168. *Decomposition Reactions of the Aromatic Diazo-compounds. Part XII. The Reaction between Diazo-compounds and Potassium Ferrocyanide.*

By M. C. Ford, William A. Waters, and H. T. Young.

The conditions under which aromatic diazo-compounds react with potassium ferrocyanide solution to yield arylazodiaryls have been studied, and it has been found that the decomposition proceeds most smoothly at pH 4—5 in the presence of a sodium acetate buffer. Yields of about 20% can be obtained with substituted aromatic amines, $R\cdot C_6H_4\cdot NH_2$, when the substituent R = Me or Cl, but both with the strongly *op*-directive substituent OMe and with the *m*-directive substituent NO_2 the yield falls to under 0·5%.

Both degradative and synthetic reactions have been carried out to establish the structures of the unsymmetrical arylazodiaryls obtained from *o*- and *p*-toluidine, *p*-chloroaniline, and α-naphthylamine. When the substituent R occupies the *p*-position to the nitrogen in the original amine, the reaction product is the 2-aryl derivative of a 4 : 4′-substituted azobenzene, and when R is an *o*-substituent the product is a 4-aryl derivative of a 2 : 2′-substituted azobenzene. Isomeric reaction products do not appear to be formed in appreciable amount. Possible mechanisms of this reaction are discussed.

In Part XI (*J.*, 1946, 1154) Saunders and Waters drew attention to the fact that 4-phenylazobenzene (I; R = H) can be prepared by treating aqueous solutions of benzenediazonium salts with potassium ferrocyanide, and suggested that free phenyl radicals might play some part in this rather unusual diazo-decomposition. We have now made an experimental study of this reaction, which since its discovery by Griess (*Ber.*, 1876, **9**, 132) has received scarcely any attention during this century, and we have established the structures of the unsymmetrical arylazodiaryls which can be prepared from diazotised *o*- and *p*-toluidine, *p*-chloroaniline, and α-naphthylamine.

The account given by Griess is very brief, and it was left to Locher (*Ber.*, 1888, **21**, 911) to show that Griess's reaction product, $C_{18}H_{14}N_2$, m. p. 150°, was probably 4-phenylazobenzene since it could be reduced to a mixture of aniline and *p*-aminodiphenyl (m. p. 50—51°). We have confirmed this work and have obtained from Griess's azo-compound pure *p*-acetamidodiphenyl having a melting point which was unchanged after admixture with an authentic specimen.

On investigating the conditions under which 4-phenylazobenzene can be obtained from aqueous solutions of benzenediazonium sulphate or chloride and potassium ferrocyanide, we found that, though the evolution of nitrogen commences immediately the reactants are mixed at, or below, room temperature, the yield of the desired reaction product is greatly increased by first buffering the diazonium salt solution to pH 4—5 by addition of an excess of sodium acetate. However, if the diazo-solution is first made neutral with sodium hydroxide or sodium hydrogen carbonate, only tarry products result. The organic reaction product usually separates as a filterable solid as the nitrogen is evolved. The reaction can in every case be completed at room temperature and it leaves a purple or brown aqueous solution which does not couple with alkaline β-naphthol. In some cases there was an indication that an intermediate solid diazonium ferrocyanide may be formed. After the reaction is over, the aqueous solution contains ferricyanide anions, showing that the reaction is essentially a reduction of the aromatic diazo-compound. The yields of the desired organic products were not appreciably altered by changing from the procedure of adding aqueous potassium ferrocyanide to a stirred buffered solution of benzenediazonium sulphate to the reverse procedure of adding the diazo-solution to the stirred ferrocyanide (contrast the Sandmeyer reaction), and so for convenience the second procedure was generally used with the other diazonium compounds.

When working with diazotised aniline and *p*-toluidine, there was no advantage in taking much more potassium ferrocyanide than the amount indicated by the simplified equation

$$3R\cdot C_6H_4\cdot N_2^+ + 2[Fe(CN)_6]^{4-} \longrightarrow R\cdot C_6H_4\cdot C_6H_3R\cdot N_2\cdot C_6H_4R + H^+ + 2[Fe(CN)_6]^{3-}$$

but when working with diazotised *p*-chloroaniline the yield of arylazodiaryl could be almost doubled by using 2 moles of ferrocyanide per mole of diazo-compound. In no case, however, was the overall yield of pure material more than 20%.

The products remaining in the aqueous layer were regularly investigated. These solutions invariably smelt of *iso*cyanide and, when heated, deposited Prussian-blue. On steam-distillation, however, they yielded only very small amounts of the nitriles, $R\cdot C_6H_4\cdot CN$, corresponding to the original amines, and no detectable amounts of the corresponding phenols,

$R{\cdot}C_6H_4{\cdot}OH$, or of hydrocarbons $R{\cdot}C_6H_4{\cdot}H$ or $R{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}R$. Small amounts of hydroxyazo-dyes were always formed. When diazonium chlorides are used instead of diazonium sulphates no significant quantities of aryl chlorides can be detected. Hence this diazo-reaction does not correspond with the normal decomposition of a diazonium cation in water: $Ar{\cdot}N_2^+ + H_2O \longrightarrow Ar{\cdot}OH + H^+$ (cf. Part X, *J.*, 1942, 266, for Type I reactions of the aromatic diazo-compounds), and is not clearly related to the Sandmeyer reaction which Cowdrey and Davies (*J.*, 1949, S 48) have recently shown to be an intramolecular decomposition of a complex salt. It is therefore probable that the initial reaction which involves the oxidation of the ferrocyanide anion is a one-electron transfer, as indicated in equations (1*a*) and (1*b*), and that the final azo-compounds result from reactions involving free organic radicals. The recent demonstration by Merz and Waters (*J.*, 1949, 2427) that free aryl radicals do not react with water molecules adds support to this view.

$$(1a) \qquad Ar{\cdot}N_2^+ + [Fe(CN)_6]^{4-} \longrightarrow Ar{\cdot}N_2{\cdot} + [Fe(CN)_6]^{3-}$$

or

$$(1b) \qquad Ar{\cdot}N{:}N{\cdot}OH + [Fe(CN)_6]^{4-} \longrightarrow Ar{\cdot}N_2{\cdot} + (OH)^- + [Fe(CN)_6]^{3-}$$

followed by

$$(2) \qquad Ar{\cdot}N{:}N{\cdot} \longrightarrow Ar{\cdot} + N_2$$

As suggested in Parts X and XI, electron-transfer potentials may be significant in determining yields in reactions such as (1) above, and in this connection it was observed that the yield of isolatable arylazodiaryl became very small indeed when the selected aromatic diazo-compound contained either a strongly electron-donating ($+T$) substituent such as methoxyl, or a strongly electron-abstracting ($-I, -T$) substituent such as the nitro-group. From diazotised *p*-anisidine only a small yield of an intractable tar containing a little azoanisole was obtained; from diazotised *p*-nitroaniline the yield of arylazodiaryl dropped to 0·2% and no 4 : 4′-dinitroazobenzene could be identified, though tarry hydroxyazobenzene derivatives were formed in quantity.

The elucidation of the structures of the azo-compounds obtained from substituted aromatic amines yielded information of considerable interest. Griess (*loc. cit.*) in his account of the reaction between benzenediazonium nitrate and potassium ferrocyanide reported that the solid product, $C_{18}H_{14}N_2$, was mixed with a little azobenzene, which he separated by steam-distillation, and also with a " red oil " of unknown constitution. This red oil was later studied by Ehrenpreis (*Chem. Zentr.*, 1907, I, 1789), who reduced it to a product of m. p. 135—138° which he believed to be triphenylhydrazine, and reported that it gave an acetyl derivative of m. p. 152°. Both Busch and Holbein (*Ber.*, 1907, **40**, 2099) and Wieland and Reverdy (*Ber.*, 1915, **48**, 1112), however, have shown that triphenylhydrazine does not have these properties. Ehrenpreis's compounds may perhaps be semidine derivatives. We have examined further the red oil which remains as the mother-liquor from the crystallisation of 4-phenylazobenzene (I; R = H) from the crude product of the Griess reaction, and have found that on distillation at low pressures it yields a considerable proportion of azobenzene and leaves a residue from which more 4-phenylazobenzene can be separated. We have also attempted to separate chromatographically further components of this oil, and have carried out repeated fractional crystallisations. In consequence of all our work we conclude that it is essentially a mixture of 4-phenylazobenzene with azobenzene, and, in particular, that no appreciable quantities of any isomers of 4-phenylazobenzene are present.

Locher (*loc. cit.*), who carried out the ferrocyanide decomposition with diazotised toluidines and with diazotised α-naphthylamine, reported that *o*-toluidine gave a " *o*-di-tolyl-*o*-azotoluene " of m. p. 104°. We have now found that this product separates in a comparatively pure state, in 22% yield, from the reaction mixture together with about 1% of 2 : 2′-azotoluene * and a very little *o*-tolunitrile. Isomers of Locher's product were sought, but none found. The main reaction product has the structure of 4-*o*-tolyl-2 : 2′-azotoluene (I; R = Me) since it could be reduced to a mixture of *o*-toluidine and an aminoditolyl (II). The latter gave *o*-toluic acid on chromic acid oxidation (thus confirming the orientation in ring B), and on bromination at room temperature it gave only a monobromo-derivative, so that the two substituents in ring A must occupy *o*- and *p*-positions to the amino-group. Nitration with copper nitrate and acetic anhydride (Menke, *Rec. Trav. chim.*, 1925, **44**, 141; Waters, *J.*, 1935, 1875) of the acetyl derivative of the base (II), followed by hydrolysis, yielded an *o*-nitro-amine, since it was successfully reduced to a diamine which condensed with phenanthraquinone to give a phenazine derivative. Assuming that the *o*-tolyl configuration is retained

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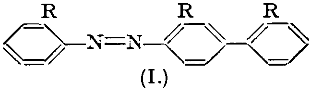
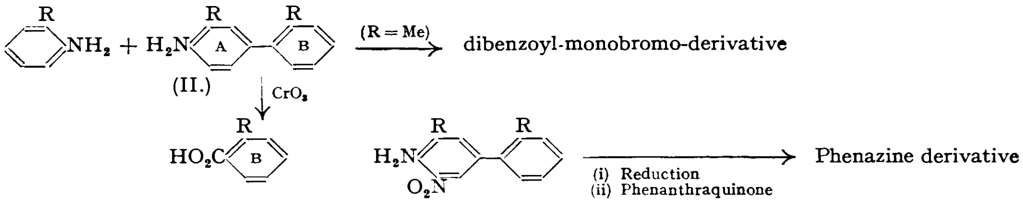
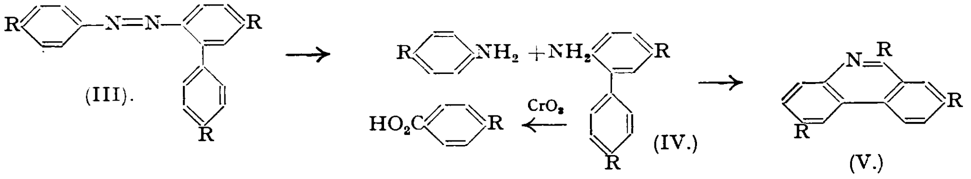
* **In the azotoluenes the prefixed numerals refer to the positions of the methyl groups.**

in regard to the methyl group in ring A of the base (II), it follows that the original " *o*-ditolyl-*o*-azotoluene " can only have the structure (I).


(I.)



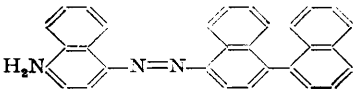
From diazotised *p*-toluidine Locher isolated a " *p*-ditolyl-*p*-azotoluene " of m. p. 118°; we found that this compound is mixed with small quantities of 4 : 4′-azotoluene and of *p*-tolunitrile, and that it is not accompanied by significant amounts of any isomers. The product is 2-*p*-tolyl-4 : 4′-azotoluene (III; R = Me) since reduction gave *p*-toluidine together with an aminoditolyl (IV; R = Me) which (i) was oxidised to *p*-toluic acid, (ii) yielded only a monobromo-derivative in the cold, and (iii) gave an acetyl derivative which could be condensed to 3 : 7 : 9-trimethylphenanthridine (V; R = Me). Morgan and Walls (*J.*, 1930, 1507) obtained the same amine (IV; R = Me) by pyrolysis of diazoamino-*p*-toluidine and established its structure by conversion into 2 : 6-dimethylcarbazole, which they then synthesised by another route.



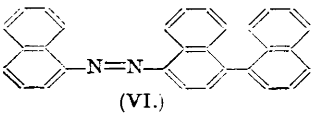
Diazotised *p*-chloroaniline, with which this reaction had not previously been performed, yielded the analogous product, 4 : *4′-dichloro-2-*p*-chlorophenylazobenzene* (III; R = Cl) with which again the reaction sequence given in the diagram above was successfully carried out. The main reaction product was, in this case, isolated by extraction (Soxhlet) with light petroleum of the bulky brown material which separates from the aqueous reaction mixture. There remains an insoluble residue which exhibits reactions indicative of a polyazo-compound but does not appear to contain isomers of (III). Again, small amounts of 4 : 4′-dichloroazobenzene and of *p*-chlorobenzonitrile were formed. *p*-Nitroaniline gives a similar product [probably (III; R = NO_2)] but only in 0·2% yield. Unfortunately, its structure cannot be established by the same reaction sequence, since reduction would also affect the nitro-groups.

From diazotised α-naphthylamine Locher obtained 1 : 1′-azonaphthalene and another substance. We found that this second compound can be extracted from the solid reaction product in about 9% yield, and it proves to be 4-α-naphthyl-1 : 1′-azonaphthalene (VI). It was synthesised by reducing 4-nitro-1 : 1′-dinaphthyl (Schoepfle, *J. Amer. Chem. Soc.*, 1923, **45**, 1566) to the corresponding *amine* (VII), coupling this with α-naphthylamine and then deaminating the resulting azo-dye (VIII). Reduction of (VI) was also attempted, but the reaction product proved to be 3-α-naphthyl-1 : 2 : 7 : 8-dibenzcarbazole (IX) and not the amine (VII). The production of a dibenzcarbazole derivative affords confirmatory evidence of the structure (VI) of the azo-compound, since carbazole formation can only occur if both β-positions adjacent to the azo-group are unsubstituted.

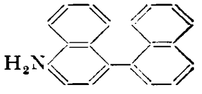
It will be seen, therefore, that in all these reactions between substituted aromatic diazo-compounds and potassium ferrocyanide an azobenzene derivative is formed in which an aryl residue occupies the *p*-position to the azo-group whenever possible. If this position is blocked in the original amine, the aryl residue occupies the *o*-position to the azo-group. Neither isomers nor symmetrical diarylazodiaryl derivatives appear to be formed. Furthermore, the nitrogen atoms of the substituted bases, $R{\cdot}C_6H_4{\cdot}NH_2$, retain throughout their original orientations relative to the group R, and the whole distinctive reaction can be viewed as an aromatic substitution by a $R{\cdot}C_6H_4{\cdot}$ group.



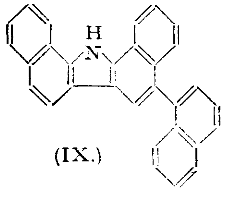
(VIII.)



(VI.)



(VII.)



(IX.)

When this investigation was commenced, it was hoped that the elucidation of the structures of the arylazodiaryls obtainable from substituted aromatic diazo-compounds would help to establish whether the substituting aryl group reacts in the form of a cation or of an electrically neutral radical, but as yet no clear discrimination between plausible alternatives can be made.

Our results show that arylation has occurred in the *p*- or *o*-position to an azo-, or diazo-, group, and not in the *p*- or *o*-position to electron-donating substituents such as Me or Cl. However, since only 1—2% of the simple arylazoaryl compounds could be isolated in comparison with 10—20% of arylazodiaryls, it is improbable that our reaction proceeds by way of arylation of a symmetrical azobenzene derivative, and indeed an attempt to phenylate azobenzene in acetone solution (cf. Part VI, *J.*, 1939, 870) failed. The most probable alternatives therefore require that the diaryl group should be formed at an early stage of the reaction, *i.e.*:

(*a*) By arylation of a diazonium cation :

$$R{\cdot}C_6H_4{\cdot} + (R{\cdot}C_6H_4{\cdot}N_2)^+ \longrightarrow (R{\cdot}C_6H_4{\cdot}C_6H_3R{\cdot}N_2)^+ + H^+$$

followed by

$$(R{\cdot}C_6H_4{\cdot}C_6H_3R{\cdot}N_2)^+ + R{\cdot}C_6H_4{\cdot} + e \longrightarrow R{\cdot}C_6H_4{\cdot}C_6H_3R{\cdot}N{:}N{\cdot}C_6H_4R$$

or (*b*) by arylation of a covalent diazo-hydroxide :

$$R{\cdot}C_6H_4{\cdot} + R{\cdot}C_6H_4{\cdot}N{:}N{\cdot}OH \longrightarrow R{\cdot}C_6H_4{\cdot}C_6H_3R{\cdot}N{:}N{\cdot}OH + H{\cdot}$$

Though the radical-type reactions suggested above seem to afford the best interpretation of our experimental work because of the absence of significant percentages of phenolic products (see p. 834) diagnostic of the presence of aryl cations, we nevertheless cannot exclude entirely cationoid substitutions by aryl ions because the observed *op*-substitution of azo-compounds is characteristic also of reactions involving cationoid attack. Thus 4 : 4′-dichloroazobenzene and 4 : 4′-azotoluene are both nitrated in position 2, adjacent to the $\cdot N{:}N\cdot$ group (see Houghton and Waters, *J.*, in the press). We would point out, however. that the simple polar substitution of a benzenediazonium cation, *i.e.*,

$$Ar^+ + (C_6H_5{\cdot}N_2)^+ \longrightarrow \text{products}$$

should give a *m*-substituted product (cf. the nitration of phenyltrimethylammonium salts) and this certainly is not formed.

EXPERIMENTAL.

Preparation of 4-*Phenylazobenzene*.—Aniline (23 g.), dissolved in hydrochloric acid (82 ml.) and water (50 ml.), was diazotised at 0—5° with sodium nitrite (18 g.) in water (50 ml.), and the resulting solution was buffered with a solution of sodium acetate (100 g.) in water (200 ml.). This cold solution was then added slowly to a stirred solution of potassium ferrocyanide (125 g.) in water (600 ml.) at room temperature. A dark red precipitate of benzenediazonium ferrocyanide formed at once, and decomposed gradually with evolution of nitrogen. The mixture was kept overnight, and the resulting brown solid was then collected, washed thoroughly with water and dilute alkali, and fractionally crystallised from alcohol (charcoal). In this way 4·4 g. (22%) of 4-phenylazobenzene were obtained in the form of orange-yellow crystals, m. p. 152° (Found : C, 83·6; H, 5·3; N, 10·9. Calc. for $C_{18}H_{14}N_2$: C, 83·75; H, 5·4; N, 10·9%). When the benzenediazonium ferrocyanide was separated at once it decomposed to give only a black tar.

The residue from the crystallisation of the 4-phenylazobenzene was a red oil which on distillation at 0·5 mm. pressure yielded 1% of azobenzene and a little more phenylazobenzene.

The aqueous filtrate from the reaction smelt strongly of phenyl *iso*cyanide. On distillation with steam it yielded a little azobenzene but not phenol, and a bulky precipitate of Prussian-blue separated.

When sodium acetate was not added the yield of 4-phenylazobenzene was only about 1%. Neutralisation of the benzenediazonium sulphate or chloride with sodium hydroxide or sodium hydrogen carbonate solutions led to formation of very tarry products.

Reduction of 4-phenylazobenzene with tin and alcoholic hydrochloric acid gave a mixture of aniline and 4-aminodiphenyl; from the latter, 4-acetamidodiphenyl, m. p. and mixed m. p. with an authentic specimen, 167°, was obtained.

4-o-*Tolyl*-2 : 2′-*azotoluene* (I; R = Me).—A solution of *o*-toluidine (1 mol.) in ice-cold 20% hydrochloric acid (540 ml., 3 mols.) was diazotised at 0—5° with sodium nitrite solution (75 g. in 200 ml. of water) and the product was buffered with a solution of hydrated sodium acetate (272 g., 2 mols.) in water (225 ml.). The resulting solution was slowly added to a mechanically stirred solution of potassium ferrocyanide (840 g., 2 mols.) in water (3 l.). Nitrogen was evolved gradually. After the mixture had been left overnight, the resulting red precipitate was collected and recrystallised from ethyl alcohol; yield, 22%. The pure product separated in orange-red platelets from methyl alcohol and had m. p. 105·5° (Ehrenpreis gives 104°) (Found: C, 84·2; H, 6·2; N, 9·2. Calc. for $C_{21}H_{20}N_2$: C, 84·0; H, 6·7; N, 9·3%).

The mother-liquors from the recrystallisations were combined, the solvent removed, and the residue distilled in a vacuum. From the combined residues from 5 mols. of *o*-toluidine there were obtained: (i) 0·5 g. of *o*-tolunitrile, b. p. 40°/1·5 mm., identified by hydrolysis to *o*-toluic acid, m. p. and mixed m. p. 103°, and (ii) 5 g. of 2 : 2′-azotoluene, m. p. and mixed m. p. 54°.

Reduction. A solution of the azo-compound (20 g.) in boiling alcohol (500 ml.) was added portion-wise to a solution of stannous chloride (112 g. of hydrate) in concentrated hydrochloric acid (112 ml.) at 100°. Each portion was immediately decolorised. (Note. Addition of stannous chloride solution to the azo-compound was unsatisfactory, as it gave an intractable mixture of involatile amines, possibly of semidine type.) The alcohol was removed from the completely reduced solution under diminished pressure, the residue was made strongly alkaline with sodium hydroxide and extracted with ether, and the bases were collected and distilled in a vacuum giving: (i) *o*-toluidine (2·5 g.), identified as its acetyl and benzoyl derivatives, and (ii) 4-amino-3 : 2′-ditolyl (7·1 g.), b. p. 92°/0·005 mm. This was a pale yellow viscous oil which rapidly darkened on storage. Its *acetyl* derivative crystallised from light petroleum (b. p. 60—80°) in fine matted needles, m. p. 143° (Found: C, 80·5; H, 7·22; N, 5·6. $C_{16}H_{17}ON$ requires C, 80·3; H, 7·2; N, 5·8%). Its *dibenzoyl* derivative, prepared by treating the base with an excess of benzoyl chloride in boiling pyridine, crystallised from alcohol in short needles, m. p. 140·5° [Found: C, 83·1; H, 5·7; N, 3·4%; *M* (Rast), 393. $C_{28}H_{23}O_2N$ requires C, 82·9; H, 5·7; N, 3·45%; *M*, 405]. Under the same conditions it was found that *N*-dibenzoyl derivatives were obtained from other *o*-substituted amines, including *o*-toluidine itself. The *picrate* of the base crystallised in stout yellow prisms, m. p. 198° (Found: N, 13·2. $C_{20}H_{18}O_7N_4$ requires N, 13·1%).

A portion of the base was oxidised with chromic acid in aqueous acetic acid solution and gave *o*-toluic acid, m. p. and mixed m. p. 102—103°. Another portion (2·0 g.) was dissolved in glacial acetic acid (50 ml.) containing anhydrous sodium acetate (2·5 g.) and a 3% solution of bromine in glacial acetic acid was added dropwise. When just over one molar equiv. (60 ml.) had been added free bromine remained in the solution. To ensure completion of the reaction a slight further excess of bromine was added, and after 5 minutes the mixture was poured into dilute alkaline sodium sulphite solution. The purple oily 5-bromo-4-amino-3 : 2′-ditolyl was collected. From a small part the *hydrochloride* was prepared and crystallised from alcoholic hydrochloric acid in glistening needles, m. p. 160° (decomp.) (Found: Cl + Br, 34·4. $C_{14}H_{14}NBr,HCl$ requires Cl + Br, 36·8%). The remainder was benzoylated as described above, and yielded 5-*bromo*-4-*dibenzamido*-3 : 2′-*ditolyl*, which crystallised from alcohol in rosettes of needles, m. p. 175° (Found: C, 69·4, 69·3*; H, 4·8, 4·7*; N, 3·0%; *M*, 485. $C_{28}H_{22}O_2NBr$ requires C, 69·5; H, 4·6; N, 2·9%; *M*, 484) (* denotes macro-analysis by Mr. F. C. Hall).

Nitration of 4-*Acetamido*-3 : 2′-*ditolyl*.—Powdered hydrated copper nitrate (7 g.) was added in small portions to a stirred suspension of acetamidoditolyl (10·5 g.) in acetic anhydride (50 ml.), kept at 25—30° in a bath of cold water. After an hour the clear green solution was poured into water, and the pale yellow 5-nitro-4-acetamido-3 : 2′-ditolyl (90%) was collected and hydrolysed by refluxing for 6 hours with a 30% solution of sulphuric acid in ethyl alcohol. After removal of the alcohol, the residue was poured into water and the resulting 5-*nitro*-4-*amino*-3 : 2′-*ditolyl* was crystallised repeatedly from aqueous methyl alcohol. It formed long orange needles, m. p. 95° (Found: C, 69·3; H, 5·9; N, 11·5. $C_{14}H_{14}O_2N_2$ requires C, 69·4; H, 5·8; N, 11·6%).

This base (0·5 g.) was reduced with an excess of zinc dust in boiling glacial acetic acid solution (25 ml.), and the purple solution was filtered into a solution of phenanthraquinone (0·4 g.) in hot glacial acetic acid (10 ml.). After the mixture had been heated for an hour it was poured into water, and a black powder separated. This was dissolved in acetone and passed down a column of activated alumina. On precipitation with water the eluted liquid gave a brown powder which was collected and crystallised repeatedly from benzene-light petroleum (b. p. 40—60°), to give eventually 12-o-*tolyl*-10-*methyl*-*phenanthrazine* (8-o-*tolyl*-6-*methyl*-1 : 2 : 3 : 4-*dibenzphenazine*) as very small light-brown needles, m. p. 192—193° (Found: C, 86·9; H, 5·0; N, 7·2. $C_{28}H_{20}N_2$ requires C, 87·4; H, 5·2; N, 7·3%). This substance gave a brilliant purple solution in concentrated sulphuric acid.

2-p-*Tolyl*-4 : 4′-*azotoluene*.—A diazotised solution of *p*-toluidine (1 mol.) was buffered with sodium acetate, as described above, and added slowly with stirring to a solution of potassium ferrocyanide (1 mol.) in water (1½ l.). A red diazonium ferrocyanide was precipitated, but quickly decomposed with evolution of nitrogen, leaving a dark brown solid and an aqueous liquid which did not react with alkaline β-naphthol. The solid (yield, 55—60%) was collected and extracted with hot alcohol. The tarry product was crystallised repeatedly from light petroleum (b. p. 60—80°) and then alcohol, to give pure 2-*p*-tolyl-4 : 4′-azotoluene in 10% yield, together with a much smaller amount of 4 : 4′-azotoluene, m. p. and mixed m. p. 142°. Attempts to isolate other products from the residual tar were not successful. The main product had m. p. 118°, in agreement with Ehrenpreis (Found: C, 83·7; H, 6·7; N, 9·6. Calc. for $C_{21}H_{20}N_2$: C, 84·0; H, 6·7; N, 9·3%).

The azo-compound was reduced with stannous chloride in alcoholic hydrochloric acid, and, after removal of the excess of alcohol, the solution was made alkaline and distilled in steam. *p*-Toluidine collected in the receiver as a white solid; its identity was confirmed. The remaining liquid was cooled, extracted with ether, and the *2-amino-5 : 4′-ditolyl* which had been formed was finally purified by distillation in a vacuum (b. p. 123—128°/0·4 mm.) (Found : C, 85·2; H, 7·6; N, 7·5. $C_{14}H_{15}N$ requires C, 85·3; H, 7·6; N, 7·1%). Its acetyl derivative crystallised from aqueous alcohol in long needles, m. p. 104° (Found : C, 80·3; H, 7·1; N, 5·6. Calc. for $C_{16}H_{17}ON$: C, 80·3; H, 7·1; N, 5·9%), and its *benzoyl* derivative formed white needles, m. p. 122° (Found : C, 83·4; H, 6·5; N, 4·8. $C_{21}H_{19}ON$ requires C, 83·7; H, 6·3; N, 4·7%). On treatment for 20 minutes with concentrated nitric acid, the acetyl derivative yielded a dinitro-compound, probably *3 : 2′-dinitro-2-acetamido-5 : 4′-ditolyl*, which crystallised from very dilute alcohol in yellow needles, m. p. 191° (Found : C, 58·7; H, 4·8; N, 13·0. $C_{16}H_{15}O_5N_3$ requires C, 58·4; H, 4·6; N, 12·8%).

On oxidation with chromic acid in aqueous acetic acid the 2-amino-5 : 4′-ditolyl (1 g.) gave *p*-toluic acid (0·2 g.), m. p. and mixed m. p. 177°.

3-Bromo-2-amino-5 : 4′-ditolyl.—2-Amino-5 : 4′-ditolyl (1 g.) was dissolved in carbon tetrachloride (20 ml.), a little powdered sodium acetate was added, and a 1% solution of bromine in carbon tetrachloride was slowly run into the mixture, cooled in ice. When excess of bromine was present, aqueous sulphurous acid was immediately stirred in to prevent further conversion into dark products. The carbon tetrachloride layer after separation, washing with water, and evaporation gave a dark residue from which white crystals of the *bromo*-base were obtained by crystallisation from aqueous methyl alcohol (charcoal); m. p. 68° (Found : C, 60·7; H, 5·1; Br, 28·8. $C_{14}H_{14}NBr$ requires C, 60·9; H, 5·1; Br, 28·9%). Its *acetyl* derivative crystallised from aqueous alcohol in white needles, m. p. 135° (Found : C, 60·2; H, 4·9. $C_{16}H_{16}ONBr$ requires C, 60·4; H, 5·0%), and its *monobenzoyl* derivative, prepared by the Schotten–Baumann method, formed white needles, m. p. 195° (Found : C, 66·0; H, 4·6. $C_{21}H_{18}ONBr$ requires C, 66·5; H, 4·5%).

3 : 7 : 9-Trimethylphenanthridine.—2-Acetamido-5 : 4′-ditolyl (1·3 g.) and phosphorus oxychloride (3 g.) were heated under reflux in nitrobenzene solution (15 ml.) with the addition of a drop of stannic chloride as catalyst. After 4 hours the evolution of hydrogen chloride had ceased. The mixture was then poured into water, nitrobenzene was removed by distillation in steam, and the remaining solid, consisting of the hydrochloride of 3 : 7 : 9-trimethylphenanthridine, was collected and crystallised from alcohol containing a little hydrochloric acid. It formed pale yellow felted needles which did not melt below 250°. The free *base* was prepared from this and purified by crystallisation from light petroleum (b. p. 60—80°); yield, 60%. It formed pale yellow prisms, m. p. 123° (Found : C, 87·0; H, 6·8; N, 6·4. $C_{16}H_{15}N$ requires C, 86·9; H, 6·8; N, 6·3%).

4 : 4′-Dichloro-2-p-chlorophenylazobenzene (III; R = Cl).—*p*-Chloroaniline (42·5 g., 0·33 mol.) in 25% hydrochloric acid (150 ml., 1 mol.) was diazotised below 5°, buffered with sodium acetate (91 g., 0·66 mol.) in water (75 ml.), and slowly added, with mechanical stirring, to a solution of potassium ferrocyanide (280 g., 0·66 mol.) in water (1 l.). Evolution of nitrogen was immediate and rapid and a few drops of butyl alcohol had to be added to control foaming. After the mixture had been left overnight, the light-brown precipitate was collected, dried (yield, 60%), and extracted thoroughly with light petroleum (b. p. 60—80°). A yellow crystalline solid was obtained, together with tar. By repeated crystallisation from acetic acid and then acetone the former gave, in 13% yield, pale yellow felted needles of *4 : 4′-dichloro-2-p-chlorophenylazobenzene*, m. p. 153° (Found : C, 60·2; 59·9; H, 3·2, 3·3; N, 7·8, 7·6; Cl, 29·4. $C_{18}H_{11}N_2Cl_3$ requires C, 59·8; H, 3·0; N, 7·8; Cl, 29·5%). The red tarry residue was evaporated and distilled in a vacuum. It gave a trace of *p*-chlorobenzonitrile, and then, at 120—170°/0·5 mm., an orange oil which solidified, and gave, on recrystallisation, orange needles of 4 : 4′-dichloroazobenzene (1%), m. p. and mixed m. p. 183°. Steam-distillation of the aqueous liquid from the initial reaction gave a further small quantity of *p*-chlorobenzonitrile, identified by hydrolysis to *p*-chlorobenzoic acid, m. p. and mixed m. p. 232°.

Reduction. 4 : 4′-Dichloro-2-*p*-chlorophenylazobenzene (10 g.) in boiling glacial acetic acid was treated, in portions, with zinc dust (15 g.). To complete the reduction a mixture of hydrochloric acid (5 ml.) in acetic acid (20 ml.) was subsequently added. The colourless solution was filtered hot, concentrated, and made strongly alkaline with 50% sodium hydroxide solution. The bases were extracted with ether, this solvent was removed, and the residue was extracted at 80° with five successive portions of hot water. The aqueous extract, on cooling, deposited *p*-chloroaniline (0·8 g.), identified by its acetyl and benzoyl derivatives (m. p.s and mixed m. p.s with authentic specimens 177° and 191°, respectively). The residue was a sticky product, and, since attempts at crystallisation failed, it was benzoylated in pyridine solution, and the benzoylated amines were fractionally crystallised from aqueous alcohol. *5 : 4′-Dichloro-2-benzamidodiphenyl* (2 g.) was thus obtained in white needles, m. p. 191° (Found : C, 66·7; H, 4·4; N, 4·0. $C_{19}H_{13}ONCl_2$ requires C, 66·7; H, 3·8; N, 4·1%) (C and H analysis by Mr. G. Ingram).

A small portion of the crude base was oxidised with chromic acid in acetic acid solution and gave *p*-chlorobenzoic acid, m. p. and mixed m. p. 232° (anilide, m. p. 195°).

3 : 7-Dichloro-9-phenylphenanthridine.—5 : 4′-Dichloro-2-benzamidodiphenyl (1 g.) and phosphorus oxychloride (3 g.) were heated under reflux for 6 hours in nitrobenzene solution (10 ml.) together with a few drops of stannic chloride. A further ml. of phosphorus oxychloride was then added, and the heating continued for another 10 hours. The product was poured into water and steam-distilled, and the solid residue was collected and recrystallised from alcoholic hydrochloric acid, yielding pale yellow needles of the hydrochloride of the phenanthridine. The free *base*, obtained by treating the salt with aqueous ammonia and extraction with ether, crystallised from benzene in colourless needles, m. p. 193°, not identical with those of the original dichlorobenzamidodiphenyl (m. p. 191°); yield, 50% (Found : C, 69·9; H, 3·6; N, 4·4. $C_{19}H_{11}NCl_2$ requires C, 70·4; H, 3·4; N, 4·3%) (C and H analysis by Mr. G. Ingram). This base gave a *picrate*, which crystallised from benzene in mustard-yellow needles, m. p. 220° (Found : N, 9·9. $C_{25}H_{14}O_7N_4Cl_2$ requires N, 10·1%). The ultra-violet absorption spectrum of the base in methyl-alcoholic solution (maxima at 2600, 3410, and 3575 A.) accorded with the phenanthridine structure.

4 : 4′-*Dinitro*-2-p-*nitrophenylazobenzene*.—*p*-Nitroaniline (46 g.) and sodium nitrite (25 g.) were ground to a smooth paste with water (100 ml.) and poured on a mixture of ice (100 g.) and concentrated hydrochloric acid (100 ml.). After being stirred for 10 minutes, the mixture was filtered into a solution of sodium acetate (91 g.) in water (100 ml.), and the product was slowly added to a mechanically stirred solution of potassium ferrocyanide (280 g.) in water (1 l.). A few drops of butyl alcohol were added to moderate the foaming which occurred. After the mixture had been left overnight, the black precipitate was collected, dried, and extracted with absolute alcohol (Soxhlet). The alcohol was then removed, the residue was boiled with 10% sodium hydroxide solution to remove hydroxyazo-compounds, and the alkali-insoluble residue was crystallised repeatedly from acetone and then from xylene. It gave the 4 : 4′-*dinitro*-2-p-*nitrophenylazobenzene* as a brick-red powder, m. p. 240° (decomp.) (yield, ¼%) (Found : N, 18·0. $C_{18}H_{11}O_6N_5$ requires N, 17·8%). In admixture with authentic 4 : 4′-dinitroazobenzene (m. p. 219°) (Calc. : N, 20·6%) the m. p. was lowered to 203°. When this was boiled with alcoholic ammonium sulphide and the product made strongly alkaline, an intense grass-green colour was produced. Under the same conditions 4 : 4′-dinitroazobenzene gave an intense blue colour.

The reaction described above for *p*-toluidine was repeated with *p*-anisidine. The product was a sticky tar from which by repeated crystallisation from methyl alcohol, yellow 4 : 4′-azoanisole, m. p. and mixed m. p. 158—159°, was eventually isolated in ½% yield, together with anisonitrile, m. p. 46°, in ¼% yield.

4-α-*Naphthyl*-1 : 1′-*azonaphthalene* (VI).—α-Naphthylamine (143 g., 1 mol.) was dissolved in hot 20% hydrochloric acid (500 ml.), cooled rapidly, and diazotised with aqueous sodium nitrite (5N.). The diazotised solution was buffered with sodium acetate (300 g.) in water (250 ml.) and then added gradually to a stirred solution of potassium ferrocyanide (928 g., 2 mols.) in water (2 l.). The evolution of nitrogen was immediate and rapid, and it was necessary to add drops of butyl alcohol to prevent foaming. After being left overnight, the brown precipitate was collected, dried (yield, 85%), and extracted for 2 days (Soxhlet) with light petroleum (b. p. 60—80°). The extract was concentrated to 250 ml., and the solid product, which contained much tar, was boiled with benzene, with the addition of charcoal (5 g.). This solution deposited a brown solid which, by successive crystallisations from alcohol, light petroleum (b. p. 60—80°), glacial acetic acid, and finally acetone, gave, in 9% yield, brick-red microscopic needles of 4-α-*naphthyl*-1 : 1′-*azonaphthalene*, m. p. 178° (Found : C, 87·3; H, 4·8; N, 6·9. $C_{30}H_{20}N_2$ requires C, 88·2; H, 4·9; N, 6·9%). This was also synthesised as follows.

4-Nitro-1 : 1′-dinaphthyl (Schoepfle, *loc. cit.*) (10 g.) in boiling alcohol (200 ml.) was treated with a solution of stannous chloride (45 g.) in concentrated hydrochloric acid (40 ml.). After refluxing for 1 hour the alcohol was removed, and the residue poured into 30% sodium hydroxide (300 ml.). The crude 4-*amino*-1 : 1′-*dinaphthyl* was collected, extracted with ether, and finally crystallised from alcohol. It formed pink nodules, m. p. 157—158° (8 g.) (Found : C, 89·3; H, 5·6; N, 5·4. $C_{20}H_{15}N$ requires C, 89·2; H, 5·6; N, 5·2%). Its *acetyl* derivative crystallised from aqueous pyridine in small white plates, m. p. 256·5° (Found : C, 84·4; H, 5·6; N, 4·6. $C_{22}H_{17}ON$ requires C, 84·9; H, 5·6; N, 4·5%), and its *dibenzoyl* derivative had m. p. 210° (Found : C, 85·9; H, 5·2. $C_{34}H_{23}O_2N$ requires C, 85·5; H, 4·9%).

The above base (7 g.) was diazotised in hydrochloric acid suspension. After 20 minutes, excess of nitrous acid was removed with urea (5 g.) and a solution of α-naphthylamine (4 g.) in glacial acetic acid (35 ml.) was added, followed by 30% sodium hydroxide solution (150 ml.). The reddish-brown aminoazo-compound was allowed to settle overnight and then was collected and dried : m. p. ca. 160° (decomp.); yield, quantitative (12 g.). It was dissolved in a mixture of alcohol (100 ml.) and concentrated sulphuric acid (5·4 g.) and treated at 0° with freshly prepared amyl nitrite (3·8 g.). After being kept for 12 hours at room temperature, the mixture was slowly warmed, and finally it was refluxed for an hour. Water was then added, the alcohols were removed under diminished pressure, and the residual black tar was washed with water and extracted with boiling alcohol. The extract, on precipitation with water, gave a bright red solid which was redissolved in 80% alcohol and passed down an alumina column, which retained both tar and azo-dye. The eluted material was repeatedly crystallised from acetone and glacial acetic acid alternately, and finally gave 4-α-naphthyl-1 : 1′-azonaphthalene as dark red granules, m. p. 178—179° not depressed on admixture with the product obtained as before. When crushed, the granules gave a brick-red powder.

Reduction of 4-α-*Naphthyl*-1 : 1′-*azonaphthalene*.—A boiling solution of the azo-compound (10 g.) in glacial acetic acid (200 ml.) was reduced by gradual addition of zinc dust (20 g.), hydrochloric acid (5 ml.) being added to complete the reaction. After filtration, the product was concentrated and treated with a large excess of 50% sodium hydroxide solution; ammonia was then evolved. The resulting solid was collected on sintered glass. No part of it was volatile in steam, and consequently α-naphthylamine was not present. The solid was purified by dissolution in alcohol and partial precipitation with water until a product was obtained which could be recrystallised from benzene–light petroleum (b. p. 40—60°). This was 3-α-*naphthyl*-1 : 2 : 7 : 8-*dibenzcarbazole* (IX), m. p. 218—219°; yield 55% (Found : C, 90·8; H, 4·8; N, 3·4. $C_{30}H_{19}N$ requires C, 91·6; H, 4·9; N, 3·6%). On crystallisation from absolute alcohol it gave brownish-yellow needles of an alcohol complex, which decomposed when heated to 136° to give the free carbazole.

The *picrate* of the carbazole derivative crystallised in maroon-coloured plates, sintering at 246° and melting at 252° (decomp.) (Found : N, 7·9. $C_{36}H_{22}O_7N_4$ requires N, 9·0%).

The carbazole in dilute alcoholic solution showed an intense blue-green fluorescence in ultra-violet light. It gave a pale red solution in concentrated sulphuric acid, which became intense indigo-blue on treatment with many oxidising agents (HNO_3, $K_2Cr_2O_7$, $K_2S_2O_8$, $FeCl_3$, V_2O_5).

Attempted Phenylation of Azobenzene.—Solid zinc benzenediazonium chloride, $(PhN_2Cl)_2,ZnCl_2$, from 18 g. of aniline, was added to a solution of azobenzene (15 g.) in dry acetone (200 ml.) containing suspended calcium carbonate (20 g.), and zinc dust (10 g.) was then added in portions with vigorous shaking. Nitrogen was evolved steadily. On the following day the mixture was heated to boiling and filtered, and the residue was washed with hot acetone. The solution on evaporation gave a brown syrup which was extracted with hot alcohol. From this extract only a brown sludge could be obtained.

Extraction of the latter with light petroleum (b. p. 60—80°), followed by repeated crystallisation, eventually led to the recovery of about 50 mg. of unchanged azobenzene; no other crystalline product could be separated.

Except where otherwise stated, all analyses are by Drs. Strauss and Weiler. M. p.s are uncorrected.

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