Benzoquinone Imines. Part IX.[1] Mechanism and Kinetics of the Reaction of *p*-Benzoquinone Di-imines with *m*-Aminophenols

By **John F. Corbett**, The Gillette Company, Personal Care Division, 456 Merchandise Mart, Chicago, Illinois 60654

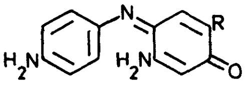
The products of the coupling of *p*-benzoquinone di-imines with *m*-aminophenols indicate that reaction occurs in the position *para* to the hydroxy-group to give aminoindoanilines while, if this position is blocked, reaction occurs at the position *para* to the amino-group to give hydroxyindamines. The reaction of di-imine with 3-amino-4,6-dimethylphenol results in an equilibrium with a compound which is probably a pseudo-quinone imine. Kinetic studies show the reaction of di-imines with *m*-aminophenols to involve electrophilic attack of the conjugate acid of the di-imine on the phenolate ion and the neutral phenol, the former predominating at pH > 8. Kinetic studies also show that, with 4- and 6-methyl-3-aminophenol, some of the postulated pseudo-quinone imine is formed, but is ultimately converted into the normal indo-dye.

Aminoindoaniline reacts with *p*-phenylenediamine or other primary arylamines to give trinuclear indoanilines such as (VII) and (VIII). In concentrated solution, hydroxyindamines undergo intramolecular cyclization to give aminophenoxazineimines.

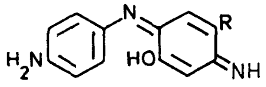
EARLIER Parts have been concerned with the mechanism of the reactions of *p*-benzoquinone di-imines with *m*-phenylenediamines[2] and with monohydric phenols.[3] It was shown that these reactions can be classified as involving electrophilic attack of the conjugate acid of the di-imine on the electron-rich coupler, followed by oxidation of the resulting diphenylamine to the aminoindamine or the indoaniline dye, respectively. *m*-Aminophenol is a particularly interesting coupler since reaction may occur either *para* to the amino-group or *para* to the hydroxy-group. We have now examined the reactions of di-imines with *m*-aminophenol and its *C*-methylated derivatives.

Structure and Spectra of Products.—There are no data on the reaction of *p*-benzoquinone di-imines with *m*-aminophenols. We have shown previously[2-4] that di-imines can be generated *in situ* by oxidation of the corresponding *p*-phenylenediamine with potassium ferricyanide or, more slowly, with molecular oxygen.

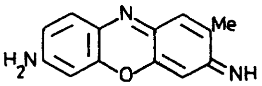
Oxidation of an equimolar solution of *p*-phenylenediamine and *m*-aminophenol with four mol. equiv. of ferricyanide, at pH 6 and 11, gave a product which was shown by t.l.c. to be a single compound. Elemental analysis corresponded to a compound with the formula $C_{12}H_{11}N_3O$ which could have either structure (I) or (II). The n.m.r. spectrum (see below) confirmed the presence of 2 primary amino-groups, indicating that aminoindoaniline structure (I) is correct. Similar oxidation of a mixture of *p*-phenylenediamine and 5-amino-2-methylphenol gave a compound, $C_{13}H_{13}N_3O$, having an n.m.r. spectrum consistent with the aminoindoaniline structure (III), which was confirmed by hydrolysis with dilute acid to give *p*-phenylenediamine and 2-hydroxy-5-methylbenzoquinone.



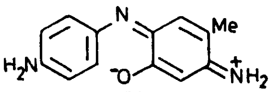
(I) R = H
(III) R = Me



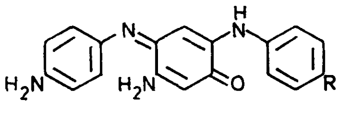
(II) R = H
(IV) R = Me



(V)



(VI)



(VII) R = NH_2
(VIII) R = Me

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[1] Part VIII, J. F. Corbett, *J. Chem. Soc.* (*B*), 1970, 1502.

[2] J. F. Corbett, *J. Chem. Soc.* (*B*), 1969, 827.

[3] J. F. Corbett, *J. Chem. Soc.* (*B*), 1970, 1418.

[4] J. F. Corbett, *J. Chem. Soc.* (*C*), 1969, 207; Proc. Joint Conference on Cosmetic Sciences, Washington, D.C. (Toilet Goods Assoc.), 1968, p. 159; *J. Soc. Cosmetic Chemists*, 1969, **20**, 253.

The n.m.r. spectra of the aminoindoanilines (I) and (III) are in Table 1. The assignments are in accord with those previously reported for simple indoanilines[3] which exhibited bands due to the protons of the amino-group on the benzenoid ring in the region τ 4·05—4·85, bands due to *ortho* pairs of benzenoid hydrogens at τ 2·94—3·52 (J 84 Hz), bands due to *ortho* pairs of quinonoid hydrogens at τ 2·58—2·89 (H-*ortho* to C=N) and τ 3·29—3·59 (H-*ortho* to C=O) with J 114 Hz. In the aminoindoanilines, the latter are shifted to slightly higher τ values by the influence of the *para*-amino-group. The lone hydrogen *ortho* to the amino-group has its absorption similarly shifted by about τ 0·7.

TABLE 1

The n.m.r. spectra of the aminoindoanilines in deuteriated dimethyl sulphoxide

Before deuteriation		After deuteriation		
τ	Integration	τ	Integration	Assignment
2-Aminoindoaniline (I)				
3·32	2 *			NH_2 (quin)
4·37	2 *			NH_2 (benz)
2·88	2	2·77	2	1 pair *ortho*
3·06		2·96		CH (quin)
3·67		3·61		(J 111 Hz)
3·86		3·79		
3·00	4	2·88	4	2 Pairs *ortho*
3·14		3·02		CH (benz)
3·20		3·12		(J 84 Hz)
3·34^m		3·26		
ca. 4·37^m	1 *	4·31		Lone CH † (quin)
2-Amino-5-methylindoaniline (III)				
3·37	2 *			NH_2 (quin)
4·47	2			NH_2 (benz)
3·00	1	3·13	1	Lone CH (quin)
3·00	4	2·92	4	2 Pairs *ortho*
3·14		3·07		CH (benz)
3·21		3·14		(J 90 Hz)
3·35^m		3·29		
4·40	1	4·31	1	Lone CH † (quin)
8·13^s	3	8·11	3	CH_3

* Obtained by difference on deuteriation. † *ortho* to NH_2 group.

m = Masked peak; s = slight splitting to doublet.

Addition of a solution of an equimolar mixture of *p*-phenylenediamine and 3-amino-4-methylphenol to a solution containing 4 molar equivalents of ferricyanide resulted in the precipitation of a product (IV) which could not be purified by sublimation or recrystallisation owing to its easy conversion into 7-amino-2-methylphenoxazine-3-imine (V). The structure of the latter was demonstrated by comparison of its visible spectrum (Figure 1) and acid dissociation constant (11·2) with that of the known 7-aminophenoxazine-3-imine,[5] and by its elemental analysis and that of its hydrochloride and picrate.

Other related indo-dyes were prepared in dilute solution by oxidation of an equimolar mixture of the *p*-diamine and the *m*-aminophenol with the theoretical amount of ferricyanide. Studies of the stoicheiometry of these reactions by the method used previously[3] indicated that all the pairs, including the *C*-methoxy-*m*-aminophenols, required 4 mol. equiv. of ferricyanide, *i.e.*, reaction (A). This indicated that the coupling of the di-imine with 3-aminomethoxyphenols did not

$$p\text{-Diamine} + m\text{-Aminophenol} \xrightarrow{-4e} \text{Indo-dye} \quad \text{(A)}$$

involve elimination of the methoxy-group since, if this were to occur, only 2 mol. equiv. of ferricyanide would be required to give the maximum yield of dye.

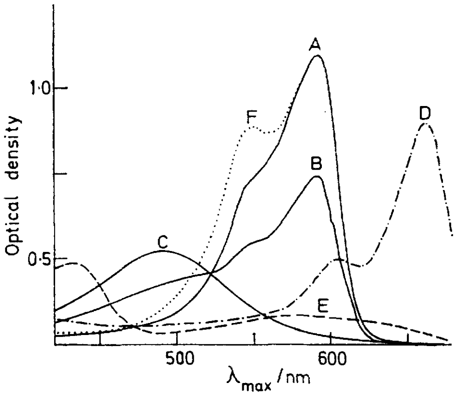

FIGURE 1 The visible spectrum of 7-amino-2-methylphenoxazine-3-imine in A and F, 0·1M-HCl; B, pH 11·2 aqueous sodium carbonate; C, 0·1M-sodium hydroxide; D, 12·0M-hydrochloric acid; and E, concentrated sulphuric acid. A—E, 5 × 10^{-6}M-solutions in 4·0 cm cell; and F, 5 × 10^{-5}M-solution in 0·5 cm cell

The visible maxima of the indo-dyes are in Table 2. As observed with indoanilines[2,3] and indophenols,[1] alkylation of the quinonoid ring produces a small hypsochromic shift, while methoxylation produces a larger hypsochromic shift. Conversely, alkylation of the benzenoid ring produces a bathochromic shift while chlorination of this ring produces a hypsochromic shift. It is noteworthy that the spectra of isomeric amino-indoanilines and hydroxyindamines are very similar in position, shape, and intensity.

TABLE 2

Visible spectra of indo-dyes formed from di-imines and 3-aminophenols

Di-imine	3-Aminophenol	$\lambda_{max.}$/nm (log ε)
Parent	Parent	511 (3·98 *)
Parent	6-Me	492 (3·96) *
2-Me	Parent	520 (3·90) *
2-Cl	Parent	500 (3·86) *
2,5-Cl_2	Parent	500 (3·86) *
2,6-Cl_2	Parent	485 (3·68) *
Parent	6-MeO	489 (3·97) *
Parent	4-Me	504 (3·99) †
2,6-Cl_2	4-Me	493 (3·64) †
Parent	4-MeO	492 (4·00) †

* Aminoindoanilines. † Hydroxyindamines.

The effect of pH on the spectrum of the aminoindoaniline (III) is shown in Figure 2. The absence of a spectral change over the pH range 6—13·5 indicates that the compound exists as a neutral species over this range.

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[5] H. Musso and H. G. Matthies, *Chem. Ber.*, 1957, **90**, 1814; H. Musso, H. G. Matthies, H. Kramer, and P. Hocks, *ibid.*, 1960, **93**, 1782.

Comparison of the spectrum with that of 3-methylindoaniline [3] ($\lambda_{max.}$ = 537 nm) shows that introduction of the strongly electron-donating amino-group causes the expected large hypsochromic shift (45 nm). At pH 2·2 the spectrum has a maximum at 428 nm (log ε 3·55) and the spectra at intermediate pH values indicates pK_a *ca.* 4·0 for the conjugate acid. Protonation of the amino-group on the quinonoid ring would be expected to produce a bathochromic shift to give a spectrum similar to that of 3-methylindoaniline. Thus, the observed hypsochromic shift suggests that the amino-group on the benzenoid ring is the basic centre in 2-aminoindoanilines. The spectrum of 2-hydroxy-3-methylindamine (IV) shifts to shorter wavelengths at pH > 12. However, owing to the instability of the dye at pH > 13 it has not been possible to determine the pK_a value. In view of the high pK_a value of aminoindamines [2] and the low value of hydroxyquinones,[6] it seems likely that (IV) exists as a zwitterion (VI) over the pH range 7—12.

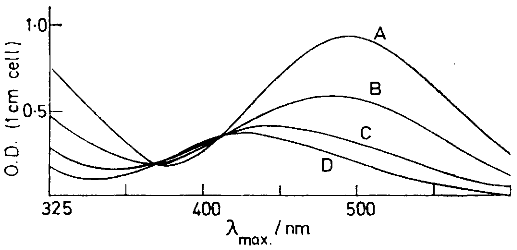

FIGURE 2 The spectrum of the aminoindoaniline (III) (1·01 × 10^{-4}M) at pH: A, 6·0—13; B, 4·0; C, 3·4; and D, 2·2

When oxygen is bubbled into an equimolar solution (0·025M) of *p*-phenylenediamine and *m*-aminophenol at pH 9, the characteristic magenta colour of the indoaniline (I) develops slowly (2% after 40 min, 5% after 80 min). As the reaction proceeds the optical density in the 350—450 nm region increases more rapidly than would be expected and a black crystalline precipitate begins to separate. The effect of reactant concentrations on the yield of this new compound (Table 3) indicates that it is formed from 2 molecules of *p*-phenylenediamine and one molecule of *m*-aminophenol. Elemental analysis and its molecular weight indicate the formula $C_{18}H_{17}N_5O$. Acid hydrolysis, giving *p*-phenylenediamine and 2,5-dihydroxybenzoquinone, suggests the structure (VII) which was confirmed by the n.m.r. spectrum (Table 4) which, by comparison with Table 1, indicates the presence of two *para*-disubstituted benzenoid rings, one disubstituted quinonoid ring, two amino (NH_2) groups attached to similar benzenoid rings, and one amino (NH_2) and one imino (NH) attached to a quinonoid ring. Further, the two lone hydrogens are shown by their high τ values to be *ortho* to an amino-group. It is thus evident that when oxidation of the *para*-diamine is slow, the initially formed aminoindoaniline (I) can react with unoxidized *p*-phenylenediamine to give (VII) the electronic spectrum of which is shown in Figure 3. This mode of formation was confirmed by allowing compound (I) to react with *p*-phenylenediamine in the absence of oxygen whereupon (VII) was formed. A similar reaction of the indoaniline with *p*-toluidine gave the analogous addition product (VIII), the structure of which was shown by its hydrolysis to *p*-phenylenediamine, *p*-toluidine, and 2,5-dihydroxybenzoquinone.

TABLE 3

Yields of compound (VII)

[*p*-Diamine]/ M	[*m*-Aminophenol]/ M	Temp. (°C)	Time (h)	Yield * (%)
0·01	0·01	30	24	82
0·05	0·05	30	24	93
0·05	0·05	75	5	96
0·08	0·04	40	24	91

* % Of *p*-phenylenediamine converted.

TABLE 4

The n.m.r. spectrum of compound (VII) in deuteriated dimethyl sulphoxide

Before deuteriation τ	Before deuteriation Integration	After deuteriation τ	After deuteriation Integration	Assignment
2·03	1			NH (quin)
2·83	2			NH_2 (quin)
4·91	4			$2NH_2$ (benz)
2·92	4	2·90	4	
3·08		3·04		(*J* 84 Hz)
3·34		3·26		
3·49		3·40		2 Sets of 2 pairs of *ortho* H (benz)
3·08^m	4	—	4	
3·22		3·19		
3·30		3·22		(*J* 90 Hz)
3·45		—		
3·99	1	3·96	1	Lone CH † (quin)
4·40	1	4·30	1	Lone CH * (quin)

* *ortho* to NH_2. † *ortho* to $NH{\cdot}C_6H_4{\cdot}NH_2$.

m = Masked.

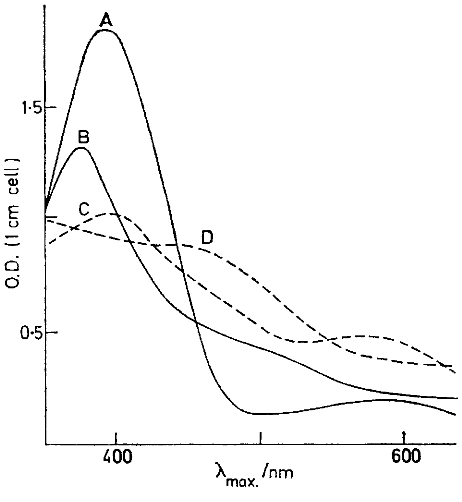

FIGURE 3 The spectrum of compound (VII) in A, 0·1M and 1·0M-hydrochloric acid; B, pH 3·08; C, pH 12·0; and D, pH 4·7.

When oxygen is bubbled into an equimolar solution of *p*-phenylenediamine and 5-amino-2-methylphenol the magenta colour of (III) develops and, as the reaction

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[6] J. F. Corbett, unpublished results.

proceeds pure compound (III) separates from the solution. Spectroscopic examination of the mother liquor at various stages confirmed the absence of other products.

When oxygen is bubbled into a dilute (10^{-4}M) equimolar solution of *p*-phenylenediamine and 3-amino-4-methylphenol, the hydroxyindamine (IV) is formed quantitatively. With more concentrated solutions (0·025M) the hydroxyindamine (IV) ($\lambda_{max.}$ 504 nm) is formed, but after *ca.* 10% reaction a slight shoulder appears at 585 nm. Finally, a precipitates separates, which consists of a mixture of (IV) and the aminophenoxazineimine (V).

Mechanism of the Reaction of Di-imines with m-*Aminophenol.*—It has been shown [7] that at pH > 8, *p*-phenylenediamine is oxidized quantitatively and almost instantaneously by ferricyanide to *p*-benzoquinone di-imine. It is therefore possible to generate the di-imine *in situ* and follow the rate of dye formation spectrophotometrically. At pH < 8, where the equilibrium (1) does not lie completely to the right, a freshly prepared aqueous solution of the pure di-imine is mixed with a solution of the coupler using a jet mixing machine.[7]

$$\textit{para}\text{-Diamine} + 2\ \text{Ferricyanide} \rightleftharpoons \text{Di-imine} + 2\ \text{Ferrocyanide} \qquad (1)$$

The rate of colour development showed that the reaction of di-imine with *m*-aminophenol is of the first order with respect to both reactants and, with stoicheiometric amounts of reactants, follows a second-order kinetic form. This, together with the stoicheiometry, indicates a two-step process, (2) and (3), in which the first step is rate-controlling and where $k[\text{Di-imine}] \gg k_{-2}$. Experiments were performed under the conditions previously defined [3] for avoiding significant hydrolysis of the di-imine or formation of Bandrowski's base during the coupling reaction.

$$\text{Di-imine} + m\text{-Aminophenol} \xrightleftharpoons[k_{-2}]{k_2} \textit{leuco}\text{-Indoaniline} \qquad (2)$$

$$\textit{leuco}\text{-Indoaniline} + \text{Di-imine} \xrightarrow{k} \text{Indoaniline} + p\text{-Diamine} \qquad (3)$$

For reactions of the type (2) followed by (3), where $k \gg k_2$, the rate of dye (In) formation is given by (4).

$$\mathrm{d}[\text{In}]/\mathrm{d}t = k_2[\text{di-imine}][m\text{-aminophenol}] \qquad (4)$$

TABLE 5

Rate data for the reaction of *p*-benzoquinone di-imine with *m*-aminophenol at 30 °C

Expt.	pH ($\pm$0·01)	10^5[Di-imine]/ M	10^5[*m*-A.P.]/ M	k_2/ l mol^{-1} s^{-1}
1	5·95	10·0 *	5·0	$1{\cdot}18 \times 10^4$
2	6·36	10·0 *	5·00	$5{\cdot}40 \times 10^3$
3	6·60	10·0 *	5·00	$3{\cdot}95 \times 10^3$
4	6·97	10·0 *	5·00	$2{\cdot}70 \times 10^3$
5	7·60	10·0 *	5·00	$1{\cdot}64 \times 10^3$
6	8·02	4·63	4·63	$1{\cdot}47 \times 10^3$
7	8·29	10·0 *	5·00	$1{\cdot}27 \times 10^3$
8	8·40	4·63	4·63	$1{\cdot}25 \times 10^3$
9	9·00	4·63	4·63	$1{\cdot}16 \times 10^3$
10	9·00	4·63 †	2·31	$1{\cdot}20 \times 10^3$
11	9·02	2·31	2·31	$1{\cdot}20 \times 10^3$
12	9·41	4·63	4·63	$1{\cdot}02 \times 10^3$
13	9·60	4·63	4·63	$8{\cdot}50 \times 10^2$
14	10·11	4·63	4·63	$4{\cdot}70 \times 10^2$
15	10·36	4·63	4·63	$3{\cdot}53 \times 10^2$
16	10·60	7·50	3·75	$2{\cdot}36 \times 10^2$
17	11·20	18·5	18·5	$5{\cdot}00 \times 10^1$

* With pure di-imine. † With *p*-diamine and ferricyanide (2 mol. equiv). All others with *p*-diamine + ferricyanide (4 mol. equiv.).

Integrated forms of this equation for various stoicheiometric conditions have been given.[1] Rate data for the reaction are in Table 5. The variation in rate with pH is typical of that for the reaction of di-imines with monohydric phenols.[3] This indicates that, at high pH, reaction (2) involves the conjugate acid of the di-imine (DH^+) and the phenoxide ion (P^-).* At lower pH values, the reaction between the conjugate acid of the di-imine and the neutral phenol (P) is the major contributor. In this case k_2 can be broken down into two components as expressed in equation (5), where k_a and k_b are the specific second-order rate constants for the reactions $\text{DH}^+ + \text{P}^-$ and $\text{DH}^+ + \text{P}$, respectively, and the α values are the fractions of the di-imine and the aminophenol which exist as the designated species at the pH to which k_2 pertains. Equation (5) was solved for k_a and k_b by use of the data in Table 5, and a programme for

$$k_2 = k_a\alpha_{\text{DH}^+}\alpha_{\text{P}^-} + k_b\alpha_{\text{DH}^+}\alpha_{\text{P}} \qquad (5)$$

a least-squares fit through the co-ordinates (0,0,0). The programme was written for an input of k_2, pH, and the pK_a values. Using pK_a values of *p*-benzoquinone di-imine [7] and *m*-aminophenol [8] of 5·75 and 9·90 respectively, we get $k_a = 1{\cdot}73 \times 10^7$ l mol^{-1} s^{-1} and $k_b = 2{\cdot}72 \times 10^4$ l mol^{-1} s^{-1}. The contributions of the two reactions were calculated and the results are compared with the experimental data in Figure 4. The excellent agreement supports the reaction Scheme 1, involving electrophilic attack by the conjugate acid of the di-imine (IX) on the position *para* to the hydroxy-group of the *m*-aminophenolate ion and of the neutral phenol to give the *leuco*-dye (X) which undergoes rapid oxidation to (I). It should be noted that under the conditions of the kinetic experiments, the addition of *p*-diamine to (I) to give (VII) is extremely slow and need not be considered. The fact that data from experiments

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* It should be noted that a reaction between the two neutral species (D + P) would have the same rate–pH profile as that for $\text{DH}^+ + \text{P}^-$. However, in our study of the coupling of di-imine with *m*-diamines and with aniline we found there to be no contribution from reactions of the neutral di-imine. It thus seems unlikely that the reaction D + P contributes significantly in the present case. Further, if this reaction did contribute, we would expect to have an even greater contribution of the reaction $\text{D} + \text{P}^-$, which would increase with increasing pH and become pH-independent at pH > 11. However, Figure 4 shows that no deviation from the $\text{DH}^+ + \text{P}^-$ profile is observed.

[7] J. F. Corbett, *J. Chem. Soc.* (*C*), 1969, 207.

[8] J. M. Bandenbelt, C. Henrick, and S. G. Vanden Berg, *Analyt. Chem.*, 1954, **26**, 726.

1—5, 7, 10, and 16 of Table 5 fit on the same curve as those from the other experiments indicates that the *p*-benzosemiquinone di-imine, which can only be formed in the former group,[4] where *p*-phenylenediamine is formed as the reaction proceeds, is not involved in the dye-forming reactions.

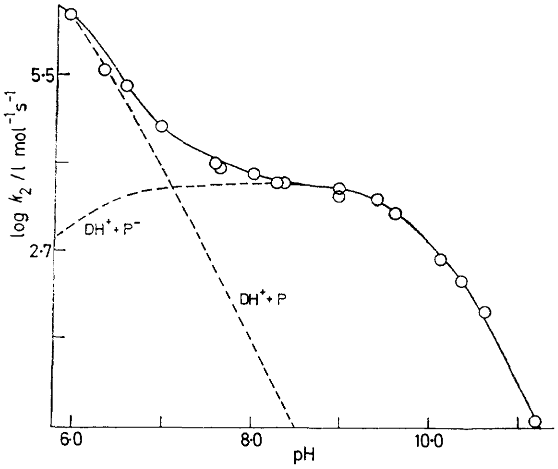


FIGURE 4 The effect of pH on the rate of reaction of *p*-benzoquinone di-imine with *m*-aminophenol at 30 °C, showing the contributions (broken lines) of the reactions between the various ionic species to the total rate (full line) calculated according to equation (5)

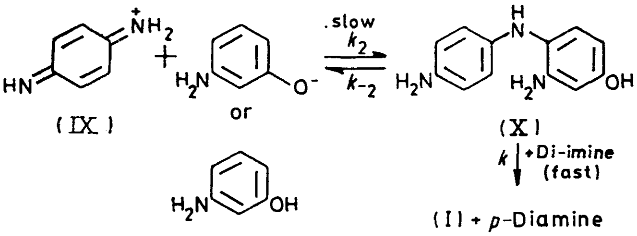
TABLE 6

Rate data for the reaction of substituted *p*-di-imines with *m*-aminophenol at 30 °C

Substituent	pH ($\pm$0·01)	10^5[Di-imine] */M	10^5[*m*-A.P.]/M	k_2/l mol^{-1} s^{-1}	(k_2/α_{P^-})/l mol^{-1} s^{-1}
2-Cl	8·85	5·00	5·00	$1·56 \times 10^3$	$1·92 \times 10^4$
2-Cl	9·81	5·00	5·00	$1·09 \times 10^3$	$2·43 \times 10^3$
2-Cl	9·94	5·00	5·00	$8·70 \times 10^2$	$1·66 \times 10^3$
2-Cl	10·39	5·00	5·00	$5·33 \times 10^2$	$7·08 \times 10^2$
2-Cl	11·41	5·00	5·00	$5·50 \times 10^1$	$5·68 \times 10^1$
2-Me	8·30	18·5	18·5	$2·82 \times 10^1$	$1·15 \times 10^4$
2-Me	9·00	18·5	18·5	$2·52 \times 10^2$	$2·25 \times 10^3$
2-Me	9·62	18·5	18·5	$2·00 \times 10^2$	$5·78 \times 10^2$
2-Me	10·02	18·5	18·5	$1·25 \times 10^2$	$2·20 \times 10^2$

* Using *p*-diamine and 4 molar proportions of potassium ferricyanide.

Rate data for the reactions of 2-chloro- and 2-methyl-*p*-benzoquinone di-imine with *m*-aminophenol are in Table 6. Plots of log (k_2/α_{P^-}) against pH are straight lines of unit slope, again indicating that, over this pH range, the conjugate acid of the di-imine and the *m*-aminophenolate ion are the reactive species. In the earlier report on the reaction of di-imines with monohydric phenols[3] the values of k_2/α_{P^-} at pH 10·05 were used to compare the effect of substituents on the reactivity of the di-imines towards phenolate ions at a particular pH. Table 6 shows that the reactivities of di-imine, chlorodi-imine, and methyldi-imine are in the ratio 1·0 : 1·5 : 0·22. Thus, as with the reaction of imines with simple phenolate ions, chlorination of the imine increases the rate of reaction while methylation decreases it at a fixed pH. Comparison of rates of reaction of these three imines with the *m*-aminophenolate ion with those for the reaction with the unsubstituted phenolate ion[3] shows that the amino-group increases the reactivity of the phenolate ion by factors of 220, 70, and 263 respectively, *i.e.*, a mean value of 188. These changes are consistent with the suggested mechanism.



SCHEME 1

Mechanism of the Reaction of p-*Benzoquinone Di-imine with* 5-*Amino*-2-*methylphenol*.—As was shown above, the final product of this reaction is 2-amino-5-methylindoaniline (III). Contrary to expectation, the formation of this dye does not follow a simple kinetic law. Thus, when stoicheiometric amounts (2 : 1) of the di-imine and the phenol are mixed there is a rapid formation of 66% of the theoretical amount of dye followed by the relatively slow formation of the remaining 34%. Repetitive scan experiments of the reaction mixture subsequent to the rapid stage (Figure 5) show the presence of an intermediate absorbing in the region 325—370 nm where neither of the reactants have significant absorption. The presence of isosbestic points at 325 and 360 nm indicate that this species is undergoing conversion into the aminoindoaniline.

The presence of the intermediate was confirmed by recording the spectrum of a 1 min old reaction mixture (10^{-4}M-di-imine and 5×10^{-5}M-aminophenol) against a reference containing $3·3 \times 10^{-5}$M-dye (III) and $3·3 \times 10^{-3}$M-*p*-phenylenediamine. The resulting spectrum (Figure 5) showed a broad absorption band having a maximum at 325 nm (ε *ca.* 7600), *i.e.*, approximately of the same intensity of the absorption of the aminoindoaniline at this wavelength, thus accounting for the isosbestic point. These results suggest that when the di-imine reacts with 5-amino-2-methylphenol, attack occurs *ca.* 66% in the 4-position, to give the dye (III) by the normal route, and *ca.* 34% in the 2-position to give a pseudo-quinone imine (XI) which subsequently undergoes slow decomposition and ultimate conversion into the indoaniline (III). The most likely course for the reaction is shown in Scheme 2. In this scheme, compound (XI) is a kinetically significant product (*i.e.*, $k_1 \sim k_2$ and $k_1 > k_{-1}$) while the dye (III) is the thermodynamically favoured product. Such a scheme would require that if di-imine and aminophenol were mixed in a 2 : 1 molar ratio, some di-imine would remain at the end of the rapid step. This was confirmed experimentally by scanning the u.v. spectrum of the reaction mixture whereupon the characteristic di-imine peaks at 257 and 265·5 nm were evident. The possibility that the conversion of (XI) into (III) might involve addition of *p*-phenylenediamine at the 3-position of (XI) and its simultaneous displacement from the (I) position to give (XII), was discounted since addition of *p*-diamine did not affect the rate of conversion.

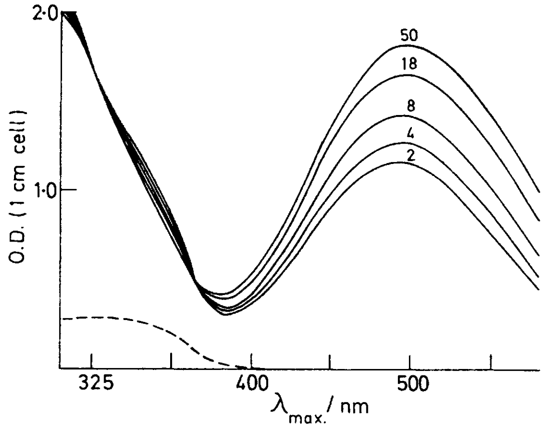
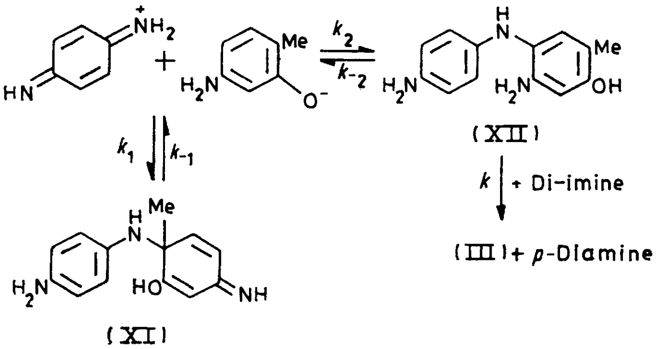


FIGURE 5 Spectrophotometric course (full lines) of the slow stage of the reaction of *p*-benzoquinone di-imine ($1{\cdot}0 \times 10^{-4}$M) with 5-amino-2-methylphenol ($5{\cdot}0 \times 10^{-5}$M) at pH 10·95 and 30 °C (times shown in min); and the difference spectrum (broken line) of the pseudo-quinone imine (XI) at 1 min



SCHEME 2

The first step of the suggested mechanism involves the competitive formation of compounds (XI) and (XII) and this is followed by the almost instantaneous oxidation of (XII) to (III). Thus, during the rapid colour development, the formation of (XI) consumes 1 mol. equiv. of di-imine while that of (III) consumes 2 mol. equiv. of di-imine. This complex stoicheiometry would give a rate of colour development exhibiting a positive deviation from the normal second-order plot as is, in fact, observed (Table 7). At both pH values (Table 7), the proportion of dye formed in the rapid stage is the same. Table 7 shows that the rate increases about 6-fold on changing from pH 10·81 to 8·26. This corresponds to an increase, by a factor of 6·26, of the product $\alpha_{\mathrm{DH^+}}\alpha_{\mathrm{P^-}}$ over the same pH range. Thus, both initial reactions involve attack by the conjugate acid of the di-imine on the aminophenolate ion. Further, at pH 10·81, the half-life for consumption of the aminophenol would be about 5 s if pure second-order kinetics were obeyed. This gives a value for $k_1 + k_2$ of *ca.* 2×10^8 l mol^{-1} s^{-1} and for k_2 of *ca.* $1{\cdot}33 \times 10^8$ l mol^{-1} s^{-1}. From this we get a value of $k_a = k_2/(\alpha_{\mathrm{DH^+}}\alpha_{\mathrm{P^-}}) \simeq 1{\cdot}77 \times 10^8$ l mol^{-1} s^{-1} for attack *para* to the hydroxy-group of the aminophenol. This is about 10 times greater than that of the value for *m*-aminophenol itself, and is between those of 30 and 3 found for analogous *C*-methylation of phenolate ion[3] and *m*-phenylenediamine[2] respectively.

TABLE 7

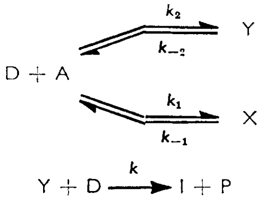
Rate of colour development in the reaction of *p*-benzoquinone di-imine with 5-amino-2-methylphenol at 30 °C *

O.D.†	Time pH 8·26	 pH 10·81	Reaction stage
0·30		1·70 s	25% A
0·60	0·70 s	4·30 s	50% A
0·90	1·70 s	10·7 s	75% A
1·05	2·90 s	18·0 s	87·5% A
1·20	18·0 s	1·5 min	(end of fast stage)
1·35	4·10 min	5·5 min	25% B
1·51	9·7 min	11·5 min	50% B
1·66	20·0 min	21·5 min	75% B
1·80			100% colour development

* [*p*-Benzoquinone di-imine] = 2[5-amino-2-methylphenol] = $1{\cdot}0 \times 10^{-4}$M. † Optical densities for 4 cm cell; times relate to $t_{1/4}$, $t_{1/2}$, and $t_{3/4}$ assuming final O.D. = 1·2 for the rapid state.

A = Fast colour development, B = slow colour development.

For the slow conversion of the adduct (XI) into the indoaniline (III), the rate data (Table 7) indicate that it follows a first-order rate law, as would be expected if $k_2 \gg k_{-1}$. At both pH values the half-life for the slow step is 10 min and, since only 66% of the dissociation products will lead directly to the formation of (III), we get k_{obs} *ca.* $1{\cdot}7 \times 10^{-3}$ s^{-1}.



SCHEME 3

The kinetic assumptions made above can be deduced from the steady-state approximation for the general Scheme 3 where D = di-imine, A = aminophenol, Y =

(XII), X = (XI), I = (III), and P = *p*-diamine. Considering first the rapid stage and assuming a steady state for Y, we get equation (6) and thence (7). Further, if $k[D] \gg k_{-2}$ we get equation (8). Also, since A and D are being consumed by two competing reactions and, assuming that $k_1[A][D] \gg k_{-1}[X]$, we get (9). Thus, the

$$[Y] = k_2[D][A]/(k_{-2} + k[D]) \qquad (6)$$

$$d[I]/dt = kk_2[D]^2[A]/(k_{-2} + k[D]) \qquad (7)$$

fast stage should follow second-order kinetics and the

$$d[I]/dt = k_2[D][A] \qquad (8)$$

$$-d[A]/dt = (k_2 + k_1)[A][D] \qquad (9)$$

rate constants for the yield of indoaniline can be obtained by combining (8) and (9) to give equation (10).

$$-d[I]/d[A] = k_2/(k_1 + k_2) = [I]_t/([I]_t + [X]_t) \qquad (10)$$

That the fast stage follows second-order kinetics was shown experimentally by doubling the reactant concentrations whereupon the times for the fast stage were halved while those for the slow stage were unchanged.

For the slow colour development we can assume a steady state for A [equation (11)] whence [Y] is given by equation (12). Assuming a steady state for Y, we

$$k_{-1}[X] + k_{-2}[Y] = (k_1 + k_2)[D][A] \qquad (11)$$

$$[Y] = \{(k_1 + k_2)[D][A] - k_{-1}[X]\}/k_{-2} \qquad (12)$$

get equation (13) and combining (12) and (13) we get (14), and thence (15). However, we also have equation

$$[Y] = k_2[D][A]/(k_{-2} + k[D]) \qquad (13)$$

$$k_2k_{-2}[D][A] = \{(k_1 + k_2)[D][A] - k_{-1}[X]\}(k_{-2} + k[D]) \qquad (14)$$

(16), and, on substituting for [A] from (15) in (16) and

$$[A] = k_{-1}[X](k_{-2} + k[D])/(\{(k_1 + k_2)(k_{-2} + k[D]) - k_2k_{-2}\}[D]) \qquad (15)$$

$$d[I]/dt = k[Y][D] = kk_2[D]^2[A]/(k_{-2} + k[D]) \qquad (16)$$

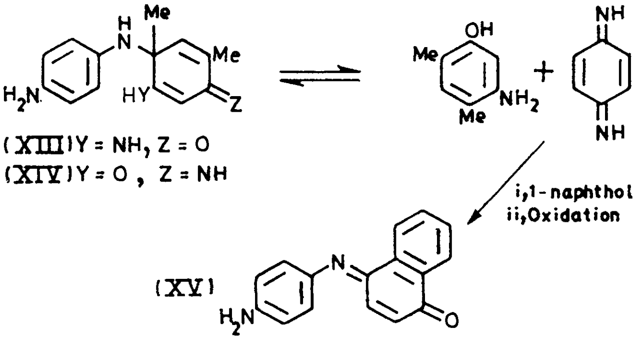
assuming $k[D] \gg k_{-2}$, we get equation (17), *i.e.*, the

$$d[I]/dt = \{k_2k_{-1}/(k_2 + k_1)\}[X] \qquad (17)$$

formation of dye in the slow stage will follow first-order kinetics and the value of k_{-1} is given by $k_{obs}(k_1 + k_2)/k_2$. Since $k_{obs} \sim 1{\cdot}7 \times 10^{-3}$ s^{-1} and $(k_1 + k_2)/k_2 = 3/2$, then $k_{-1} \sim 2{\cdot}5 \times 10^{-3}$ s^{-1}.

Equations (16) and (17) show that the presence of an excess of the aminophenol should affect the rate of colour development in the slow stage since it invalidates the assumption that $k[D] \gg k_{-2}$. An experiment with a reaction mixture containing 10^{-4}M of both di-imine and the aminophenol showed the expected increase in the amount of dye formation in the fast stage but a decrease, by a factor of *ca.* 2 in the rate of the slow stage. On the other hand, with a reaction mixture comprising equal amounts of *p*-phenylenediamine and 5-amino-2-methylphenol and an excess (>4 mol. equiv.) of ferricyanide, the fast stage gave the same colour yield as did that for a 2 : 1 mixture of di-imine and the aminophenol, but the onset of the slow colour development was considerably delayed. This can be ascribed to the fact that both D and A are completely consumed in the fast step and the condition $k_1[A][D] \gg k_{-1}[X]$ no longer holds and a sigmoid colour development curve is observed. These results support the mechanism in Scheme 2.

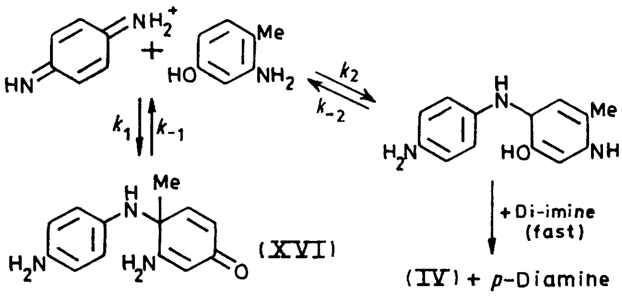
The hypothesis that a pseudo-quinone imine, such as (XI), is formed is further supported by the observation that when a 5×10^{-5}M-di-imine solution is injected into a solution containing 1 molar equivalent of 3-amino-4,6-dimethylphenol, the spectrum of the di-imine disappears immediately and is replaced by a peak at 327 nm (log ε 3·85). The spectral features of the species, which may have the structure (XIII) or (XIV) or be a mixture of both, are closely similar to those deduced above for (XI). Further it was found that if the reaction mixture is treated with a known coupler, such as 5-amino-2-methylphenol or 1-naphthol, the dye formed from di-imine and that coupler, *i.e.*, (III) or (XV), is slowly formed. These observations are explained in Scheme 4.



SCHEME 4

Mechanism of the Reaction of p-*Benzoquinone Di-imine with* 3-*Amino*-4-*methylphenol*.—As shown above, the initial product of this reaction is the hydroxyindamine (IV), which is capable of subsequent intramolecular cyclization to the phenoxazineimine (V). Kinetic experiments, following the rate of formation of the indamine, showed colour development to follow a similar course to that observed for the reaction with 5-amino-2-methylphenol. Thus there is observed a rapid formation of 60% of the dye (second-order kinetics) followed by a slower formation of the remaining 40% (first-order kinetics). Again, the rate of the fast step changes with pH in proportion to the product $\alpha_{DH^+}\alpha_{P^-}$, while the rate of the slow step is independent of pH. From the data the following rate constants were obtained: $k_a = 2{\cdot}0 \times 10^8$ l mol^{-1} s^{-1} for attack of the conjugate acid of the di-imine at the 6-position of the 3-amino-4-methylphenolate ion, and $k_{-1} = 3{\cdot}8 \times 10^{-3}$ s^{-1} for dissociation of the adduct (XVI) which absorbs maximally near 335 nm. On the basis of these results the mechanism shown in Scheme 5 is suggested.

When a concentrated solution (10^{-1}M) of the hydroxyindamine (IV) is heated, the cyclized product (V) is formed rapidly. However when a dilute solution (10^{-4}M) of (IV) is heated under similar conditions the indamine decomposes and no phenoxazine is formed. The rate of colour loss follows a first-order rate law.



SCHEME 5

This observation suggests that only in concentrated solutions, where associated dimers of the indamine might be formed, can the cyclization occur. To test this proposition, data for the yield of phenoxazineimine as a function of initial indamine concentration were obtained (Table 8). For the suggested mechanism, intramolecular cyclization to the phenoxazineimine P, *via* an associated dimer of the indamine I, competes with first-order decomposition to give an ill-defined product B (Scheme 6).

TABLE 8

Effect of initial concentration on the yield of the phenoxazineimine (V)

Concn. (M)	10^{-3}	$2{\cdot}5 \times 10^{-3}$	5×10^{-3}	10^{-2}	10^{-1}
Yield (%)	*ca.* 0 *	2·6 *	5·7 *	11·4 *	60 †

* Determined spectrophotometrically. † Determined gravimetrically.

$$2\mathrm{I} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Dimer}$$

$$\text{Dimer} \xrightarrow{k_2} 2\mathrm{P} \text{ (or Dimer} \xrightarrow{k_2} \mathrm{P} + \mathrm{I})$$

$$\mathrm{I} \xrightarrow{k'} \mathrm{B}$$

SCHEME 6

For the equilibrium $[\text{Dimer}]_t/[\mathrm{I}]^2 = K = k_1/k_{-1}$, $\mathrm{d}[\mathrm{P}]/\mathrm{d}t = 2k_2[\text{Dimer}]_t = 2k_2K[\mathrm{I}]_t^2$, and $\mathrm{d}[\mathrm{B}]/\mathrm{d}t = k'[\mathrm{I}]_t$. Assuming a steady state for the dimer we get equation (18) whence (19) and (20). Putting $k_c = 2k_2k_1/(k_{-1} + k_2)$

$$k_1[\mathrm{I}]_t^2 - k_2[\text{Dimer}]_t - k_{-1}[\text{Dimer}]_t = 0 \qquad (18)$$

$$[\text{Dimer}]_t = k_1[\mathrm{I}]_t^2/(k_{-1} + k_2) \qquad (19)$$

$$-\mathrm{d}[\mathrm{I}]/\mathrm{d}t = \{2k_2k_1[\mathrm{I}]_t^2/(k_{-1} + k_2)\} + k'[\mathrm{I}]_t \qquad (20)$$

$$-\mathrm{d}[\mathrm{I}]/\mathrm{d}t = k_c[\mathrm{I}]_t^2 + k'[\mathrm{I}]_t \qquad (21)$$

we get equation (21). It follows that $-\mathrm{d}[\mathrm{B}]_t/\mathrm{d}[\mathrm{I}]_t = k'/(k_c[\mathrm{I}]_t + k')$ which on integration between the limits $[\mathrm{I}]_t = [\mathrm{I}]_0$ when $t = 0$ and $[\mathrm{I}]_t = 0$ when $t = \infty$ gives equation (22), and since $[\mathrm{P}]_\infty = [\mathrm{I}]_0 - [\mathrm{B}]_\infty$, from the stoicheiometry, we get equation (23). Equation (23)

$$[\mathrm{B}]_\infty = (k'/k_c) \ln \{(k_c[\mathrm{I}]_0 + k')/k'\} \qquad (22)$$

$$\frac{[\mathrm{P}]_\infty}{[\mathrm{B}]_\infty} = \frac{[\mathrm{I}]_0 - (k'/k_c) \ln \{(k_c[\mathrm{I}]_0 + k')/k'\}}{(k'/k_c) \ln \{(k_c[\mathrm{I}]_0 + k')/k'\}} = \frac{k_c[\mathrm{I}]_0}{k' \ln (1 + k_c[\mathrm{I}]_0/k')} - 1 \qquad (23)$$

can be solved for various values of $k_c[\mathrm{I}]_0/k'$, and a plot of $\log [\mathrm{I}]_0$ against $\log$ (% P) for a value of $k_c/k' = 15{\cdot}9$ is shown in Figure 6. The experimental values from Table 8 can be superimposed on the theoretical plot, as shown by the points in Figure 6, thus supporting the suggested mechanism. It should be noted that the same theoretical curve would be obtained if the cyclization step were to give one molecule of phenoxazineimine and one molecule of indamine (*i.e.*, Dimer ⟶ P + I). Experiments with 3-amino-4-methylphenol and a variety of *p*-phenylenediamines have shown that the oxidation can be used as a general method for the synthesis of 7-aminophenoxazineimines.

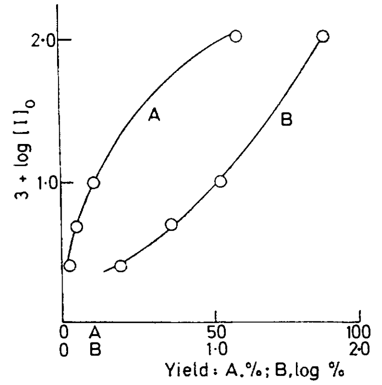


FIGURE 6 Theoretical plots [from equation (23)] and experimental points (from Table 8) for the yield of the phenoxazineimine (V) from the indamine (IV) as a function of initial indamine concentration

EXPERIMENTAL

Materials.—5-Amino-2-methylphenol, m.p. 162° (lit.,[9] 159—161°), 3-amino-4-methylphenol, m.p. 157° (lit.,[10] 157°), and 3-amino-4,6-dimethylphenol, m.p. 164° (lit.,[11] 166·5—167°) were prepared by catalytic reduction ($\mathrm{H_2}$/10% Pd–C in ethyl acetate) of the corresponding nitrophenols which were obtained by diazotization and replacement of the amino-group of the corresponding nitroanilines by a hydroxy-group.[11] 3-Amino-4-methylphenol was also prepared as described in a patent.[12] 3-Amino-4-methoxyphenol hydrochloride and 5-amino-2-methoxyphenol hydrochloride have been described.[13] *p*-Benzoquinone diimine was prepared as described.[14] All other materials were commercial samples which were recrystallized to constant m.p.

Spectra and Dissociation Constants of Aminophenols.—The

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[9] O. Wallach, *Ber.*, 1882, **15**, 2832.

[10] W. A. Jacobs, M. Heidelberger, and I. P. Rolf, *J. Amer. Chem. Soc.*, 1919, **41**, 459.

[11] E. Bamberger and E. Reber, *Ber.*, 1907, **40**, 2267.

[12] L'Oreal, B.P. 1,143,589.

[13] J. F. Corbett, B.P. 1,056,250.

[14] J. F. Corbett, *J. Chem. Soc.* (*C*), 1969, 213.

dissociation constants of the phenolic group of the aminophenols were determined spectrophotometrically at 30·0 ± 0·1 °C in buffer solutions prepared by appropriate admixture of 0·1M-solutions of AnalaR disodium hydrogen phosphate and sodium phosphate. The spectra of the aminophenolate and hydroxyanilinium ions were determined in 0·1M-sodium hydroxide and 0·1M-hydrochloric acid respectively. The spectra of the neutral aminophenols were determined in a phosphate buffer of pH = 7·5. Results are in Table 9.

TABLE 9

Spectra and dissociation constants of aminophenols

3-Aminophenol	Cation	Neutral	Anion	pK_a (±0·02)
Parent	270 (3·26), 275^{s}	281 (3·27)	290 (3·50)	9·90
4-Methyl	275 (3·36), 282^{s}	285 (3·49)	292 (3·57)	10·20
6-Methyl	270 (3·29), 275^{s}	286 (3·36)	294 (3·55)	10·06
4,6-Dimethyl	277 (3·36)	289 (3·54)	301 (3·70)	

s = Shoulder.

Oxidation of Mixtures of p-*Phenylenediamine and* m-*Aminophenols with Ferricyanide*.—(i) m-*Aminophenol*. 0·0125M-*p*-Phenylenediamine (80 ml) and 0·0125M-*m*-aminophenol (80 ml) were mixed and the pH was adjusted to *ca*. 9 with sodium carbonate; 0·4M-potassium ferricyanide solution (20 ml) was added, the solution filtered, and the filtrate extracted with ether (3 × 150 ml). The dried (Na_2SO_4) extract was evaporated to 25 ml and cooled to give 2-*amino*-N-(4-*aminophenyl*)*benzoquinone monoimine* (I) (24 mg) as black needles with a green reflex, m.p. 131° (Found: C, 67·9; H, 4·92; N, 19·4. $C_{12}H_{11}N_3O$ requires C, 67·6; H, 5·16; N, 19·7%).

(ii) 5-*Amino-2-methylphenol*. The above procedure gave 2-*amino*-N-(4-*aminophenyl*)-5-*methylbenzoquinone monoimine* (III) as black needles with a green reflex, m.p. 210° (unchanged after recrystallization from methanol) (Found: C, 68·7; H, 5·91; N, 18·5. $C_{13}H_{13}N_3O$ requires C, 68·7; H, 5·72; N, 18·5%). The compound was heated with 0·15M-hydrochloric acid with the condenser set for distillation. Spectroscopy showed the distillate to contain 2-hydroxy-5-methyl-1,4-benzoquinone ($\lambda_{max.}$ in acid 268 and 394, in alkali 274 and 490 nm).[15] Chromatography showed an ether extract of the basified residue to contain *p*-phenylenediamine and a purple compound identical with that formed from heating a solution containing *p*-phenylenediamine and 2-hydroxy-5-methyl-1,4-benzoquinone.

(iii) 3-*Amino*-4-*methylphenol*. A solution of *p*-phenylenediamine dihydrochloride (3·62 g) and 3-amino-4-methylphenol hydrochloride (3·19 g) in water (50 ml) was added slowly to a solution of potassium ferricyanide (27 g) in water (300 ml), the pH of the mixture being maintained at 8—9 by addition of ammonium hydroxide. The precipitated indamine (IV) (2·75 g, 59%) was filtered off, washed with dilute ammonium hydroxide, and allowed to dry in an evacuated desiccator. The filtrate from the reaction mixture was heated on a water-bath for 1 h. On cooling, the phenoxazineimine (V) separated as a black solid (0·53 g). The crude product was dissolved in 0·5M-hydrochloric acid (1 l), and the solution was filtered and treated with ammonium hydroxide to pH 8. On cooling, 7-*amino*-2-*methylphenoxazine*-3-*imine hydrochloride* separated as black microcrystals, m.p. >360° (Found: C, 59·5; H, 4·69; Cl, 13·5. $C_{13}H_{12}ClN_3O$ requires C, 59·7; H, 4·59; Cl, 13·6%). The free base was obtained by triturating the salt with 0·25M-sodium hydroxide and filtering. The still wet solid was extracted with ethyl acetate (3 × 250 ml) in the presence of a few sodium hydroxide pellets and the solution was dried (Na_2SO_4) and filtered while hot. On cooling, 7-*amino*-2-*methylphenoxazine*-3-*imine* (V) separated as brown needles, m.p. 228° (decomp.) (Found: C, 69·4; H, 4·76; N, 18·4. $C_{13}H_{11}N_3O$ requires C, 69·3; H, 4·89; N, 18·7%). The *picrate* separates from ethanol as greenish yellow needles, m.p. 310° (decomp.) (Found: C, 50·2; H, 3·24; N, 18·5. $C_{19}H_{14}N_6O_8$ requires C, 50·2; H, 3·08; N, 18·5%). In an experiment in which the intermediate indamine was not isolated, a 63% yield of the phenoxazineimine hydrochloride was obtained.

Oxidation of Mixtures of p-*Phenylenediamine and* m-*Aminophenols with Molecular Oxygen*.—(i) m-*Aminophenol*. *p*-Phenylenediamine dihydrochloride (7·24 g) and *m*-aminophenol (2·18 g) were dissolved in 0·1M-disodium hydrogen phosphate (500 ml) and the pH was adjusted to 8 with sodium hydroxide. Oxygen was bubbled through the solution for 24 h and the solution was filtered to give 2-*amino*-N-(4-*aminophenyl*)-5-(4-*aminoanilino*)*benzoquinone monoimine* (VII) (5·8 g) as black needles, m.p. 237° [Found: C, 68·2; H, 5·62; N, 20·5%; *M*, 319·1433 (mass spectrum). $C_{18}H_{17}N_5O$ requires C, 67·9; H, 5·34; N, 22·0%; *M*, 319·1433]. Yields of compound (VII) from other experiments are given in Table 3. Compound (VII) was also obtained from mixing deaerated solutions of *p*-phenylenediamine and the crude indamine (IV) and allowing the mixture to stand for 1 h.

Compound (VII) was dissolved in 10% hydrochloric acid and the solution was heated under reflux for 15 min and then set for distillation. After 100 ml of distillate had been collected, it was examined spectrophotometrically to confirm the presence of 2,5-dihydroxy-1,4-benzoquinone ($\lambda_{max.}$ in acid 284 and 402, in alkali 313, 325, and 397 nm).[16] A portion of the residue was treated with alkali and ammonia was evolved on warming. A second portion was made alkaline and extracted with ether and the extract evaporated to give a solid which, on sublimation, gave *p*-phenylenediamine. The remainder of the residue was examined chromatographically and shown to be almost identical with that obtained from the hydrolysis of Bandrowski's base or from heating a mixture of *p*-phenylenediamine and 2,5-dihydroxybenzoquinone in acid.[17]

(ii) 5-*Amino*-2-*methylphenol*. *p*-Phenylenediamine dihydrochloride (1·81 g) and 5-amino-2-methylphenol hydrochloride (1·59 g) were dissolved in water (200 ml) and the pH adjusted to 9·3 with ammonium hydroxide. Oxygen was bubbled through the solution for 24 h to give 0·4 g of the indoaniline (III), m.p. and mixed m.p. 210°.

(iii) 3-*Amino*-4-*methylphenyl*. *p*-Phenylenediamine dihydrochloride (0·45 g) and 3-amino-4-methylphenol hydrochloride (0·40 g) were dissolved in water and the pH was adjusted to 9·3 with ammonium hydroxide. Oxygen was

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[15] J. F. Corbett, *J. Chem. Soc.* (*C*), 1970, 2101.

[16] J. F. Corbett, *J. Chem. Soc.* (*C*), 1967, 1909.

[17] J. F. Corbett, *J. Soc. Dyers and Colourists*, 1969, **85**, 71.

bubbled through the solution and the reaction was monitored by examining the visible spectrum at intervals. After 24 h, the precipitate (0·074 g) was filtered off, dried, and dissolved in methanol. Chromatography of basic alumina gave the indamine (IV) and the phenoxazineimine (V). When oxygenation was performed at 90 °C a 41% yield of the phenoxazineimine hydrochloride was obtained after 30 min. To examine the conversion of the indamine (IV) into the phenoxazineimine (V), appropriate weights of (IV) were dissolved in 200 ml of a 0·1-M phosphate buffer (pH = 9), and heated on a water-bath for 30 min. A sample of the solution was diluted and the yield of phenoxazineimine was determined from its absorption band at 592 nm.

Preparation of Indoanilines and Indamines.—Spectral data for other derivatives of compounds (I) and (II) were obtained by mixing equal volumes of a 3×10^{-4}M-solution of the *p*-diamine, a 3×10^{-4}M-solution of the *m*-aminophenol, and a 6×10^{-4}M-solution of potassium ferricyanide, all at pH 8·5, and recording the spectrum when maximum colour had developed. Data are in Table 2.

Synthesis of 2-Alkyl-3,7-diaminophenoxazinium Salts.—The appropriate *p*-phenylenediamine dihydrochloride (0·02 mol) and 4-alkyl-3-aminophenol hydrochloride (0·02 mol) were dissolved in water (50 ml) and the solution was added, with stirring, to a solution of potassium ferricyanide (27 g) in water (300 ml), the pH being maintained at 8—9 by the addition of ammonia. The mixture was heated on a boiling-water bath for 30 min, and sodium chloride was added during subsequent cooling to precipitate the 2-alkyl-3,7-diaminophenoxazinium chloride. Data are in Table 10.

Kinetic Experiments.—All kinetic measurements were made at 30·0 ± 0·1 °C by use of previously described techniques.[3] Buffer solutions were prepared from 0·1M-solutions of sodium dihydrogen phosphate, disodium hydrogen phosphate, and sodium phosphate. Individual kinetic runs were reproducible to within ±4% and it is estimated that the rate constants are accurate to within ±9% over the pH range 6·5—10 and ±15% outside this range. Typical experimental data are in Table 11.

TABLE 10

Data for the synthesis of 2-alkyl-3,7-diaminophenoxazinium chlorides

Reactants		Product	
p-Diamine	3-Aminophenol	Yield (%)	$\lambda_{max.}$/nm
Parent	4-Me	65	554^s, 592
Parent	4-Pr^i	60	554^s, 591
2,5-Me_2	4-Me	60	552^s, 591
2,6-Me_2	4-Me	55	553^s, 593
2-Cl	4-Me	65	550^s, 591

s = Shoulder.

TABLE 11

Typical experimental data for the reaction between *p*-benzoquinone di-imine and *m*-aminophenol at 30 °C

Optical density †	Reaction %	t/s	10^3k_2/l mol^{-1} s^{-1}
	pH 8·40 *		
0·47	25	5·5	1·32
0·74	50	17·6	1·24
1·21	75	52·0	1·25
1·435	87·5	120·0	1·27
	pH 6·60 ‡		
0·475	25	~0·7	—
0·95	50	2·25	4·45
1·425	75	6·80	4·23
1·66	87·5	15·0	3·50

* [*p*-Phenylenediamine] = [*m*-aminophenol] = $4·63 \times 10^{-5}$ M; [ferricyanide] × 1·85 = 10^{-4}M. † In a 4 cm cell. ‡ [*p*-Benzoquinone di-imine] = $1·0 \times 10^{-4}$M; [*m*-aminophenol] = $5·0 \times 10^{-5}$M.

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