741. *Studies in Peroxidase Action. Part XI.* The Oxidation of a Mixture of Amines.*

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The products obtained by the oxidation of aniline and of *p*-toluidine separately are well established. The peroxidase oxidation of the two together has now been investigated, and it has been shown that (apart from 4 : 4′-dimethylazobenzene) none of the products from each amine separately has been obtained, but instead compounds of " intermediate " structure.

PREVIOUS papers in this series have dealt with the oxidation of single substrates by hydrogen peroxide in the presence of peroxidase. For example, peroxidase oxidation of aniline alone [1] gives rise to 2-amino-5-anilino-*p*-benzoquinone dianil, *pseudo*mauveine, induline, and an " ungreenable " aniline black; that of *p*-toluidine alone [2] gives 4-amino-2 : 5-toluquinone di-*p*-tolylimine, 4-*p*-toluidino-2 : 5-toluquinone bis-*p*-tolylimine, 4 : 4′-dimethyldiphenylamine, and small quantities of 4 : 4′-dimethylazobenzene and 2 : 5-toluquinone *p*-tolylimine. It is therefore of interest to oxidise the two amines together to determine whether or not the separate products of the single oxidations are formed. Such results might provide further evidence concerning the mechanism of the reaction.[3]

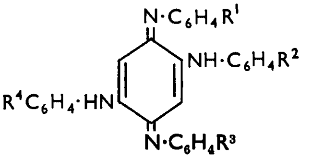
The experimental procedure followed closely that established for the oxidation of single amines as substrates. It soon became apparent, however, that the " mixed " oxidation, if allowed to proceed too far, gave tarry products of high molecular weight: since these arose from simpler intermediates, subsequent oxidations were allowed to proceed to only 20% completion; at this stage a clean solid had separated.

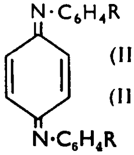
The product was split into fractions by solvent extraction, and each fraction examined chromatographically. A large number of compounds was formed, many, however, only in traces. We were able to isolate in significant amounts: 4 : 4′-dimethylazobenzene and substances (A), (B), and (C).

(Ia): $R^1 = R^2 = R^3 = R^4 = H$

(Ib): $R^1 = R^3 = H$, $R^2 = R^4 = Me$

(Ic): $R^1 = R^2 = R^3 = R^4 = Me$





(IIa): R = H

(IIb): R = Me

Substance (A) was isolated as red needles, m. p. 237°, though some specimens had m. p.s over the range 223° to 243°. It was obvious, therefore, that a careful investigation was required. Elementary analysis, *C*-methyl analysis, and molecular weight determinations gave a formula $C_{30}H_{28}N_4Me_2$. Physical properties and general chemical behaviour suggested that substance (A) was a dimethyl derivative of azophenine (Ia).

To assist in locating the methyl groups, azophenine (Ia), the di-*p*-methylazophenine (Ib) and tetra-*p*-methylazophenine (Ic) were prepared. *NN*′-Diphenyl-*p*-phenylenediamine was oxidised by mercuric oxide to quinone dianil (IIa) which with *p*-toluidine gave the azophenine (Ib). The same compound was prepared independently by treating quinone di-*p*-tolylimine (IIb) with aniline. However, it was found that if the reaction time for these additions was longer than five minutes, the two products were not identical, having different infrared spectra and giving a depressed mixed m. p. To investigate this further, the di-imine (IIb) was treated with *p*-toluidine for (*a*) five minutes and (*b*) one hour. The products were identical, namely, tetra-*p*-methylazophenine (Ic). Pure azophenine (Ia) was then prepared from the di-imine (IIa) and aniline. With the spectra of these compounds it was possible to interpret with precision the course of the earlier reactions.

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* Part X, *J.*, 1956, 940.

[1] P. J. G. Mann and Saunders, *Proc. Roy. Soc.*, 1935, *B*, **119**, **47**.

[2] Saunders and P. J. G. Mann, *J.*, 1940, 769.

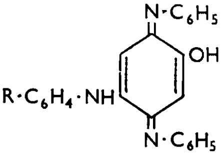
[3] Hughes and Saunders, *J.*, 1954, 4630.

It was clear that the addition of *p*-toluidine to the di-imine (IIa) gave initially the required di-*p*-methylazophenine (Ib), but subsequently replacement of the imine groups occurred so that the product was progressively converted into tri- and tetra-*p*-methylazophenine. Similarly the reaction of aniline with the tolylimine (IIb) leads, ultimately, to azophenine (Ia).

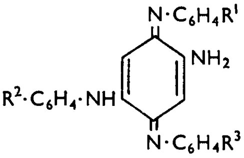
Comparison of the infrared spectra of the product (A) from peroxidase action with those of the products obtained as just described showed that it was a mixture of *p*-methylated azophenines.

The light absorption of azophenine (I) is of interest in that the longest-wavelength maxima (*ca.* 390 mμ) are at shorter wavelengths than those in the corresponding anils (II), indicating the chromophore Ar·N:C·CH:CH·C:N·Ar present in the imine is suppressed in the azophenine. This suggests that there is considerable steric strain between adjacent aromatic rings, and this was borne out when models showed that the molecules are far from planar.

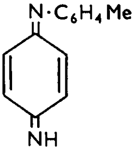
Compound (B) was isolated as red needles, m. p. 215—217°. Elementary analysis and molecular weight determination gave $C_{25}H_{21}ON_3$, and its colour reactions with concentrated sulphuric acid suggested strongly that it was a homologue of 2-hydroxy-5-anilino-*p*-benzoquinone dianil[4] (III; R = H).



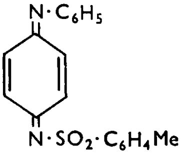
(III)



(IV)



(V)



(VI)

Heller[5] described the compound (III; R = Me), m. p. 214°, and repetition of his work yielded a product identical with that obtained by peroxidase action. (We have changed the earlier name of 2 : 5-dianilino-*p*-benzoquinone mono-*p*-tolylimine to 2-hydroxy-5-*p*-toluidino-*p*-benzoquinone dianil, for the infrared spectra of this and allied compounds exhibit no maxima corresponding to a carbonyl group. The spectra of allied compounds known to contain this type of carbonyl group all show maxima between 6·07 and 6·10 μ.)

Compound (C) was isolated as red needles, m. p. 173—174°, and had a partial formula $C_{24}H_{19}N_4$·Me. Its colour reactions with concentrated sulphuric acid suggested a mono-*p*-methyl analogue of 2-amino-5-anilino-*p*-benzoquinone dianil[6] (IV; $R^1 = R^2 = R^3 = H$) (again we have changed the name, for compounds of this type exhibit three maxima in the 3 μ region).

None of the three chemical methods that suggested themselves to us for determining which of the three R groups was methyl yielded satisfactory results. We were unable to hydrolyse the compound (C) to simple products. Since it has already been shown that the substance (IV; $R^1 = R^2 = R^3 = OMe$) is not readily hydrolysed in a simple manner[7] it is possible that the early work of Goldschmidt and Wurzschmitt[8] is in error.

Compounds of this type react with amines to give azophenines. Although compound (C) reacted with both aniline and *p*-toluidine, the products were mixtures, and the infrared spectrum of the product from *p*-toluidine action showed that it was a mixture of poly-*p*-methylated azophenines. It appeared therefore that the other groups suffered replacement as readily as did the amino-group.

Lastly, it was not possible to synthesise either the compound (C) or one of its derivatives. Although *p*-benzoquinone imine *p*-tolylimine (V) was prepared successfully, it did not react

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[4] Zincke and Von Hagen, *Ber.*, 1885, **18**, 787.
[5] Heller, *Annalen*, 1919, **418**, 265.
[6] Bornstein, *Ber.*, 1901, **34**, 1268.
[7] Daniels and Saunders, *J.*, 1951, 2112.
[8] Goldschmidt and Wurzschmitt, *Ber.*, 1922, **55**, 3216.

with aniline in a simple manner. Again, working with the model compound toluene-*p*-sulphonimido-*p*-benzoquinone anil (VI), it was not possible to add aniline before replacement of the toluene-*p*-sulphonimido- by an anilino-group. This result is in agreement with the findings of Adams and Schowalter.[9]

Although compound (C) has not yet been synthesised, the above work has given a sufficiently large number of reference compounds to interpret in detail its infrared spectrum. This shows that the compound has a *p*-toluidino-group *para* to an amino-group and so is 2-amino-5-*p*-toluidino-*p*-benzoquinone dianil (IV; $R^1 = R^3 = H, R^2 = Me$).

EXPERIMENTAL

Infrared spectra were determined on a Perkin-Elmer Model 21 spectrophotometer, as mulls in Nujol. Light absorption spectra were determined on a Unicam Model S.P. 600 spectrophotometer.

Peroxidase-catalysed Oxidation of Equimolar Quantities of Aniline and p-*Toluidine*.—Aniline (4·65 g., 0·05 mole) and *p*-toluidine (5·35 g., 0·05 mole) were dissolved in acetic acid (12 ml.) and diluted with water (500 ml.). The pH was adjusted to 4·5 and hydrogen peroxide (2 ml.; 20-vol.) added. There was no visible change. The addition of enzyme (2 ml.; P.N. *ca.* 3—5), however, produced an immediate dark red colour, and after about 5 min. a pale brown precipitate was formed.

At hourly intervals the effects of enzyme, hydrogen peroxide, and of both reagents together, were determined on small samples of the mixture; the result determined which reagent or reagents were to be added to the bulk reaction mixture.

The initial fast reaction became progressively slower, and the precipitate darker, and ultimately tar was formed. Hence, the oxidations were not carried to completion. The material used in the examination detailed below was obtained by conducting a number of oxidations to one-fifth completion.

Filtering the reaction mixture through " Hyflo Supercel " gave a clear, deep permanganate-coloured solution. This was distilled, and from the distillate unchanged amines were recovered. During the distillation a mauve-black precipitate was formed which was examined chromatographically. It was a complex mixture containing traces of a large number of unidentified compounds of the induline type.

The red filtrate (above) was extracted with chloroform, and the extract, on evaporation, gave a red gum (31 mg. from 50 g. of mixed amines). This was chromatographed on alumina, giving a green solid (22 mg.), which dissolved in ethanol to give a red solution. Qualitatively the light absorptions of this compound and phenosafranine in ethanol, and in dilute hydrochloric acid solution, were similar, but not identical.

Examination of the solid oxidation product. The solid (27·7 g.), together with " Hyflo Supercel " (24·8 g.), was extracted (Soxhlet) with light petroleum (b. p. 40—60°; 7 × 750 ml. + 7 × 300 ml.). The combined red extracts were concentrated under reduced pressure, benzene (150 ml.) was added, and the evaporation continued. The tarry residue was freed from solvents at 80°/2 mm. during 8 hr. The black residue (19·7 g., 71%) was dissolved in benzene (350 ml.) and light petroleum (b. p. 40—60°; 200 ml.), and the solution examined as described below (fraction i).

The black petroleum-insoluble material was extracted (Soxhlet) with ether (750 ml.), and the extract on evaporation gave another black residue (5·68 g., 20%) (fraction ii).

The remaining 9% of the original product proved intractable.

Fraction (i). A portion (150 ml.) of the benzene–petroleum solution was chromatographed on alumina (7 × 35 cm.), the column being eluted successively with light petroleum (b. p. 40—60°)–benzene (50, 60, 70% benzene) mixtures, benzene, and benzene–ethanol (1, 2, 5% ethanol) mixtures.

The lowest bands on the column were yellow, green, and pale brown respectively. These were succeeded by a number of dark bands, one of which was separated from the remainder by further chromatography with benzene as eluant. Evaporation of the four eluates gave, in order, 4 : 4′-dimethylazobenzene and substances (A), (B), and (C).

4 : 4′-Dimethylazobenzene was obtained as yellow-orange crystals, m. p. 135° (180 mg.). After two recrystallisations from light petroleum (b. p. 40—60°) and sublimation the m. p. was 137—141° (Found : C, 79·8; H, 6·5; N, 13·5. Calc. for $C_{14}H_{14}N_2$: C, 80·0; H, 6·7; N, 13·3%).

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[9] Adams and Schowalter, *J. Amer. Chem. Soc.*, 1952, **74**, 2597.

In concentrated sulphuric acid, it gave a deep orange solution. An authentic sample was prepared by the following improvement of Barsilowsky's[10] method.

A solution of potassium ferricyanide (164·5 g.) and potassium hydroxide (42·0 g.) in water (1·8 l.) was added to a stirred solution of *p*-toluidine hydrochloride (37·0 g.) in water (500 ml.) during 1 hr. The tarry red precipitate was filtered off, washed, and dried (20·0 g.). Extraction (Soxhlet) with light petroleum (b. p. 40—60°; 750 ml.), and evaporation of solvent gave a black crystalline residue (12·8 g.), which was chromatographed in benzene (215 ml.) on alumina, with light petroleum (b. p. 40—60°)–benzene (1 : 1) as eluant. The first band gave, on evaporation, yellow-orange crystals of 4 : 4'-dimethylazobenzene, m. p. 138—141°, which on recrystallisation from light petroleum had m. p. 141—143°, mixed m. p. with enzyme product 139—142.°

Identification of Substance (A).—The red crystalline residue (288 mg.) containing (A) was recrystallised from *cyclo*hexane. The m. p.s of various specimens were in the range 223—243°, only some of which were raised by recrystallisation from *cyclo*hexane, light petroleum (b. p. 100—120°), or light petroleum (b. p. 60—80°)–toluene [Found: C, 82·0; H, 6·1; N, 12·0; *C*-Me, 6·2%; *M*, 488 (±35). Calc. for $C_{32}H_{28}N_4$: C, 82·0; H, 6·0; N, 12·0; *C*-Me, 6·4%; *M*, 468]. Comparison of the infrared spectrum with those of various azophenines, whose preparation is described below, combined with the analytical data, show that (A) was a mixture of *p*-methylated azophenines.

Quinone Dianil.—A mixture of *NN'*-diphenyl-*p*-phenylenediamine (6·1 g.), yellow mercuric oxide (12·0 g.), and dry benzene (150 ml.) was stirred and heated under reflux for 8 hr., cooled, and filtered. The filtrate was evaporated and the residue, crystallised from ethanol, had m. p. 181·5—182·5° (5·28 g., 87%) (Bandrowski[11] gave m. p. 176—181°) (Found: C, 83·9; H, 5·6; N, 11·0. Calc. for $C_{18}H_{14}N_2$: C, 83·7; H, 5·5; N, 10·9%). Light absorption in 95% EtOH: $\lambda_{max.}$ 304, 443 (ε 26,800, 8000); $\lambda_{min.}$ 238, 360 mμ (6790, 2000). Infrared max.: 6·32s, 6·70s, 6·90s, 7·56w, 7·65w, 8·25w, 8·55w, 8·65w, 8·96w, 9·30m, 9·77w, 10·16w, 10·35w, 10·50m, 10·96m, 11·56m, 11·67s, 12·76s, 13·35w, 13·76s, and 14·35 μ s (s = strong, m = medium, w = weak here and below).

p-*Benzoquinone Di*-p-*tolylimine.*—*NN'*-Di-*p*-tolyl-*p*-phenylenediamine was prepared by the method of Hatschek and Zega.[12] The product (40—60% yield), recrystallised from benzene, had m. p. 181°. Oxidation with yellow mercuric oxide gave the *di*-p-*tolylimine* as red needles (from ethanol), m. p. 123—123·5° (94%) (Found: C, 83·9; H, 6·7; N, 9·75. $C_{20}H_{18}N_2$ requires C, 83·9; H, 6·3; N, 9·8%). Light absorption in 95% ethanol: $\lambda_{max.}$ 310, 464 (ε 27,500, 11,600); $\lambda_{min.}$ 218, 240, 277, 368 (ε 11,900, 7800, 15,900, 2070); $\lambda_{infl.}$ 233, 270 mμ (ε 12,200, 16,200). Infrared max.: 6·35s, 6·67s, 7·60s, 8·24w, 9·06m, 9·60w, 9·87w, 10·15w, 10·47m, 11·54m, 11·63s, 11·71s, 12·00s, 12·15s, 12·70m, 13·57m, and 14·35 μ m.

Reaction of Benzoquinone Dianils with Aromatic Amines.—The dianil was dissolved in the minimum of dilute acetic acid, and a large excess of the amine added. The mixture was heated on a water-bath for the stated time, cooled, and filtered. The residue was washed with hot ethanol and recrystallised from light petroleum (b. p. 100—120°). All azophenines crystallised as red needles. Products are recorded in the annexed Table.

Reactants	Time (min.)	Azophenine produced	M. p.
p-Benzoquinone dianil + aniline	5, 60	Ia	236—237°
,, ,, *p*-toluidine	5	Ib	233—235, 236
,, ,, ,,	15	Mixture Ib & c	236—237
,, ,, ,,	60	,,	253
p-Benzoquinone di-*p*-tolylimine + *p*-toluidine	5, 60	Ic	264—265
,, ,, aniline	5	Ib	234, 235
,, ,, ,,	60	Ia	235·5, 235·5—236

Properties of azophenines: Azophenine, m. p. 236—237° (lit., between 225° and 250°) (Found: N, 12·6. Calc. for $C_{30}H_{24}N_4$: N, 12·7%). Light absorption in ether: $\lambda_{max.}$ 290, 384—388 (ε 33,900, 20,400); $\lambda_{min.}$ 250, 332 (ε 17,600, 10,800); $\lambda_{infl.}$ 400—404 mμ (18,300). Infrared max.: 3·05s, 6·27s, 6·44s, 6·65s, 6·75s, 6·92s, 7·44m, 7·74m, 8·05w, 8·30w, 8·56m, 8·66m, 9·30m, 9·80w, 10·65w, 10·97w, 11·51m, 11·76m, 11·87m, 12·07,m 12·83m, 13·05s, 13·28s, 13·61w, 13·99m, 14·15m, 14·40s, 14·71m, and 15·01 μ w.

Tetra-*p*-methylazophenine, m. p. 264—265° (lit., 249°,[13] 259—260°[14]) (Found: N, 11·35.

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[10] Barsilowsky, *Annalen*, 1881, **207**, 103.
[11] Bandrowski, *Monatsh.*, 1886, **7**, 375.
[12] Hatschek and Zega, *J. prakt. Chem.*, 1886, **33**, 209.
[13] Fischer and Hepp, *Ber.*, 1887, **20**, 2480.
[14] Ruggli and Buchmeier, *Helv. Chim. Acta*, 1945, **28**, 850.

Calc. for $C_{34}H_{22}N_4$: N, 11·3%). Light absorption in ether : $\lambda_{\text{max.}}$ 290, 395 (ε 33,000, 20,700); $\lambda_{\text{min.}}$ 244, 388 (ε 16,400, 8700); $\lambda_{\text{infl.}}$ 222—227, 398—404 mμ (ε 23,100, 20,400). Infrared max.: 3·02s, 6·27s, 6·45s, 6·72s, 7·47s, 7·71m, 8·09w, 8·25w, 8·34w, 8·55w, 9·03w, 9·83w, 10·57w, 11·70m, 12·17s, 12·35s, 12·78w, 13·15s, 13·70s, 13·93w, and 14·10 μ m.

Di-*p*-methylazophenine, m. p. 236°. Light absorption in ether : $\lambda_{\text{max.}}$ 290, 388—390(ε 29,800, 18,700); $\lambda_{\text{min.}}$ 252, 336 mμ (ε 15,500, 8100). Infrared max. : 3·05 μ (N–H) and (in the 11—15 μ region) 11·03w, 11·47w, 11·67m, 11·81m, 12·33s, 12·87m, 13·15m, 13·98m, 14·40s, and 14·83 μ w. The maximum at 3·05 μ strongly suggests that the compound is 2 : 5-dianilino-*p*-benzoquinone di-*p*-tolylimine.

*Reaction between the Di-*p*-methylazophenine and *p*-Toluidine.*—The azophenine (61 mg.) was dissolved in dimethylformamide (100 ml.), and *p*-toluidine (2 g.) and acetic acid (5 ml.) were added. The solution was heated on a water-bath for 3 hr., then concentrated to 5 ml. Ethanol (20 ml.) was added and the red crystals were filtered off, dried (56 mg.), and recrystallised from benzene–light petroleum (b. p. 100—120°) as red needles, m. p. 227—232°. These were dissolved in dimethylformamide (150 ml.), and *p*-toluidine (2 g.) and acetic acid (10 ml.) were added. After being heated at 100° for 18 hr., the product was isolated as above as red needles (30 mg.), m. p. 259—260°, mixed m. p. with tetra-*p*-methylazophenine, 263—264°.

Identification of Substance (B).—The compound (B) was obtained as red needles, m. p. 211—212° (150 mg.). Recrystallisation from either *cyclo*hexane or ethanol–chloroform raised the m. p. to 215—217°. In concentrated sulphuric acid, compound (B) gave a blue-red solution, unaltered on being heated [Found : C, 79·4; H, 5·8; N, 11·2%; *M* (Rast), 370 (±30). Calc. for $C_{25}H_{21}ON_3$: C, 79·1; H, 5·6; N, 11·1%; *M*, 379. Calc. for $C_{24}H_{19}ON_3$: C, 78·9; H, 5·1; N, 11·5%; *M*, 365].

These facts suggest that (B) was 2-hydroxy-5-*p*-toluidino-*p*-benzoquinone dianil ($C_{25}H_{21}ON_3$), which we synthesised by the method of Heller,[15] who gave m. p. 214°.

Crude 4-hydroxy-4′-methyldiphenylamine was oxidised to *p*-benzoquinone mono-*p*-tolylimine, red needles [from light petroleum (b. p. 40—60°)], m. p. 81° (Found : N, 7·3. Calc. for $C_{13}H_{11}ON$: N, 7·1%). Infrared max. : 5·21w, 6·09s, 6·17s, 6·35m, 6·67m, 7·07w, 7·60s, 7·66m, 7·99w, 8·28w, 8·53m, 8·63m, 9·04w, 9·63w, 10·17w, 10·31w, 10·53m, 11·52s, 11·99s, 12·66w, 12·95w, 13·14m, 13·50w, and 14·23 μ m.

p-Benzoquinone mono-*p*-tolylimine reacted with aniline, to give 2-hydroxy-5-*p*-toluidino-*p*-benzoquinone dianil, m. p. 213°, mixed m. p. with specimen from peroxidase action, 214° (Found : N, 10·7%). Light absorption in ether : $\lambda_{\text{max.}}$ 289, 387 (ε 35,150, 19,800); $\lambda_{\text{min.}}$ 251, 338 (ε 30,250, 12,500); $\lambda_{\text{infl.}}$ 265 mμ (ε 31,600). Infrared max. : 3·05s, 6·26s, 6·40s, 6·60s, 7·45s, 7·69s, 8·08m, 8·33m, 8·55m, 9·01w, 9·34w, 9·75w, 9·85w, 10·60w, 11·05w, 11·69m, 11·08m, 12·17s, 12·28s, 12·85m, 13·15m, 13·97m, and 14·37 μ s.

Identification of Substance (C).—Crude (C), m. p. 157—162° (632 mg.), was purified by chromatography on alumina in benzene. The eluate from the main band was evaporated to a red glass which crystallised on addition of *cyclo*hexane (15 ml.). The crystals (400 mg.) had m. p. 173—174°, unaltered on recrystallisation from either *cyclo*hexane or ethanol–chloroform (Found : C, 79·6; H, 6·0; N, 14·7; *C*-Me, 4·7. $C_{25}H_{22}N_4$ requires C, 79·4; H, 5·8; N, 14·8; *C*-Me, 4·0%). Light absorption in ether : $\lambda_{\text{max.}}$ 228, 279, 356 (ε 28,000, 22,600, 19,900); $\lambda_{\text{min.}}$ 222, 252, 320 mμ (ε 20,900, 16,100, 8970). Infrared max. : 2·89m, 3·025s, 6·24s, 6·43s, 6·60s, 6·68s, 7·42s, 7·54m, 7·88m, 8·10s, 8·30s, 8·47m, 8·61w, 9·01w, 9·35w, 9·76w, 9·84w, 10·65w, 10·87w, 11·15w, 11·69m, 11·90m, 12·10s, 12·15m, 12·90m, 13·00m, 13·85m, 14·13m, 14·45s, and 14·99 μ w.

Substance (C) gave a magenta solution in concentrated sulphuric acid, which became red on dilution, blue-violet on heating, and on more prolonged heating blue-black. Both blue solutions became red on dilution and fluoresced slightly.

The above suggested that (C) was a homologue of 2-amino-5-anilino-*p*-benzoquinone dianil and was shown to be a compound of this type by acetylation and by reaction with *p*-toluidine.

The compound (73 mg.) was heated under reflux with acetic anhydride (2 ml.) for 10 min., the mixture cooled, ethanol (5 ml.) added, and the mixture filtered. The red residue of *2-acetamido-5-*p*-toluidino-*p*-benzoquinone dianil* recrystallised from ethanol as scarlet needles, m. p. 174—176° (Found : N, 13·1. $C_{27}H_{24}ON_4$ requires N, 13·3%).

The compound (C) (111 mg.), *p*-toluidine (0·25 g.), water (12·5 ml.), and acetic acid (12·5 ml.) were heated together on a water-bath for 2 hr. The red amorphous precipitate was filtered off, washed, dried (m. p. 226—227°), and recrystallised from toluene–light petroleum (b. p. 80—100°)

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[15] Heller, *Annalen*, 1919, **418**, 265.

as red needles, m. p. 233—234° (Found: *C*-Me, 6·6. Calc. for $C_{32}H_{28}N_4$: 2*C*-Me, 6·4%). Infrared max. in the 11—15 μ region: 11·69m, 11·80w, 12·15s, 12·30m, 12·85w, 13·15w, 13·75s, 14·10s, 14·37m, and 14·85 μ w. This spectrum is similar to that of the fourth product in the Table, which had max. at 11·49w, 11·70m, 12·15s, 12·34m, 13·92w, 14·10m, and 14·37 μ w, *i.e.*, the above product is a mixture.

2-*Amino*-5-*anilino*-p-*benzoquinone Dianil.*[16]—To a stirred solution of aniline (60 g.) in water (1·2 l.) and glacial acetic acid (40 g.), at 0°, lead dioxide (160 g.) was added portionwise during 0·5 hr. The mixture was filtered, and the residue extracted with cold benzene (1 l.) and filtered. This filtrate was passed through a column of alumina (6·5 × 11·0 cm.), and the eluate concentrated to 300 ml. The concentrate was chromatographed on alumina in benzene containing ethanol (2%). The main band was preceded by a small quantity of azobenzene. The eluate containing the main band was evaporated, to yield a dark red amorphous residue, which was recrystallised from ethanol–chloroform. The first crop of crystals had m. p. 163—164° (2·3 g.) (Found: C, 78·7; H, 5·7. Calc. for $C_{24}H_{20}N_4$: C, 79·1; H, 5·5%). Light absorption in ether: $\lambda_{\text{max.}}$ 228, 277, 356 (ε 24,400, 22,000, 21,900); $\lambda_{\text{min.}}$ 256, 316 (ε 19,500, 9370); $\lambda_{\text{infl.}}$ 240—244 mμ (ε 21,950). Infrared max.: 2·87s, 2·97s, 3·035s, 6·17s, 6·26s, 6·40s, 6·57s, 6·67m, 6·74s, 7·35m, 7·40m, 7·55m, 7·65m, 7·83w, 7·87w, 8·10m, 8·25m, 8·57w, 8·67w, 9·35m, 9·76m, 10·95w, 11·14w, 11·65w, 12·17s, 12·67w, 12·80s, 12·92m, 13·15s, 14·30s, 14·40s, and 14·98 μ w.

p-*Nitro*-N-p-*tolylaniline.*—*p*-Bromotoluene (56 g.), *p*-nitroaniline (20 g.), potassium carbonate (10 g.), copper powder (0·2 g.), and potassium iodide (0·5 g.) were heated together under reflux, with stirring, for 14 hr. The mixture was then steam-distilled to remove unchanged *p*-bromotoluene. The residue was filtered, the insoluble material was heated with 3N-hydrochloric acid (300 ml.) for 0·5 hr., and the mixture cooled and filtered. The residue (9·0 g.) was chromatographed on alumina in benzene to give two main bands (i) and (ii). Band (i), on evaporation, gave p-*nitro*-NN-*di*-p-*tolylaniline* (2·49 g., 5·5%) as yellow hexagonal plates, which on recrystallisation from ethanol–benzene, had m. p. 163·5—164·5° (Found: C, 75·4; H, 5·5; N, 8·6. $C_{20}H_{18}O_2N_2$ requires C, 75·5; H, 5·7; N, 8·8%). Band (ii), on evaporation, gave *p*-nitro-*N*-*p*-tolylaniline (7·04 g., 21%) as orange prisms, which on recrystallisation from dilute ethanol had m. p. 137° (Goldberg[17] gave m. p. 138°) (Found: C, 68·6; H, 5·4; N, 12·0. Calc for $C_{13}H_{12}O_2N_2$: C, 68·4; H, 5·3; N, 12·3%).

N-*Toluene*-p-*sulphonyl*-N′-p-*tolyl*-p-*phenylenediamine.*—*N*-*p*-Tolyl-*p*-phenylenediamine[18] (713 mg.) was dissolved in pyridine (2 ml.), and a solution of toluene-*p*-sulphonyl chloride (700 mg.) in pyridine (4 ml.) added. The mixture was set aside for an hour, ethanol (2 ml.) added, and the mixture poured into water; the derivative crystallised. N-*Toluene*-p-*sulphonyl*-N′-p-*tolyl*-p-*phenylenediamine* recrystallised from dilute ethanol as leaflets, m. p. 163—165° (1·07 g., 85%) (Found: C, 68·3; H, 5·5; N, 8·2. $C_{20}H_{18}O_2N_2S$ requires C, 68·6; H, 5·2; N, 8·0%).

p-*Benzoquinone Imine* p-*Tolylimine.*—*N*-*p*-Tolyl-*p*-phenylenediamine was oxidised by silver oxide as described by Willstätter and Kubli.[19] The di-imine formed yellow crystals (from ether), m. p. 107—109° (Willstätter reported m. p. 114°) (Found: C, 79·8; H, 6·35; N, 14·4. Calc. for $C_{13}H_{12}N_2$: C, 79·6; H, 6·2; N, 14·3%). Light absorption in ether: $\lambda_{\text{max.}}$ 278, 434 (ε 18,500, 2870); $\lambda_{\text{min.}}$ 356 mμ (ε 930).

4-*Toluene*-p-*sulphonamidodiphenylamine.*—4-Aminodiphenylamine (8·4 g.) was treated with toluene-*p*-sulphonyl chloride (9·5 g.) as above. The *amide* recrystallised from dilute ethanol as rectangular plates, m. p. 145—145·5° (14·0 g., 91%) (Found: C, 67·2; H, 5·3; N, 8·4. $C_{19}H_{18}O_2N_2S$ requires C, 67·4; H, 5·4; N, 8·3%).

Oxidation of 4-*Toluene*-p-*sulphonamidodiphenylamine.*—The amide (451 mg.) was treated in dry benzene (300 ml.) with lead tetra-acetate (594 mg.), heated under reflux, with stirring, for 10 hr., cooled, and filtered, and the filtrate was evaporated. Addition of ether (5 ml.) and scratching caused the red *toluene*-p-*sulphonimido*-p-*benzoquinone anil* to crystallise. The ether was evaporated and the quinone collected (m. p. 93—95°; 400 mg., 89%); recrystallised from ether, it had m. p. 98° (Found: C, 67·9; H, 5·0; N, 8·3. $C_{19}H_{16}O_2N_2S$ requires C, 67·9; H, 4·8; N, 8·3%). Light absorption in ether: $\lambda_{\text{max.}}$ 223, 317, 480 (ε 14,600, 25,600, 4600); $\lambda_{\text{min.}}$ 240, 400 mμ (ε 6350, 1620). Infrared max.: 6·15m, 6·28w, 6·37s, 6·65s, 7·63s, 7·67s, 7·77s, 8·26w, 8·45w, 8·54m, 8·66s, 8·72s, 9·06m, 9·20s, 9·80m, 10·02w, 10·45w, 10·87w, 11·50s, 11·72s, 11·83s, 11·93m, 12·30m, 12·51s, 13·01w, 13·19w, 13·97s, 14·30s, and 14·79 μ s.

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[16] Improvement on the method of Majima and Aoki, *Ber.*, 1911, **44**, 3080.

[17] Goldberg, G.P. 1906, 185,663, *Chem. Zentr.*, 1907, II, 957.

[18] Ullmann and Dahmen, *Ber.*, 1908, **41**, 3751.

[19] Willstätter and Kubli, *Ber.*, 1909, **42**, 4135.

The identity of the quinone was also established by reduction. Toluene-*p*-sulphonimido-*p*-benzoquinone anil (20 mg.) was shaken in ether (3 ml.) with sodium dithionite (50 mg.) in water (3 ml.). The ether layer was washed with water, dried (Na_2SO_4), and evaporated. The residue, recrystallised from dilute ethanol, had m. p. and mixed m. p. with 4-toluene-*p*-sulphonamidodiphenylamine, 145°.

Reaction of p-*Benzoquinone Toluene*-p-*sulphonimide Anil with Aniline.*—The anil (30 mg.) in dioxan (5 ml.) was warmed with a solution of aniline (1 ml.) in acetic acid (1 ml.) for 5 min., water (20 ml.) was added, and the mixture filtered. The red residue was washed with water, cold ethanol, and hot ethanol, giving, in each case, colourless washings. The residue, m. p. 225—235°, recrystallised from light petroleum (b. p. 100—120°) as red needles, m. p. and mixed m. p. with azophenine, 236°.

Reaction of the Above Anil with p-*Bromoaniline.*—The anil (128 mg.) was treated as above, the aniline being replaced by *p*-bromoaniline. *Tri*-p-*bromoazophenine* was obtained as red needles, m. p. 232—236° (Found : Br, 36·6. $C_{30}H_{21}N_4Br_3$ requires Br, 35·4%).

Examination of Fraction ii (p. 3816).—Fraction ii (5·68 g.) was chromatographed on alumina (7 × 40 cm.) in benzene. The lowest band, on evaporation, gave red needles, m. p. 229—233° (143 mg.). An infrared spectrum showed that this substance was a mixture of *p*-methylated azophenines.

It was not possible to separate the remaining bands either by silica or alumina chromatography.

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