XXII.—*Acyl Derivatives of Paradiazoimino-benzene.*

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THE monosulphonamides of *p*-phenylenediamine and its homologues give rise on diazotisation to diazonium salts, which change by internal condensation into *p*-diazoimides on diminishing the acidity of the diazo-solution. The course of this reaction may be indicated by the following general equation:

The diazonium salt (II) has been isolated in several instances, but when diazotisation occurs in the absence of strong acids condensation takes place forthwith and the *p*-diazoimide is produced.

As the result of applying this process to a large number of *p*-aminosulphonamides (I) and similarly constituted compounds, it has been demonstrated that the reaction is a very general one. The course of the reaction taking place throughout the series of sulphonamides examined may be summarised in the following generalised diagram:

X is a bivalent aromatic hydrocarbon group with (*a*) homonuclear substituents, such as 1:4-phenylene, C₆H₄; 1:4-tolylene, C₇H₆; 1:4-xylylene, C₈H₈; or 1:4-naphthylene, C₁₀H₆, or with

(b) heteronuclear substituents, such as 4:4'-diphenylene (benzidine residue), $C_6H_4 \cdot C_6H_4$; or 1:8-naphthylene, $C_{10}H_6$.

n = the valency of the radicle R attached to the sulphonic group. Instances have been selected where $n = 1, 2$, or 3 .

With $n = 1$, R' has been methyl, benzyl, phenyl, *o*- and *p*-tolyl, 1:3-xylyl, α - and β -naphthyl, and β -camphoryl.

With $n = 2$, R'' has been methylene, CH_2 , and 1:3-phenylene, C_6H_4 .

With $n = 3$, R''' has been the tervalent group, 1:3:5- C_6H_3 , derived from benzene.

The practical details by means of which the foregoing general reaction has been demonstrated are described in the following communications: T., 1905, **87**, 73, 921, 1302; 1906, **89**, 4, 1158; 1907, **91**, 1505, 1512; 1908, **93**, 614; 1910, **97**, 48; *Ber.*, 1906, **39**, 2869. It was also demonstrated that the diazoimide condensation does not occur with *m*-aminosulphonamides; it is a function of the more sympathetic ortho-, para-, dipara- (benzidine), and peri- (naphthalene) positions (T., 1906, **89**, 1289). In addition to these researches, the investigation has been extended to *p*-aminodiphenylamine and its nitro-derivatives, with the result that it was found that these substances give rise on diazotisation to internal condensation products, namely, the *p*-diazoimines, in accordance with the following general reaction:

where $n = 0, 1, 2$, or 3 (*Ber.*, 1902, **35**, 888; T., 1908, **93**, 602).

It was obviously of interest to examine the behaviour under similar conditions of acyl-*p*-diamines containing carboxyl groups, but when the procedure of diazotising in aqueous solutions was applied to these compounds it failed completely to yield the corresponding acyl-*p*-diazoimides. In these circumstances, only ill-defined diazoamines were obtained from formyl-*p*-phenylenediamine and acetyl-*p*-phenylenediamine. More definite and interesting results were obtained from benzoyl-*p*-phenylenediamine, which yielded benzoyl-*p*-aminobenzenediazonium nitrite and the corresponding hydrogen carbonate (T., 1905, **87**, 933). Even more striking was the behaviour of benzoyl-1:4-naphthylenediamine, which gave rise to well-defined, stable, coloured diazonium salts (T., 1907, **91**, 1316), but neither of these benzoyl-*p*-diamines showed any tendency to furnish benzoyl-*p*-diazoimides in aqueous solution.

It has now been found that formyl-*p*-phenylenediamine and its homologues can be converted into *p*-diazoimides by diazotising with liquid nitrous anhydride in non-aqueous solvents, such as dry acetone.

Formyl-p-phenylenediazoimide (formula IV), obtained in this way from formyl-*p*-phenylenediamine, is an unstable, pale yellow substance, darkening on exposure to light and losing diazo-nitrogen even at the ordinary temperature:

This compound, the simplest possible acyl-*p*-phenylenediazoimide, is the least stable member of the series.

The next homologue, *acetyl-p-phenylenediazoimide* (formula V), is of special interest as showing how dependent is the course of the diazo-reaction on experimental conditions. The parent substance, acetyl-*p*-phenylenediamine, has long been diazotised on a considerable scale in the manufacture of azo-colours, having a *p*-phenylene residue as the middle component. This diazotisation is, however, always effected in aqueous solutions, and accordingly the cyclic diazoimide has not been produced under these conditions.

Acetyl-p-phenylenediazoimide is a pale yellow, crystalline compound, which, like the formyl compound, is unstable at the ordinary temperature, slowly losing diazo-nitrogen even in dry air. Considerable increase in stability is, however, produced by substituting a benzoyl group for the formyl and acetyl groups of the preceding compounds.

Benzoyl-p-phenylenediazoimide (formula VI) is obtained by the same experimental method from benzoyl-*p*-phenylenediamine. It is a well-defined, pale yellow, crystalline substance, quite stable in air at the ordinary temperature:

Inasmuch as this non-aqueous diazotisation with liquid nitrous anhydride changed completely the course of diazotisation of benzoyl-*p*-phenylenediamine from that which obtains in aqueous or in acid

solutions (see above), it seemed of interest to extend the study to the parallel case of benzoyl-1:4-naphthylenediamine. This naphthalenoid amine had in aquo-acid solutions given rise to an exceptionally stable and well-defined series of coloured diazonium salts, but in these conditions it had shown no tendency to furnish a cyclic diazoimide. This compound becomes the main product when the diazotisation is conducted under the new conditions. Liquid nitrous anhydride in dry acetone leads to *benzoyl-1:4-naphthylenediazoimide* (formula VII), a compound resembling the preceding benzenoid analogue and stable in air at the ordinary temperature :

The foregoing acyl-*p*-phenylenediazoimides and the corresponding naphthylene analogue have chemical properties closely resembling those of the alkyl- and aryl-sulphonyl-*p*-phenylenediazoimides; they combine additively with phenols and naphthols and with reactive bases, such as the naphthylamines and *m*-phenylenediamine and its homologues to furnish azo-derivatives. The production of these comparatively simple acyl-*p*-diazoimides is another step nearer to the hypothetical *p*-phenylenediazoimine (*p*-diazoiminobenzene),

which has not hitherto been isolated.

EXPERIMENTAL.

Formanilide dissolved in 2 parts of cold concentrated sulphuric acid was nitrated with 1 part of nitric acid (D 1.42) diluted with an equal volume of concentrated sulphuric acid; the nitration mixture was stirred thoroughly and maintained at 15–20°. The crude *p*-nitroformanilide, when precipitated on ice and crystallised from toluene, melted at 196°. An alternative method of preparing this nitro-compound consisted in boiling one molecular proportion of *p*-nitroaniline dissolved in toluene with formic acid (2 mols.) for three hours, when the formyl derivative crystallised on cooling. The yellow, crystalline powder, when washed with alcohol, melted at 197°, the yield being about 88 per cent. of the calculated amount.

Formyl-*p*-phenylenediamine was best obtained from the preced-

ing nitro-compound by suspending 20 parts of the latter in 70 parts of hot water containing 1 part of formic acid and by adding slowly 20 parts of iron borings. The reduction was complete in about forty minutes, after which 1 part of solid calcium carbonate was added and the precipitate of iron hydroxides filtered off quickly from the boiling solution. From the cooled filtrate 6—7 parts of formyl-*p*-phenylenediamine crystallised, whilst a further portion was obtained by evaporating the mother liquor in a current of carbon dioxide. The total yield of formyl-*p*-phenylenediamine was 70 per cent. of the calculated quantity.

The formylated base was purified by extraction with dry benzene in a Soxhlet apparatus. This solvent, which removed the base in a purified, colourless condition (m. p. 125—126°) without melting out the tarry impurity, is for this reason to be preferred to toluene, in which the base is rather more soluble, because at the higher boiling point of toluene the tarry impurity melts and becomes mixed with the extracted material.

Earlier experiments in aqueous solution having shown (*loc. cit.*) that this medium was not suitable for inducing internal condensation to a diazoimide, attempts were made in various organic solvents. Formyl-*p*-phenylenediamine (0.5 gram) dissolved in 6 c.c. of alcohol to which were added 20 c.c. of ether was treated with nitrous fumes generated from arsenious oxide and nitric acid, the ether-alcohol solution being cooled by ice and salt. A brown powder separated, which after drying in a vacuum desiccator blackened at 94—95° and decomposed at 120—124°. This result indicated the formation of an unstable diazo-compound, and further experiments were made. Half a gram of purified formyl-*p*-phenylenediamine dissolved in 10 c.c. of dry acetone and cooled by ice and salt was treated with excess of liquefied nitrous anhydride. A pale yellow, crystalline solid separated, the precipitation being completed by the addition of cooled dry ether. The product, after drying on a porous tile, decomposed with explosive violence at 128°, and coupled with β -naphthol either on powdering the reagents together or more rapidly on moistening these substances with pyridine, the product being a bright red azo-derivative. Similar azo-couplings occurred equally readily with α - and β -naphthylamines, yielding respectively deep red and brown azo-derivatives. When exposed to light the diazo-compound darkened, becoming orange, brown, and finally black.

On repeating the preparation in acetone with liquefied nitrous fumes derived in the usual way from arsenious oxide and concentrated nitric acid, it was found that the method was very uncertain. Occasionally, a well-defined, yellow, crystalline diazo-deriv-

ative separated, but more often the product was tarry and indefinite. Moreover, the crystalline material was not stable on exposure, and after a few days its colour had changed to deep yellow even in the absence of light.

More satisfactory results were obtained by freeing the liquefied nitrous fumes from nitrogen peroxide by passing nitric oxide through the green liquid until it assumed a deep blue colour (H. B. Baker and M. Baker, T., 1907, **91**, 1862).

To a solution of blue nitrous anhydride in cooled dry acetone was added powdered formyl-*p*-phenylenediamine. The base dissolved, and the addition was continued until the liquid assumed a pale green colour. Cooled dry ether was then added, when a heavy, yellow, crystalline solid separated. This product, which was hard and gritty, was collected rapidly, washed with cold ether, and transferred to a vacuum desiccator over phosphoric oxide. Even when kept in complete darkness the yellow diazoimide assumed a darker brownish-orange shade within a few hours. Freshly prepared specimens gave on analysis the following results for total and diazo-nitrogen :

0.1038 gave 21.4 c.c. N_2 * at 18° and 761.5 mm. $N = 23.85$.

0.1134 „ 14.4 c.c. diazo- N_2 at 14° and 760 mm. $N = 14.95$.

$C_7H_5ON_3, 1\frac{1}{2}H_2O$ requires $N_3 = 24.14$; $N_2 = 16.09$ per cent.

The diazo-nitrogen was estimated by warming the diazoimide in the volumeter with diluted sulphuric acid (1 vol. H_2SO_4 ; 3 vols. H_2O) for ten minutes on the water-bath. The result showed that the ratio of diazo-nitrogen to total nitrogen is approximately 2:3, thus excluding the possibility of the diazo-compound being a diazo-amino-derivative, $COH \cdot NH \cdot C_6H_4N_2 \cdot NH \cdot C_6H_4 \cdot NH \cdot COH$, in which case the ratio should be 2:5. The remaining possibilities are that this diazo-product is either a primary nitrosoamine,

or a hydrated diazoimide, $COH \cdot \overline{N \cdot C_6H_4 \cdot N_2} \cdot 1\frac{1}{2}H_2O$, either of these compounds giving the ratio of diazo to total nitrogen at 2:3. The mode of formation and the ease with which the product couples with β -naphthol and aromatic amines excludes the nitrosoamine configuration.

On the other hand, the presence of water of hydration is quite compatible with the presence of an internal diazoimide complex. The anhydride of *p*-diazophenol was shown by Hantzsch and Davidson to contain four molecular proportions of water,

* In all the nitrogen estimations recorded in this paper the gas was moist being measured over water.

(Ber., 1896, **29**, 1530), and the diazoimides of the arylsulphonylbenzidines contain two molecular proportions of water, having the composition $\overline{\text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{SO}_2\text{R}} \cdot 2\text{H}_2\text{O}$ (Morgan, Hird, and Micklethwait, T., 1907, **91**, 1509; 1908, **93**, 619).

In the present instance, the presence of water in the diazoimide is quite compatible with its mode of formation,

If the water eliminated from the reacting molecules remained in the product, the latter would have a composition corresponding with the analytical results.

Formyl-p-phenylenediazoimide, when prepared in acetone solution, was generally obtained as a pale yellow, crystalline solid, darkening even in the absence of light, and evolving nitrogen at the ordinary temperature. Various specimens decomposed explosively between the limits 125° and 128°. All attempts to recrystallise the compound failed, even at low temperatures, the products being resinous, ill-defined materials.

Formyl-p-aminobenzeneazo-β-naphthol from Formyl-p-phenylene-diazoimide.

Formyl-*p*-phenylenediazoimide was intimately mixed with β-naphthol (1 mol.), and the mixture treated with dilute aqueous sodium hydroxide. Frothing occurred, showing loss of diazo-nitrogen, and the azo-β-naphthol derivative separated, the yield being about 50 per cent. of the calculated amount. A more complete coupling occurred on moistening the mixture of diazoimide and β-naphthol with pyridine. A slight frothing was observed, and, after washing the separated azo-β-naphthol with water, aqueous sodium hydroxide and water, the yield was found to be 67·4 per cent.:

0·0959 gave 11·2 c.c. N₂ at 14° and 772 mm. N=14·30.

C₁₇H₁₃O₂N₃ requires N=14·42 per cent.

Formyl-p-aminobenzeneazo-β-naphthol, when crystallised successively from glacial acetic acid and alcohol, separated in dark brownish-red, nodular crystals, and melted at 242—243°. With concentrated sulphuric acid, it developed a deep blood-red coloration.

Crude acetyl-*p*-phenylenediamine, produced by the reduction with iron and very dilute acetic acid of *p*-nitroacetanilide, was purified

by extraction with dry benzene in a Soxhlet apparatus, when the solvent deposited colourless, acicular crystals melting at 162° . For this purification, benzene was preferred to toluene, because at the higher boiling point of the latter solvent the tarry impurity in the crude acetyl *p*-phenylenediamine was melted out and found its way into the crystallised product.

The purified acetyl-*p*-phenylenediamine was dissolved in quantities of about 0.5 gram in the least possible amount of acetone at the ordinary temperature. The acetone solution was cooled by surrounding the beaker with ice and salt, and excess of liquid nitrous anhydride was added, this reagent having been first carefully freed from nitrogen peroxide by passing in nitric oxide until the green colour of the liquid changed to blue. The acetone solution of diazo-compound containing excess of nitrous anhydride was treated with dry, well-cooled ether, when the acetyl-*p*-phenylene-diazoimide separated as a yellowish-white, voluminous, crystalline precipitate, the yield being about 75 per cent. of the calculated amount. After drying on a cold porous tile in a vacuum desiccator over phosphoric oxide, the product decomposed explosively at 127° .

Acetyl-p-aminobenzeneazo-β-naphthol from Acetyl-p-phenylene-diazoimide.—The coupling with β-naphthol took place even in the dry state at the ordinary temperature when the two reagents were ground together in a mortar. In the presence of aqueous sodium hydroxide, the reaction proceeded very readily, although a certain amount of frothing indicated that some diazo-nitrogen was eliminated before the condensation to azo-β-naphthol was complete: 0.1608 gram of diazoimide yielded 0.1658 gram of azo-derivative, being 55 per cent. of the calculated amount. The acetyl-*p*-aminobenzeneazo-β-naphthol thus obtained melted at $259\text{--}260^{\circ}$ (Meldola, T., 1905, **87**, 4), and gave on analysis $N=13.85$, $C_{18}H_{15}O_2N_3$ requiring $N=13.77$ per cent.

This azo-coupling took place with less loss of diazo-nitrogen in the presence of pyridine.

Acetyl-p-phenylenediazoimide was unstable at the ordinary temperature, and slowly evolved nitrogen, with the formation of amorphous, ill-defined products. When the total and diazo-nitrogen were estimated on the day of preparation, the following analytical results were obtained. The latter estimation was made by decomposing the freshly prepared diazoimide in the volumeter at 100° with diluted sulphuric acid (1 vol. H_2SO_4 , 4 vols. H_2O):

0.1020 gave 21.8 c.c. N_2 at 12° and 742.5 mm. $N=24.80$.

0.1327 „ 17.0 c.c. diazo- N_2 at 8° and 773 mm. $N=15.73$.

$C_8H_7ON_3 \cdot H_2O$ requires $N_3=23.46$; $N_2=15.64$ per cent.

Analyses made on older specimens gave lower percentages of

nitrogen, the amount of loss of this constituent depending on the lapse of time.

When dissolved in cold acetone and reprecipitated by ether, the diazoimide was further decomposed, and could not be recrystallised by purified from its decomposition products. These changes were due, not to hydrolysis of the acetyl group, but to the unstable nature of the diazo-complex. An acetyl determination by A. G. Perkin's method on the partly decomposed diazoimide gave Ac = 29.29, the calculated amount being 25.5 per cent.

The ordinary method of combustion for carbon and hydrogen failed for this diazoimide, inasmuch as the compound exploded violently when warmed in contact with copper oxide and a stream of air.

Acetyl-*p*-phenylenediamine dissolved in alcohol and treated with an ethereal solution of nitrous anhydride gave a pale pink, crystalline precipitate, separating on the addition of more ether. This product, which resembled the diazoimide formed in acetone solution, decomposed explosively at 95° and contained 23.18 per cent. of nitrogen; it coupled readily with β -naphthol.

Carefully purified benzoyl-*p*-phenylenediamine (0.5 gram) was added little by little to an acetone solution of blue nitrous anhydride free from nitrogen peroxide, the mixture being thoroughly cooled in ice and salt. The benzoyl derivative dissolved, and on pouring well cooled ether into the clear bluish-green solution a yellow, crystalline solid separated, which was rapidly collected, washed successively with ether and light petroleum, and dried in a darkened desiccator over phosphoric oxide:

0.1134 gave 18.7 c.c. N_2 at 19° and 759 mm. $\text{N} = 18.92$.

$\text{C}_{13}\text{H}_9\text{ON}_3$ requires $\text{N} = 18.83$ per cent.

Benzoyl-p-phenylenediazoimide is a pale yellow, crystalline powder decomposing explosively at 139°. When stirred into a suspension of β -naphthol in pyridine a red azo-derivative was obtained melting at 211°. Concentrated sulphuric acid gave a blue coloration, changing to violet. The azo-compound was evidently benzoyl-*p*-aminobenzeneazo- β -naphthol, identical with the product obtained by coupling with alkaline β -naphthol the benzoyl-*p*-aminobenzene-diazonium nitrite and hydrogen carbonate previously described (T., 1905, 87, 934).

When coupled with alkaline β -naphthol, the diazoimide underwent partial decomposition as shown by frothing, and the yield of

benzoyl- β -aminobenzeneazo- β -naphthol is only about 62 per cent. In pyridine the coupling proceeded more smoothly, the yield of azo-derivative being 76.5 per cent. of the calculated amount.

Recrystallised benzoyl-1:4-naphthylenediamine (0.5 gram) was added slowly to an excess of liquefied nitrous anhydride freed from nitrogen peroxide and dissolved in dry acetone cooled by ice and salt. The benzoyl derivative dissolved, and from the clear bluish-green solution the diazoimide was separated as an orange, flocculent precipitate by the addition of dry ether. This product was rapidly collected, washed with dry ether, and dried over phosphoric oxide. The yield was considerably less than in the preceding experiment:

0.1012 gave 12.8 c.c. moist N_2 at 12° and 753 mm. $\text{N} = 14.88$.

$\text{C}_{17}\text{H}_{11}\text{ON}_3$ requires $\text{N} = 15.38$ per cent.

Benzoyl-1:4-naphthylenediazoimide decomposed at 123° , but without explosion. It coupled with β -naphthol and resorcinol to give deep red and nut-brown azo-derivatives respectively, the colorations with concentrated sulphuric acid being violet and crimson.

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