144. *A New Reaction of Certain Diazosulphonates derived from β-Naphthol-*1*-sulphonic Acid. Part X. Preparation of Phthalazine Derivatives from* 4-*Aminoazobenzene and* 4′-*Nitro*-4-*aminoazobenzene.*

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In testing qualitatively the generality of the reaction by which complex phthalazine derivatives are formed from certain diazosulphonates, we found that the only compounds which gave rise to this reaction, and which did not contain a nitro-group, were derivatives of 4-aminoazobenzene and its sulphonic acid (J., 1926, 692). The reaction has now been examined more closely, the diazosulphonate from 4-aminoazobenezene being used, and also its 4′-nitro-derivative for purposes of comparison.

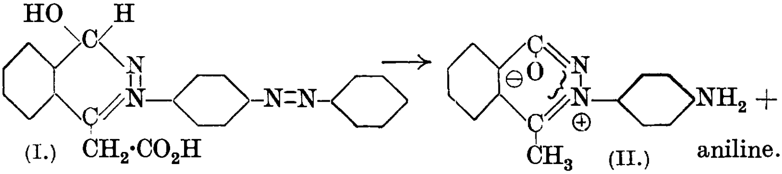
Pure aminoazobenzenes and their derivatives of any desired orientation are prepared conveniently by coupling any diazo-compound with the ω-sodium methanesulphonate of any benzenoid amino-compound, followed by hydrolysis with hot dilute hydrochloric acid or with boiling aqueous sodium hydroxide (compare Bucherer, D.R.-P. 157,909; Akt. Ges. für Anil.-Fabr., D.R.-P. 131,860). The ω-sodium methanesulphonates are formed quantitatively, and coupling, which in some cases is preferably accelerated by the use of sodium bicarbonate in place of sodium acetate, and subsequent hydrolysis also are almost quantitative.

Benzeneazobenzene-2-naphthol-1-diazosulphonate is formed readily from diazotised 4-aminoazobenzene and β-naphthol-1-sulphonic acid in acid solution, but it does not dissolve in sodium carbonate, and the conversion into sodium 1-(benzeneazobenzeneazo)-β-naphthaquinone-1-sulphonate is slow. This conversion must be allowed to occur completely, however, as even under the best conditions *sodium hydrogen* 3-(*benzeneazobenzene*)-1 : 3-*dihydrophthalazine*-1-*sulphonate*-4-*acetate* is formed by the subsequent action of sodium hydroxide only to a minor extent (yield, 19·3%), the principal product being benzeneazobenzeneazo-β-naphthol (Sudan III), which is formed by decomposition. The sodium hydrogen salt is converted readily into a *barium* salt, but otherwise resembles the corresponding nitro-compounds previously prepared in general properties, except that its orange-yellow dyeings are very sensitive to mineral acids, being coloured deep violet. The replacement of the sodium-1-sulphonate group by hydroxyl, which requires care owing to the sparing solubility of the free sulphonic acid in presence of mineral acid, gives 1-*hydroxy*-3-(*benzeneazobenzene*)-1 : 3-*dihydrophthalazine*-4-*acetic acid* (I), from which *esters*, an *acetyl* derivative, and an *anilide* were obtained.

Sodium hydrogen 3-(4′-*nitrobenzeneazobenzene*)-1 : 3-*dihydrophthalazine*-1-*sulphonate*-4-*acetate*, as anticipated, is formed much more readily (yield, 63·4%) and gives 1-*hydroxy*-3-(4′-*nitrobenzeneazobenzene*)-1 : 3-*dihydrophthalazine*-4-*acetic acid*, from which an *acetyl* derivative and an *anilide* were obtained, but the esters are very sensitive to acids and have not yet been obtained pure.

In agreement with the constitutions attributed to them, 1-hydroxy-3-(benzeneazobenzene)-1 : 3-dihydrophthalazine-4-acetic acid and its 4′-nitro-derivative are reduced to 1-hydroxy-3-(4′-aminophenyl)-tetrahydrophthalazine-4-acetic acid (*loc. cit.*, p. 702) and aniline or *p*-phenylenediamine respectively. In the latter case reduction proceeds satisfactorily with alkaline hydrosulphite (hyposulphite), but in the former case stannous chloride and hydrochloric acid are necessary.

When 1-hydroxy-3-(4′-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic acid is boiled with dilute sulphuric acid (b. p. 140°), acetic acid is eliminated and 4′-nitro-3-phenylphthalaz-1-one is formed (J., 1928, 2553), whereas treatment with cold acid dichromate results in decarboxylation of the acetic acid side-chain with formation of 4′-nitro-3-phenyl-4-methylphthalaz-1-one (J., 1931, 1070). In view of these results, the behaviour of 1-hydroxy-3-(benzeneazobenzene)-1 : 3-dihydrophthalazine-4-acetic acid (I) and its 4′-nitro-derivative when boiled with dilute sulphuric acid under similar conditions is remarkable, for the product in each case is 4′-amino-3-phenyl-4-methylphthalaz-1-one (II) (*ibid.*, p. 1072), together with aniline or *p*-nitroaniline respectively; *e.g.*,


(I.) (II.) + aniline.

In neither case was there any trace of the anticipated phthalazone derivative with the azobenzene residue in position 3. It is noteworthy, not only that decarboxylation occurred in the present instance instead of the elimination of acetic acid as in all other examples yet examined, but that fission of the azo-group also occurred. We have found only two references in the literature to the fission of azo-compounds by acid : Limpricht (*Ber.*, 1882, **15**, 1155) obtained sulphanilic acid, or a mixture of sulphanilic and metanilic acids respectively, by heating azobenzene-4 : 4′- or 4 : 3′-disulphonic acid with dilute hydrochloric acid (1 : 2) in a sealed tube at 150°; and Wallach and Kölliker (*Ber.*, 1884, **17**, 395), in investigating the formation of indulines, found that refluxing 4-aminoazobenzene hydrochloride with hydrochloric acid also gave aniline, *p*-phenylenediamine and various chlorinated quinols. These cases were regarded as reductions, but although with 1-hydroxy-3-(4′-nitrobenzeneazobenzene)-1:3-dihydrophthalazine-4-acetic acid some *p*-phenylenediamine also can be detected, the main product of this portion of the molecule is *p*-nitroaniline, so that this fission can scarcely be due to reduction, because it would not be anticipated that an azo-group would be reduced preferentially in presence of a nitro-group.

In view of the complex nature of these azo-compounds, we have also examined qualitatively the behaviour of some simple azo-compounds of various types when boiled with dilute sulphuric acid and found that a corresponding fission appears to be an unsuspected general reaction of azo-compounds. For example, benzene-azo-β-naphthol and its 4′-nitro-derivative (Para red) give aniline and *p*-nitroaniline respectively, together with a little *p*-phenylenediamine in the latter case. A comprehensive investigation of this reaction is now in progress, and it appears that with ordinary azo-dyes the fission is more probably due to hydrolysis than to reduction.

EXPERIMENTAL.

Sodium Hydrogen 3-(*Benzeneazobenzene*)-1 : 3-*dihydrophthalazine*-1-*sulphonate*-4-*acetate*.—A filtered solution of commercial 50% sodium β-naphthol-1-sulphonate (55 g.) in water (250 c.c.) was stirred slowly at 0° into a suspension of the sulphate of diazotised 4-aminoazobenzene. The latter was obtained by pouring a solution of 4-aminoazobenzene (19·7 g.) in cold concentrated sulphuric acid (50 c.c.) on ice (200 g.), adding a concentrated aqueous solution of sodium nitrite (7·1 g.), and stirring for 2 hours until the sulphate of the base was replaced by red crystals of the diazosulphate. The benzeneazobenzene-2-naphthol-1-diazosulphonate separated as a brown precipitate and the mixture was stirred for ½ hour. The precipitate was filtered off, washed free from acid with brine, made into a paste with cold water (350 c.c.), and stirred into a cold solution of anhydrous sodium carbonate (30 g.) in water (80 c.c.). The mixture was left for ¼ hour until the brown suspension was replaced by an orange precipitate of sodium 1-(benzeneazobenzeneazo)-β-naphthaquinone-1-sulphonate. The alkaline suspension was then added to a cold solution of sodium hydroxide (20 g.) in water (40 c.c.); a complete solution was not obtained, and the deep brown mixture was left over-night until the colour had changed completely to yellowish-brown. The pure product was isolated in the usual manner, after separation from much benzeneazobenzeneazo-β-naphthol. *Sodium hydrogen* 3-(*benzeneazobenzene*)-1 : 3-*dihydrophthalazine*-1-*sulphonate*-4-*acetate* (yield, 9·1 g.; 19·3%, calculated on the 4-aminoazobenzene) crystallised from alcohol in orange-brown leaflets containing 2½ mols. of alcohol of crystallisation and formed an amorphous black powder after removal of the alcohol (Found: loss at 125°, 19·6. $C_{22}H_{17}O_5N_4SNa,2\frac{1}{2}C_2H_6O$ requires C_2H_6O, 19·6%. Found in material dried at 125°: S, 6·6. $C_{22}H_{17}O_5N_4SNa$ requires S, 6·8%). It was readily soluble in water, but less soluble in alcohol, forming orange-yellow solutions, deepened in colour by the addition of alkali. It is a level-dyeing, orange-yellow acid dye of good tinctorial power, but fugitive to light and very sensitive to mineral acids, which colour it deep violet, although the shade is unaltered by acetic acid. On addition of barium chloride solution to a boiling solution of the sodium hydrogen salt (5 g.) in water (50 c.c.), the sparingly soluble *barium* salt separated in light orange-brown leaflets, which, when recrystallised from boiling water, contained 7 mols. of water of crystallisation, and formed a black semi-crystalline powder after removal of the water [Found : loss at 125°, 10·9. $(C_{22}H_{17}O_5N_4S)_2Ba,7H_2O$ requires H_2O, 10·85%. Found in material dried at 125° : S, 6·3 ; Ba, 13·0. $(C_{22}H_{17}O_5N_4S)_2Ba$ requires S, 6·2 ; Ba, 13·2%].

1-*Hydroxy*-3-(*benzeneazobenzene*)-1 : 3-*dihydrophthalazine*-4-*acetic Acid* (I).—A solution of the preceding sodium hydrogen salt (20 g.) in water (200 c.c.) was boiled, and concentrated hydrochloric acid (5 c.c.) added drop by drop (to avoid precipitation of the free sulphonic acid) until sulphur dioxide was evolved steadily and an oil separated. Concentrated hydrochloric acid (35 c.c.) was then added gradually, and boiling continued until the evolution of sulphur dioxide had ceased and the product had formed a light brown powder. The latter was washed with boiling water, dissolved in dilute sodium carbonate solution, boiled (charcoal), and filtered, and the filtrate precipitated with acetic acid. 1-*Hydroxy*-3-(*benzeneazobenzene*)-1 : 3-*dihydrophthalazine*-4-*acetic acid* crystallised from ethyl acetate in orange-yellow plates or flat needles, m. p. 177° (yield, 10·5 g.; 64·2%) (Found : C, 68·6 ; H, 4·7 ; N, 14·5. $C_{22}H_{18}O_3N_4$ requires C, 68·4 ; H, 4·7 ; N, 14·5%), readily soluble in alcohol, acetone, or glacial acetic acid, but very sparingly soluble in benzene. It was very sparingly soluble in water, forming a solution acid to litmus, but dissolved in sodium carbonate with an orange-brown colour, in sodium hydroxide with a deep red colour, and in cold concentrated sulphuric acid with an orange colour, being reprecipitated unaltered on dilution.

Derivatives of 1-*Hydroxy*-3-(*benzeneazobenzene*)-1 : 3-*dihydrophthalazine*-4-*acetic Acid.*—*Methyl ester.* A solution of the acid (3 g.) in dry methyl alcohol (50 c.c.) was saturated with dry hydrogen chloride at 0°, left over-night, and then boiled under reflux for 2 hours. The alcohol was removed, and the resinous residue repeatedly taken up with dry methyl alcohol and evaporated under reduced pressure until all trace of acid was removed. The *ester* then crystallised from methyl alcohol in long orange-yellow needles, m. p. 153° (Found : C, 68·8 ; H, 5·0 ; N, 14·15. $C_{23}H_{20}O_3N_4$ requires C, 69·0 ; H, 5·0 ; N, 14·0%). The *ethyl* ester, similarly prepared (60 c.c. of ethyl alcohol), crystallised from ethyl alcohol in stout orange prisms, m. p. 142—143° (Found : C, 69·55 ; H, 5·5 ; N, 13·6. $C_{24}H_{22}O_3N_4$ requires C, 69·6 ; H, 5·3 ; N, 13·5%). Both esters were insoluble in sodium carbonate solution, but dissolved in hot sodium hydroxide with a deep red colour. The *acetyl* derivative crystallised from alcohol in orange-brown plates, m. p. 229° (Found : C, 67·4 ; H, 4·75 ; N, 13·0. $C_{24}H_{20}O_4N_4$ requires C, 67·3 ;

H, 4·7; N, 13·1%). It dissolved in hot sodium carbonate solution with a yellow colour and in cold sodium hydroxide with a deep red colour. The *anilide* crystallised from ethyl acetate in flat orange prisms or plates, m. p. 250° (Found: C, 72·95; H, 5·1; N, 15·1. $C_{28}H_{23}O_2N_5$ requires C, 72·9; H, 5·0; N, 15·2%), insoluble in sodium hydroxide.

Reduction of 1-*Hydroxy*-3-(*benzeneazobenzene*)-1 : 3-*dihydrophthalazine*-4-*acetic Acid.*—The finely powdered acid (4 g.) was added to a boiling solution of stannous chloride (16 g.) in concentrated hydrochloric acid (40 c.c.) and boiled for ¼ hour until completely dissolved. After cooling, the colourless solution was rendered alkaline with sodium hydroxide and filtered, the precipitate washed with sodium carbonate, and dilute hydrochloric acid added to the united filtrate and washings until an almost white precipitate had separated completely. This crystallised from a large volume of boiling water in colourless prisms, m. p. 239° (yield, 2·2 g.; 71%), not depressed by admixture with 1-hydroxy-3-(4′-aminophenyl)-tetrahydrophthalazine-4-acetic acid (J., 1926, 702) and identical with the latter in all respects. The filtrate from which this compound was isolated was rendered alkaline and distilled with steam. The distillate contained aniline, confirmed by conversion into acetanilide, m. p. 115°. Reduction with alkaline sodium hydrosulphite (hyposulphite) also gave some aniline, but 1-hydroxy-3-(4′-aminophenyl)tetrahydrophthalazine-4-acetic acid could not be isolated from the mixture in this case.

Action of Boiling Aqueous Sulphuric Acid on 1-*Hydroxy*-3-(*benzeneazobenzene*)-1 : 3-*dihydrophthalazine*-4-*acetic Acid.*—A solution of the acid (10 g.) in concentrated sulphuric acid (50 c.c.) was diluted with water (60 c.c.) and boiled (b. p. 140°) under reflux. A violet-red solution was soon obtained, which gradually changed to red, and was almost colourless after 1½ hours' boiling. The mixture was diluted with water (200 c.c.), boiled (charcoal), and filtered, and the filtrate neutralised with sodium hydroxide and then rendered strongly alkaline with sodium carbonate. The brownish-yellow precipitate crystallised first from alcohol and then from pyridine in yellow needles, m. p. 277°, not depressed by admixture with 4′-amino-3-phenyl-4-methylphthalaz-1-one (II) (J., 1931, 1072); the identity was confirmed by conversion into the acetyl derivative, colourless prismatic needles, m. p. and mixed m. p. 316—317° (*loc. cit.*).

Sodium Hydrogen 3-(4′-*Nitrobenzeneazobenzene*)-1 : 3-*dihydrophthalazine*-1-*sulphonate*-4-*acetate.*—This was prepared from 4′-nitro-4-aminoazobenzene (24 g.) suspended in concentrated hydrochloric acid (70 c.c.) and water (250 c.c.), and diazotised in the usual way, but otherwise the procedure was similar to that employed for the corresponding un-nitrated compound (*loc. cit.*). 4′-Nitrobenzeneazobenzene-2-naphthol-1-diazosulphonate separated as a red precipitate, which did not dissolve in sodium carbonate solution, although the colour deepened. With sodium hydroxide the temperature rose several degrees and the deep brown mixture was left over-night until the colour had changed completely to deep red. The product was isolated as usual, after separation from 4′-nitrobenzeneazobenzeneazo-β-naphthol. *Sodium hydrogen* 3-(4′-*nitrobenzeneazobenzene*)-1 : 3-*dihydrophthalazine*-1-*sulphonate*-4-*acetate* (yield, 32·5 g.; 63·4%) crystallised from alcohol in small red prisms containing 1½ mols. of alcohol of crystallisation and formed an amorphous, deep blackish-red powder after removal of the alcohol (Found: loss at 125°, 11·9. $C_{22}H_{16}O_7N_5SNa,1\frac{1}{2}C_2H_6O$ requires C_2H_6O, 11·8%. Found in material dried at 125° : S, 6·4. $C_{22}H_{16}O_7N_5SNa$ requires S, 6·2%). It was readily soluble in water and moderately readily soluble in alcohol, forming orange-red solutions, deepened in colour by the addition of alkali. It is a level-dyeing orange-red acid dye of good tinctorial power, but fugitive to light and very sensitive to mineral acids, which colour it deep violet to blue according to the concentration.

1-*Hydroxy*-3-(4′-*nitrobenzeneazobenzene*)-1 : 3-*dihydrophthalazine*-4-*acetic Acid*.—This was prepared from the preceding sodium hydrogen salt (75 g.). It crystallised from ethyl acetate in red plates, m. p. 222—223° (yield, 35 g.; 56%) (Found: C, 61·2; H, 4·1; N, 16·35. $C_{22}H_{17}O_5N_5$ requires C, 61·25; H, 3·9; N, 16·2%), readily soluble in alcohol, acetone or glacial acetic acid, but sparingly soluble in benzene. It was very sparingly soluble in water, forming a solution acid to litmus, but dissolved in sodium carbonate with a brownish-red colour (cold) or blue (hot), and in cold sodium hydroxide with a deep blue colour. It dissolved in cold concentrated sulphuric acid with a magenta-red colour, being reprecipitated unaltered on dilution. The esters are very sensitive to acids and have not yet been obtained pure. The *acetyl* derivative, obtained by refluxing with equal volumes of acetic anhydride and pyridine, crystallised from ethyl acetate in small, bright red prisms, m. p. 197° (decomp.) (Found: C, 60·95; H, 4·0; N, 14·7. $C_{24}H_{19}O_6H_5$ requires C, 60·9; H, 4·0; N, 14·8%). It dissolved in hot sodium carbonate solution with a yellowish-brown colour and in cold sodium hydroxide with a deep blue colour. The *anilide* crystallised first from toluene and then from ethyl acetate in brick-red prisms, m. p. 281° (decomp.) (Found: C, 66·35; H, 4·4; N, 16·5. $C_{28}H_{22}O_4N_6$ requires C, 66·4; H, 4·35; N, 16·6%), insoluble in sodium hydroxide.

Reduction of 1-*Hydroxy*-3-(4′-*nitrobenzeneazobenzene*)-1 : 3-*dihydrophthalazine*-4-*acetic Acid*.—Hydrosulphite was added gradually to a solution of the acid (5 g.) in water (75 c.c.) and sodium hydroxide (5 g.) at 90° until the deep blue colour had changed through red to yellow, the mixture being kept alkaline throughout by the addition of sodium hydroxide. The solution was filtered, and hydrochloric acid added to the cold filtrate until a white precipitate had separated completely. This crystallised from a large volume of boiling water in colourless prisms, m. p. 239° (yield, 1·8 g.; 51·9%), not depressed by admixture with 1-hydroxy-3-(4′-aminophenyl)tetrahydrophthalazine-4-acetic acid. The filtrate from which this compound was isolated contained *p*-phenylenediamine. This was isolated in the usual way and identified by conversion into the diacetyl derivative, m. p. and mixed m. p. 305°.

Action of Boiling Aqueous Sulphuric Acid on 1-*Hydroxy*-3-(4′-*nitrobenzeneazobenzene*)-1 : 3-*dihydrophthalazine*-4-*acetic Acid*.—The reaction was carried out under similar conditions to those described for the corresponding unnitrated compound (p. 1123), except that boiling was continued for 2 hours. The precipitate, isolated as before, consisted of a mixture of two compounds, which were readily separated by means of their difference in solubility in ethyl acetate. The more soluble compound crystallised from water in yellow prismatic needles, m. p. 147°, and was *p*-nitroaniline, as it did not depress the m. p. of the latter, and acetylation gave *p*-nitroacetanilide, m. p. and mixed m. p. 210°. The less soluble compound crystallised from pyridine in yellow needles, m. p. 277°, not depressed by admixture with 4′-amino-3-phenyl-4-methylphthalaz-1-one; acetyl derivative, m. p. and mixed m. p. 316—317°.

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