage (4)].

The reaction in a strongly acid medium is distinguished by a high reactivity of the diazotising agent and a high rate of nitrosation. Nitrosonium sulphate (nitrosylsulphuric acid), which consists of ionic components, is usually employed as the nitrosating agent[12]. The generation of active nitrosonium cations has been demonstrated by ultraviolet spectroscopy of solutions in sulphuric acid[13]:

$$HNO_2 + 2H_2SO_4 \rightleftarrows NO^{\oplus} + H_3O^{\oplus} + 2HSO_4^{\ominus}.$$

In terms of its activity, the nitrosonium cation exceeds all known nitrosating agents[9]:

$$NO^{\ominus} > \begin{matrix} H \\ H \end{matrix}\!\!>\!O^{\oplus}{-}NO > BrNO > ONONO > HONO.$$

Kinetic studies have shown that in a strongly acid medium the *N*-nitrosation stage does not determine the reaction rate. It has been suggested[14] that an arylamine is rapidly nitrosated to give a low equilibrium concentration of the nitrosoammonium ion, which is converted into the diazonium ion with a slow transfer and elimination of protons. These two stages determine the rate of diazotisation in a strongly acid medium.

With increase of the acidity of the medium, the equilibrium concentration of the nitrosoammonium ion and the rate of loss of a proton diminish.

† Not isolated hitherto[9].

It is noteworthy that the formation of nitrosoammonium salts is possible also in reactions with weak acids, for example, in the reaction of nitrous acid with acetic acid or acetic anhydride[15]:

$$HNO_2 + AcOY \rightleftarrows AcONO + HOY ;$$
$$AcONO \rightleftarrows NO^{\oplus}AcO^{\ominus} ;$$
$$Y=H, Ac .$$

The unexpectedly high activity of nitrosonium acetate in the diazotisation reaction has been noted[15].

III. METHODS OF SYNTHESIS OF DIAZONIUM SALTS

Weakly basic aromatic and heterocyclic amines are usually diazotised in concentrated sulphuric acid, a mixture of sulphuric and phosphoric acids, a mixture of sulphuric and acetic acids, and also in concentrated nitric acid.

1. Diazotisation in Concentrated Sulphuric Acid

Diazotisation in concentrated sulphuric acid is suitable only for weakly basic amines. Aromatic amines with a high basicity are either precipitated from sulphuric acid in the form of salts (for example, aniline[16]) or are nitrosated in the *p*-position in the ring (for example, α-naphthylamine, *m*-toluidine, and *m*-anisidine[1]).

The diazotisation is as a rule carried out in the following manner. The amine is added with stirring and cooling to a solution of nitrosylsulphuric acid in sulphuric acid, prepared by the method of Fierz-David and Blangley[17], and the reaction mixture is then allowed to stand for the required time. The diazonium salt is either precipitated with ether or is made to undergo further reactions in concentrated sulphuric acid.

The time required for the complete diazotisation depends on the structure of the amine. Table 1 presents data on the diazotisation of weakly basic amines in concentrated sulphuric acid.

Table 1. Diazotisation of amines in sulphuric acid.

Amine	τ*, h	Refs.
3-Amino-2-carboxypyrazole	0.25	[4]
2,3,4,5-Tetrachloroaniline	1	[18]
2,3,5,6-Tetrachloroaniline	1	[18]
2,4,5-Trichloroaniline	1	[18]
2,3,4-Trichloroaniline	1	[18]
4-Fluoro-2-nitroaniline	1	[19]
2,4-Dinitroaniline	3	[17]
5-Chloro-2,4-dinitroaniline	4	[20, 21]
2,3,4,5-Tetrachloroanthranilic acid	16	[22]
4-Amino-2-iodoquinoline	—	[23]
p-Phenylenediamine	—	[24]**
2-Methyl-3,5-dinitroaniline	—	[25]

* Total diazotisation time.
** A bisdiazonium salt is formed.

The rate of diazotisation can be increased by diluting sulphuric acid with water[1]. However, this procedure is limited by the solubility of amines[21] and also by the decomposition of certain diazonium salts, for example 2,4,6-trinitrobenzenediazonium sulphate[3].

It has been noted[26] that the diazotisation of nitroanilines in concentrated sulphuric acid requires certain precautions: the reaction mixtures are very explosive in the case of dinitroanilines.

2. Diazotisation in a Mixture of Sulphuric and Acetic Acids

Weakly basic amines are diazotised successfully and at a high rate in a mixture of sulphuric and acetic acids. There are two methods, developed by Hodgson and co-workers, whereby the reaction can be carried out, depending on the solubility of the amine in acetic acid.

A. When the amine is soluble in acetic acid, its solution is added to the sulphuric acid solution of nitrosylsulphuric acid and care is taken to avoid the formation of a precipitate of the amine sulphate[27,28]. For example, *o*-phenylenediamine[27] and 4-nitro-1-naphthylamine[29] are diazotised in this way.

B. If the amine is sparingly soluble in acetic acid, it is recommended that it be initially dissolved in the sulphuric acid solution of nitrosylsulphuric acid and that an approximately equal amount of acetic acid is then added, as in the diazotisation of 1,6-dinitro-2-naphthylamine[30] or *p*-aminobenzaldehyde[31].

A list of weakly basic aromatic and heterocyclic amines, diazotised by the first and second methods in a mixture of sulphuric and acetic acids, is given in Table 2.

The method of diazotisation in acetic acid is used quite widely; it makes it possible to diazotise successfully not only weakly basic but also strongly basic aromatic and heterocyclic amines, provided that they do not decompose in sulphuric acid.

Table 2. Diazotisation of amines in a mixture of sulphuric and acetic acids.

Amine	Method	Refs.
3,5-Dibromo-1-nitroaniline	A	[32]
2,4-Diaminoquinoline	B	[23]
4-Amino-2-methoxyquinoline	B	[23]
o-Nitroaniline	A	[33]
m-Nitroaniline	A	[33]
p-Nitroaniline	A	[33]
2,4-Dinitronaphthylamine	A, B	[34, 35]
2,5-Dichloroaniline	A	[33]
3,5-Dinitro-*p*-toluidine	A	[33]
4-Trifluoromethyl-2-nitroaniline	A	[19]
4-Amino-2-nitrobenzaldehyde	A	[19]
4,5-Dinitronaphthylamine	A	[36]
4,4'-Diamino-3,3'-dinitrobiphenyl	B	[27]
2,3-Dinitroaniline	A	[37]
2,4,6-Tribromoaniline	A	[38]
p-Aminobenzaldehyde	B	[31]
2-Aminobenzo-1,4-dioxane	B	[39]
4-t-Butyl-1-nitroaniline	A	[40]

Diazonium sulphates can be isolated in the solid state by precipitation with ether or by other suitable solvents[41-43].

The relatively high freezing point of acetic acid, even in solution in sulphuric acid, must be regarded as a disadvantage of this method. If it is necessary to carry out the reaction at a low temperature, a mixture of acetic and propionic acid is used, for example, in the diazotisation of ethyl 5-aminothiophen-2-carboxylate[44].

3. Diazotisation in a Mixture of Sulphuric and Phosphoric Acid

The method of diazotisation in a mixture of sulphuric and phosphoric acids was developed by Schoutissen for weakly basic aromatic amines and diamines[16,31,35,45]. Diazotisation in a mixture of sulphuric and phosphoric acid takes place much more rapidly than in sulphuric acid alone. As in a mixture of sulphuric and acetic acids, the reaction is carried out by two methods: (1) a solution of the amine in sulphuric acid is added to a solution of nitrosylsulphuric acid in sulphuric acid; (2) phosphoric acid is added to a solution of the amine and nitrosylsulphuric acid in sulphuric acid.

Table 3 gives a list of the weakly basic aromatic and heterocyclic amines which have been diazotised by this method. The advantages of the method include the possibility of working at low temperatures.

Table 3. Diazotisation of amines in a mixture of sulphuric and phosphoric acids.

Amine	Refs.
2,4-Dinitroaniline	[16]
2,4,6-Trinitroaniline*	[16]
1,4-Diamino-2,5-dichlorobenzene**	[16]
o-Phenylenediamine**	[8]
p-Aminobenzaldehyde	[31]
2-Amino-1,3-selenazole	[46]
2-Amino-4-phenyl-1,3-selenazole	[46]
2,3-Dinitroaniline	[47]
2,6-Dinitroaniline	[47]
2,4-Difluoro-5-nitroaniline	[48]
2,6-Di-iodo-4-nitroaniline	[49]

* 2,4,6-Trinitroaniline is first dissolved in nitrobenzene.
** Bisdiazonium salts are formed.

4. Diazotisation in Concentrated Nitric Acid

It has been shown[50,51] that certain amines can be smoothly diazotised in concentrated nitric acid. The reaction takes place much faster than in concentrated sulphuric acid and is actually faster than in mixtures of sulphuric acid with acetic or phosphoric acid. The diazotisation frequently reaches completion after several minutes, which can be explained by the high solvent power of concentrated nitric acid.

Despite these advantages, the method is used rarely, because there is a risk that part of the amine is nitrated before being diazotised[52,53].

The reaction in nitric acid is carried out using different diazotising agents. Thus 2,6-nitro-4-toluidine is diazotised by nitrous oxides[50]; 4-amino-3,5-dibromobenzoic acid is diazotised with potassium nitrite[54]; 3,4,5-tri-iodoaniline is diazotised with sodium nitrite[55]; 2-methyl-3,5-dinitroaniline[25] and 13-aminobenzanthrone[56] are diazotised with nitrosylsulphuric acid formed when potassium thiosulphate is introduced into nitric acid. It is noteworthy that the diazotised amine is nitrated very slowly[56] owing to the powerful negative mesomeric effect of the diazo-group[57].

5. Diazotisation in Organic Solvents

This method is used fairly rarely for weakly basic amines. Thus 6-bromo-2,4-dinitroaniline[2] is diazotised by a mixture of nitrosylsulphuric and formic acids in tetrahydrothiophen 1,1-dioxide, while 2,4,6-trinitroaniline[16] is diazotised by a mixture of nitrosylsulphuric and phosphoric acids in nitrobenzene.

It has been reported[58] that 2,4,6-trinitroaniline can be smoothly diazotised by nitrosylsulphuric acid in a mixture of pyridine and sulphuric acid and the product of the azo-coupling of the diazonium salt with β-naphthol was actually isolated. Later, when an attempt was made to confirm this investigation, it was established[59] that diazotisation does not take place in this instance and that the so-called "product of the azo-coupling reaction" is an equimolar adduct of β-naphthol and picramide.

The attempt to obtain diazonium salts from 2,4,6-trichloro- and 2,4,6-tribromoanilines with the aid of nitrosylsulphuric acid in ethanol[18] should also be mentioned: after the decomposition of the reaction mass, only the corresponding diaryltriazenes were isolated, which indicates a low rate of diazotisation.

The question of the limits of the applicability of the reaction is obscure and the possibility of the diazotisation of weakly basic amines in organic solvents must be elucidated in each individual instance.

Thus weakly basic aromatic and heterocyclic amines can be most conveniently diazotised by nitrosylsulphuric acid in a mixture of concentrated sulphuric and phosphoric ($d = 1.7$) or acetic acids. Phosphoric acid mixtures make it possible to carry out the reaction at a low temperature. Other diazotising mixtures are rarely employed.

IV. REACTIONS OF DIAZONIUM SALTS

The reactions of diazonium ions have been investigated for a very long time. Various reactions of diazonium salts, leading to compounds which cannot be obtained by other methods, are known.

There exist several classifications of the reactions of diazonium ions. The most complete modern classification was devised by Zollinger[60] in 1973.

The present review deals only with those reactions which are known for diazonium salts obtained from weakly basic aromatic and heterocyclic amines by diazotisation in strongly acid media. They are frequently divided into three types:

1. Reactions involving addition to the β-atom of the diazo-group (azo-coupling with electron-donating π-electron systems, the formation of triazenes and azido-derivatives);
2. reactions with heterolytic dissociation of the bond between the ring carbon atom and a nitrogen atom of the diazo-group (hydrolysis);
3. reactions with homolytic dissociation of the same bond (substitution by halogen-, nitro-, and cyano-groups and reduction of diazonium salts).

1. Azo-Coupling with π-Electron Systems

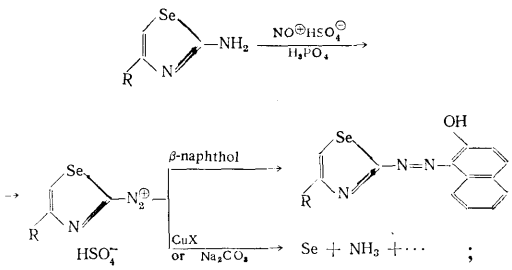
One of the most characteristic reactions of diazonium salts is that of azo-coupling. The azo-coupling reaction is usually carried out in nearly neutral media, because in an acid medium the amines and the phenols employed as the azo-components are protonated and to a large extent lose their activity.

The reaction is accelerated when the arenediazonium cation contains one or several electron-accepting groups. Thus the 2,4,6-trinitrobenzenediazonium ion reacts even with a relatively inactive azo-component such as mesitylene[61].

When the diazonium salts are difficult or impossible to obtain in the solid state or in an aqueous solution of moderate acidity, their azo-coupling is carried out in strongly acid

solutions by adding the azo-component in the solid state or in solution in pyridine[16] or methylene chloride[62]. β-Naphthol or phenol are usually employed as the azo-component. The precipitate of the azo-coupling product is usually bright red.

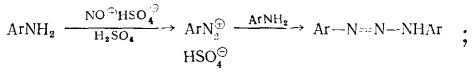
Among the chemical methods, this reaction constitutes the most reliable procedure for the detection of diazonium salts. In many cases the presence of diazonium salts is tested by the azo-coupling reaction. Thus the formation of diazonium salts in the diazotisation of 2-amino-1,3-selenazoles by a mixture of nitrosylsulphuric and phosphoric acids was confirmed solely by the reaction with β-naphthol, while the interaction with other reagents leads only to decomposition products[43]:



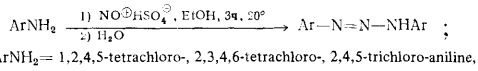
R=H, Ph .

2. The Formation of Triazenes

Triazenes are usually formed on diazotisation of amines (particularly weakly basic amines) in a weakly acid medium. The use of strong acids, prevents this reaction. If the diazotisation has not been carried out to completion or additional amine is introduced into the reaction mass which has fully reacted, there is a possibility of the formation of 1,3-disubstituted triazenes when the strongly acid solutions are poured into water[18]:

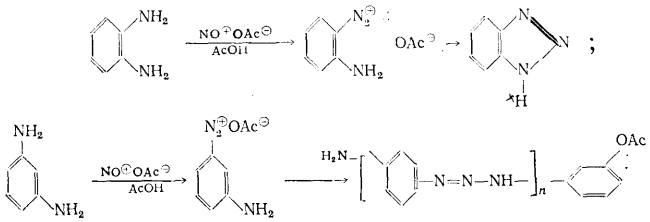


$ArNH_2$ = 2,4,6-trichloro- or 2,4,6-tribromo-aniline;



$ArNH_2$ = 1,2,4,5-tetrachloro-, 2,3,4,6-tetrachloro-, 2,4,5-trichloro-aniline, etc.

It is particularly important to take this reaction into account in the decomposition of monodiazonium salts obtained from diamines. This entails the formation of both cyclic (from *o*-phenylenediamines) and linear triazenes[7,63]:

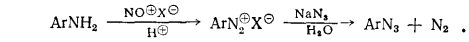


3. The Formation of Azido-Derivatives

Diazonium salts interact with ammonia, hydrazine and many of their derivatives, such as hydroxylamine, arenesulphonamides, phenylhydrazine, and aromatic acid hydrazides with formation of azides.

However, these methods are applicable to weakly basic or neutral solutions of diazonium salts, because in strong acids ammonia and hydrazine derivatives are protonated and do not react with diazonium cations.

For weakly basic amines, the most common reaction of diazonium salts is that with hydrazoic acid and its salt. The yields of azidoarenes are high, frequently nearly quantitative:



For example, 1-azido-4-trifluoromethyl-2-nitrobenzene, 1-azido-4-formyl-2-nitrobenzene, 1-azido-4-fluoro-2-nitrobenzene[19], and 1-azido-4,6-dibromo-2-nitrobenzene[32] are obtained in this way.

In the case of 2,2′-diaminoazobenzene and 2,4,6-triaminomesitylene it is possible to introduce two[64] or three[65] azido-groups respectively.

4. Substitution by the Hydroxy-Group

Virtually all diazonium salts react with water, exchanging the diazo-group for a hydroxyl. For diazonium salts obtained from weakly basic amines, this reaction can actually interfere with its normal reactions and can compete with the reaction involving substitution under the influence of other nucleophiles[3,4].

Strongly acid solutions of diazonium salts obtained from weakly basic amines are decomposed by being poured into water, as in the case of 3-carboxypyrazole-2-diazonium sulphate[4], or into a solution of copper sulphate, as in the case of 2,3,4,5-tetrachlorobenzenediazonium sulphate[22]. When necessary, dilute solutions of diazonium salts are refluxed. For example, *p*-hydroxybenzaldehyde[31] and 2- and 4-hydroxyquinolines[23] are obtained in this way.

5. Substitution by the Chloro-, Bromo-, Nitro-, and Cyano-Groups (The Sandmeyer Reaction)

When a solution of a diazonium salt is treated with an appropriate nucleophile X^- (X = Cl, Br, NO_2, or CN) in the presence of a copper catalyst, the diazo-group is replaced by the chloro-, bromo-, cyano-, or nitro-group. The catalyst can consist of metallic copper, copper(I) oxide, copper(II) oxide, or copper(II) sulphate as well as copper(I) salts (the chloride, bromide, and cyanide).

The Sandmeyer reaction is carried out as a rule in a neutral or weakly acid medium. The diazonium salts obtained from weakly basic amines by diazotisation in strongly acid media are also decomposed by being poured into a solution of the corresponding nucleophile in the presence of the copper catalyst.

The substitution by chlorine (or bromine) is usually carried out by adding a solution of copper(I) chloride (bromide) in hydrochloric (hydrobromic) acid to a solution of the diazonium salt.

Nitro-compounds are best obtained with preliminary precipitation of the diazonium salt from strongly acid solutions with ether.

The reaction involving the substitution of the diazo-group by the cyano-group is rarely used. It is usually carried out in a rigorously neutral medium by adding a solution of an alkali metal cyanide and copper sulphate (copper monocyanide is sometimes used). For example, *o*-, *m*-, and *p*-nitroanilines[66], 3-aminopyridine, and 5-amino-2-methylpyridine[67] are diazotised in this way.

Data for the Sandmeyer reaction of hydrochloric acid solutions of diazonium salts are presented in Table 4.

The Sandmeyer reaction does not occur when the competing hydrolytic reaction proceeds at a higher rate, as for 2-carboxypyrazolediazonium sulphate[4], or when the heterocycle is ruptured[46].

Table 4. The Sandmeyer reaction for weakly basic aromatic and heterocyclic amines.

Amine	Diazotising mixture	Substituting anion	Decompn. mixture	Refs.
2,3-Dinitroaniline	$NOHSO_4+H_3PO_4$	$Cl^\ominus$	HCl+CuCl	[47]
ditto	$NOHSO_4$+AcOH	$Br^\ominus$	HBr+CuBr	[37]
2,6-Dinitroaniline	$NOHSO_4+H_3PO_4$	$Cl^\ominus$	HCl+CuCl	[47]
4,5-Dinitronaphthylamine	$NOHSO_4$+AcOH	$Cl^\ominus$	ditto	[36]
ditto	ditto	$Br^\ominus$	HBr+CuBr	[36]
4,4'-Diamino-3,3'-dinitrobiphenyl	»	$Cl^\ominus$	HCl+CuCl	[27]
2,4-Dinitronaphthylamine	»	$Cl^\ominus$	ditto	[27]
ditto	»	$Br^\ominus$	HBr+CuBr	[27]
4-Amino-2-methoxyquinoline	»	$Cl^\ominus$	HCl+CuCl	[23]
ditto	»	$NO_2^\ominus$	$NaNO_2+Cu_2O$	[23]
2,4-Diaminoquinoline	»	$Cl^\ominus$	HCl+CuCl	[23]
ditto	»	$NO_2^\ominus$	$NaNO_2+Cu_2O$	[23]
4-Bromo-2,6-dinitroaniline	$NOHSO_4$	$Br^\ominus$	HBr+CuBr	[68]
2-Amino-3,4,5,6-tetrachlorobenzoic acid	ditto	$Br^\ominus$	ditto	[69]
4-Amino-3-nitroanisole	»	$Br^\ominus$	»	[70]
2,4,6-Tribromoaniline	$NOHSO_4$+AcOH	$Br^\ominus$	»	[38]
p-Phenylenediamine	ditto	$CN^\ominus$	KCN+CuCN	[66]
m-Phenylenediamine	$NOHSO_4$+AcOH	$CN^\ominus$	»	[66]
3,5-Dinitronaphthylamine	ditto	$NO_2^\ominus$	$NaNO_2+CuSO_3$	[71]
7-Amino-6-nitrotetralin	»	$NO_2^\ominus$	»	[71]

Table 5. Substitution of the diazo-group by iodine in diazonium salts obtained in a strongly acid medium.

Amine	Diazotising mixture	Refs.
2-Amino-4,5-dinitrobenzoic acid	$NOHSO_4+H_2SO_4$	[72]
2,4-Difluoro-6-nitroaniline	$NOHSO_4+H_3PO_4$	[48]
2,6-Di-iodo-4-nitroaniline	ditto	[49]
4-Amino-3,5-dibromobenzoic acid	$NOHSO_4+H_2SO_4$	[73]
2,3-Dinitroaniline	$NOHSO_4$+AcOH	[37]
p-Aminobenzaldehyde	$NOHSO_4+H_3PO_4$(AcOH)	[31]
2-Aminobenzo-1,4-dioxan	$NOHSO_4$+AcOH	[39]
4-Amino-2-methoxyquinoline	ditto	[23]
2,4-Diaminoquinoline	»	[23]
2,4-Dinitro-1-naphthylamine	»	[74]
1,6-Dinitro-2-naphthylamine	»	[74]

6. Substitution by Iodine

The substitution of the diazo-group by iodine does not require the presence of copper catalysts. It takes place when strongly acid solutions of diazonium salts are poured into a solution of potassium iodide. A list of weakly basic amines which have been made to undergo this reaction is presented in Table 5.

7. Substitution by Hydrogen (Reduction)

Diazonium salts can be reduced with the aid of many reagents. The most common are alcohol and hypophosphorous acid. (In relation to the initial amine, this reaction is referred to as deamination.)

Diazonium salts obtained from weakly basic amines such as 2,4-dinitrotoluidine[50] and 5-t-butyl-2-nitroaniline[40] are usually reduced by heating with ethanol. Copper catalysts are sometimes used, for example, copper(II) oxide for *o*-, *m*-, and *p*-nitroanilines, 2,4-dinitronaphthylamine, and 2,5-dichloroaniline[33] or copper sulphate for 2,6-dibromo-4-carboxyaniline[54].

2,4,6-Trinitroaniline can be conveniently deaminated with hypophosphorous acid[75].

Summarising the above discussion, one may say that the diazonium salts obtained from weakly basic amines in strongly acid media are capable of undergoing various reactions both with and without the evolution of molecular nitrogen. The reactions without the evolution of a nitrogen molecule (azo-coupling and the formation of triazenes) as a rule take place readily. The methods for the substitution of the diazo-group by various functional groups have been developed less fully owing to the low stability of the diazonium salts in aqueous media.

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