Benzoquinone Imines. Part 13.[1] Reactions of *N*-Methylated 2-Aminoindamines in Aqueous Solution

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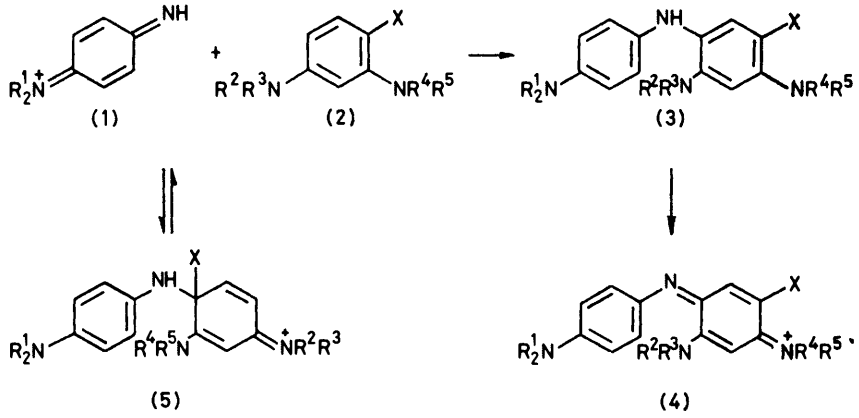
N-Methylated 2-aminoindamines [2-amino-*N*-(4-aminophenyl)-*p*-benzoquinone di-imines] undergo hydrolysis at the azomethine bridge at pH < 4, intramolecular cyclization to diaminophenazines at pH 4—9.5, and hydrolysis of the terminal imino-group at high pH. The effect of *N*-methylation of either amino- or imino-group on the rate of these reactions is consistent with the proposed mechanisms. Acid hydrolysis involves reaction of the dication with a hydroxonium ion and with water, cyclization involves an intramolecular coupling of the 2-amino-nitrogen of the monocation, to the 2-carbon atom, followed by oxidation, and alkaline hydrolysis involves reaction of a hydroxide ion with the monocation. The N^4N^4-dimethylindaminium ions form a neutral species at pH > 11 by loss of a proton from the tautomeric form 4-dimethylamino-N^1-(4-aminophenyl)-*o*-benzoquinone di-imine. 2-Dimethylaminoindamines undergo rapid intramolecular cyclization to give the colourless 2,8-diamino-10,10-dimethyl-5,10-dihydrophenazinium ion. This is slowly converted into a 10-methylphenazinium salt, a methyl group being eliminated as methanol.

In a previous paper[1] we reported that the decomposition of 2-aminoindamines (4; R^1—R^5 = H) in aqueous solution resulted from hydrolysis at the azomethine bridge at low pH, intramolecular cyclization of the conjugate acid at moderate pH, and hydrolysis of the terminal imino-group at high pH. In view of this diversity of reaction and of the number of nitrogen functions it was of interest to examine the effect of *N*-alkyl substituents on the course and rate of these reactions.

In the course of our kinetic studies, we prepared dilute solutions of some of the aminoindamines *in situ*, by oxidative coupling of the *p*-diamine with the *m*-diamine, using potassium ferricyanide as oxidant.[2] In coupling reactions with *p*-phenylenediamine and all the *N*-methylated *m*-diamines we found, as with the unsubstituted *m*-diamines,[2] that the rate of indamine formation increases with decreasing pH, over the pH range 6—10, confirming that the rate controlling step involved reaction of the di-iminium ion (1; R^1 = H) with the neutral *m*-diamine (2) (Scheme 1).



a; R^1–R^5 = X = H
b; R^1–R^5 = H, X = Me,
c; R^1–R^4 = H, R^5 = X = Me
d; R^1–R^3 = H, R^4 = R^5 = X = Me
e; R^1–R^3 = X = H, R^4 = R^5 = Me
f; R^1 = Me, R^2–R^5 = X = H
g; R^1 = X = Me, R^2–R^5 = H
h; R^1 = R^4 = R^5 = Me, R^2 = R^3 = X = H
i; R^1 = R^4 = R^5 = X = Me, R^2 = R^3 = H
j; R^1 = R^2 = R^4 = R^5 = H, R^3 = X = Me
k; R^1 = R^4 = R^5 = H, R^2 = R^3 = X = Me

SCHEME 1 Formation of 2-aminoindamines (4) by coupling of *p*-di-imines (1) with *m*-diamines (2)

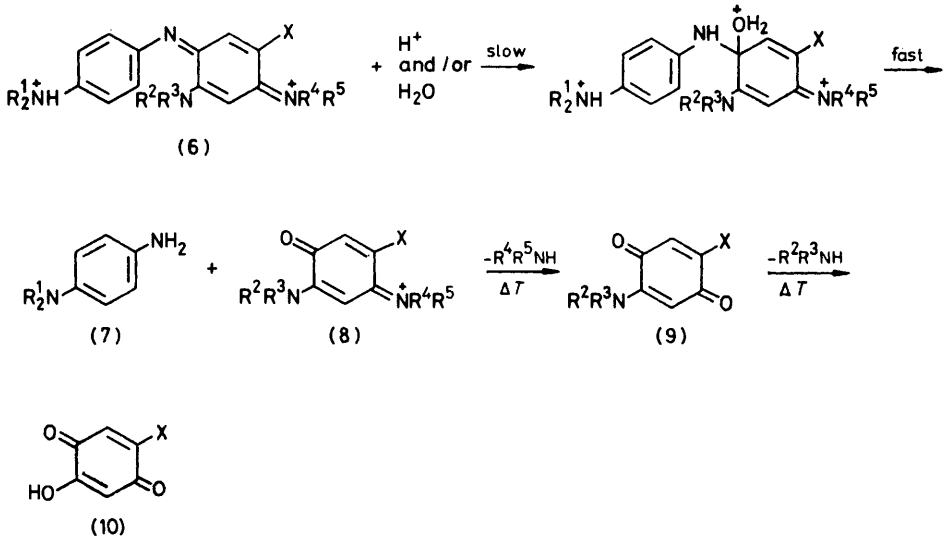
However, the rate of indamine formation in the oxidative coupling of *NN*-dimethyl-*p*-phenylenediamine with the various *m*-diamines was found to be independent of pH over the pH range 8—12, indicating a rate-

[1] Part 12, J. F. Corbett, S. Pohl, and I. Rodriguez, *J.C.S. Perkin II*, 1975, 728.

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

controlling step involving the *NN*-dimethyl-*p*-benzoquinone di-iminium ion (1; R^1 = Me) and the neutral *m*-diamine, the concentrations of which are pH independent in this pH range.

In the coupling reactions with some of the *N*-methylated 2,4-diaminotoluenes (2; X = Me) it was noted that colour developed rapidly up to 65—85% indamine formation and then at a considerably slower rate for the remaining 15—35%. This is believed to indicate that while most of the coupling occurs at the normal unsubstituted carbon atom to give the diphenylamine (3), some occurs at the methylated carbon to give an unstable pseudoquinone imine (5), having an absorption near 350 nm, which slowly reverts to the original reactants and finally is converted completely, *via* (3), to the indamine (4).



SCHEME 2 Acid catalysed hydrolysis of 2-aminoindamines

The structure of the 2-aminoindamines formed by coupling *p*-phenylenediamine or its *NN*-dimethyl derivative with various *N*-methylated derivatives of 2,4-diaminotoluene are unequivocal. However the coupling reactions with *NN*-dimethyl-*m*-phenylenediamine could occur *para* to the amino-group or *para* to the dimethylamino-group. In spite of previous reports to the contrary,[3,4] the present work shows unequivocally that coupling occurs *para* to the dimethylamino-group.

Visible Spectra and pK_a Values of 2-Aminoindamines.—Table 1 lists spectral data for the indamines studied in the present work. We have reported previously [2] that, over the pH range 0—13, the simple 2-aminoindamines exist in three forms: a red diprotonated form (6) which has pK_a *ca.* 3.5, a violet monoprotonated form (4) which has pK_a *ca.* 10.5, and a red neutral form. We now find that the *N*-methylated compounds (except the *NN*-dimethylimino-derivatives) exist as analogous species and that, while the pK_a of the dication is little affected by *N*-methylation, the acidity of the monocation is reduced considerably by methylation of any of the nitrogen functions. The dimethyliminium compounds (4d, e, h, and i) exist as analogous dications and monocations, while at high pH (>12) there is evidence that an addition product with an hydroxide ion or a neutral form of a tautomer is formed (see later).

It should be noted that the spectra for compounds (4e and h) are similar to those of compounds (4d and i), rather than to that of compound (4k), thus supporting the conclusion that coupling to *NN*-dimethyl-*m*-phenylenediamine occurs *para* to the dimethylamino-group.

Hydrolysis of 2-Aminoindamines in Acid Solution.—As with the simple 2-aminoindamines,[1] we find that the *N*-methylated derivatives undergo hydrolysis at pH <4. The reaction can be followed spectrophotometrically (Figure 1) and, at pH 1.5 and 30 °C, is essentially complete within 2 h. The products are the *p*-diamine (7) and the conjugate acid (8) of the corresponding 2-aminobenzoquinone 4-imine which, unlike the neutral form, is relatively stable. The presence of the two products was demonstrated chromatographically. At the boil, (8) is converted into the corresponding 5-substituted 2-hydroxybenzoquinone (10), presumably

TABLE 1

Spectral data and pK_a values for the 2-aminoindamines (4) in aqueous buffer solution

Compound (4)	$\lambda_{max.}$/nm (log ε) and pK_a				
	Dication	pK_a	Cation	pK_a	Neutral
a	453 (3.70)	3.4	548 (4.13)	10.9	460 (3.97)
b	450 (3.70)	3.6	539 (4.09)	10.6	452 (3.87)
c	454 (3.82)	3.5	528 (4.15)	11.4	452 (3.95)
d	‡	†	545 (4.21)		*
e	460 (3.92)	3.5	558 (4.20)	†	*
f	454 (3.81)	3.6	646 (4.41)	11.2	478 (3.96)
g	447 (†)	3.7	640 (4.35)	10.9	468 (3.97)
h	458 (3.75)	3.4	656 (4.39)	†	*
i	†	3.6	644 (4.07)	†	*
j	458 (3.80)	3.8	536 (4.16)	11.25	458 (3.78)
k	‡	†	521 (4.05)	†	*

* Does not exist as a stable neutral indamine. † Not determined. ‡ These indamines could not be isolated nor studied at low pH.

[3] M. Bil, *J. Appl. Chem. Biotechnol.*, 1972, **22**, 853.

[4] P. Karrer, *Ber.*, 1917, **50**, 420.

via the aminobenzoquinone (9). Spectral data for the quinone imines (9) are given in Supplementary Publication No. SUP 22013 (8 pp.).*

At a particular pH, the hydrolysis of the indamines follows first-order kinetics and the rate is proportional to

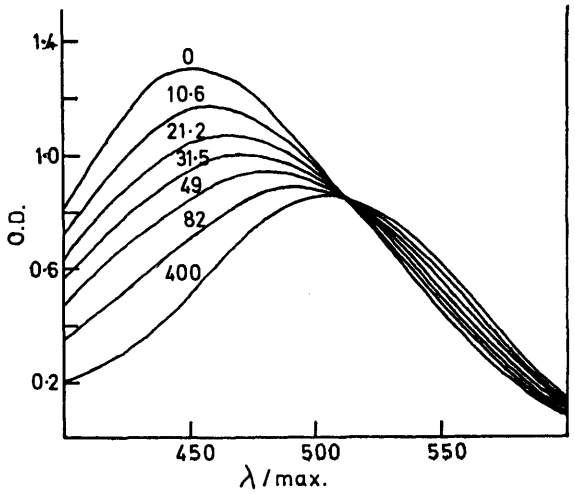
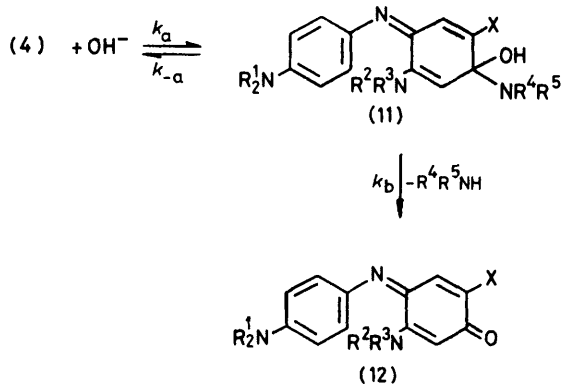


FIGURE 1 Spectrophotometric course of the hydrolysis of the 2-aminoindamine (4c) at pH 1.86 and 30 °C (time in min)

the hydrogen ion concentration over the pH range 0—2, provided the ionic strength is constant. The reaction evidently involves attack of a hydroxonium ion on the azomethine bridge carbon of the dicationic form (7) of the indamine, or of a water molecule on the analogous carbon of the tricationic form which is a minority species at pH >0 (Scheme 2). As will be seen



SCHEME 3 Hydrolysis of 2-aminoindamines (4) in alkaline solution

later, the hydrolysis at the azomethine bridge also involves reaction of the dicationic form (6) with a water molecule. This reaction contributes significantly in the pH range 2—4.

For the purpose of comparing the reactivities of different indamines, the rate of reaction was measured in hydrochloric acid–sodium chloride mixtures having unit ionic strength, and the specific second order rate constant k_1 was evaluated using equation (i) assuming that the reaction involves attack of a hydroxonium ion on the dication (6) as the rate controlling step. From SUP 22013 it is evident that *N*-methylation of 2-aminoindamine has little effect on the reactivity of the azomethine bridge since values of k_1 are in the range 0.014—0.028 l mol^{-1} s^{-1}.

Hydrolysis of the 2-Aminoindamines in Alkaline Solution.—It was shown previously [1] that the simple

$$k_1 = k_{obs.}/[H^+] \quad \text{(i)}$$

indamines (4a and b) are unstable in alkaline solution and undergo hydrolysis at the terminal imino-group to give the corresponding 2-aminoindoaniline (12). The rate of reaction as a function of pH and the comparison of the rate constants with those of other imine hydrolyses suggested the mechanism shown in Scheme 3, involving rate-controlling attack of hydroxide ion on the conjugate acid of the indamine (4), rather than the alternative of attack by a water molecule on the neutral

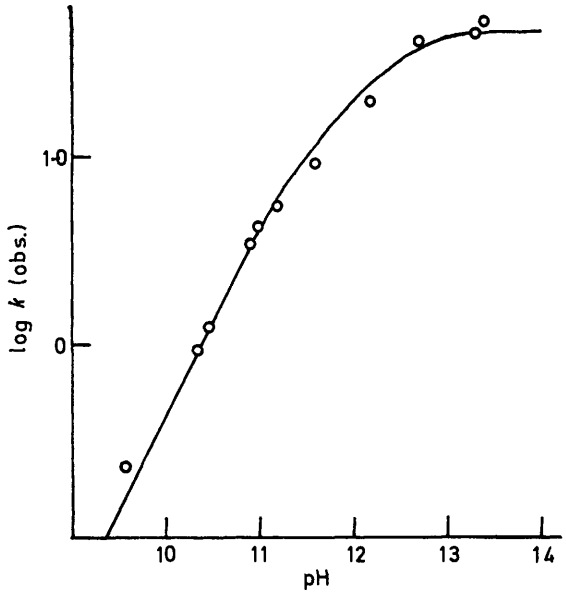


FIGURE 2 Effect of pH on the rate of alkaline hydrolysis of 2-amino-5,N^4N^4-trimethylindamine at 30 °C

indamine. Thus the observed rate k_{obs} is given by equation (ii) where k_a is the specific second-order rate

$$k_{obs} = k_a(\alpha_{I+}[OH^-]) \quad \text{(ii)}$$

constant and α_{I+} is the fraction of indamine present as the cation at the pH to which k_{obs} and [OH$^-$] pertain.

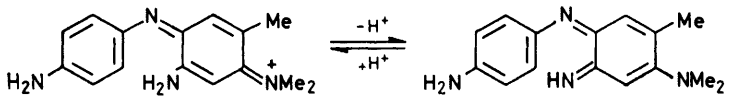
On examining the decomposition of the *N*-methylated 2-aminoindamines (4c, f, g, j, and k), all of which can form the neutral indamine by loss of a proton from the imino group, we find that they undergo hydrolysis at high pH. In the case of the ^2N-methylated derivatives (4j and k), phenazine formation is also significant up to pH 12. In each case the experimental rate constant for hydrolysis increases with increasing pH and approaches a limiting value (Figure 2) as predicted by equation (ii).

The 2-aminoindamines (4d, e, k, and i) all contain the dimethyliminium group which cannot lose a proton in

* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1976, Index issue. Items less than 10 pp. are supplied as full-size copies.

alkaline solution. However, contrary to our expectation, we find that these compounds do exhibit an instantaneous and reversible spectral change on increasing the pH above 10.5.

We consider that the new species formed in appreciable quantity from the indamine (4d) at high pH is not the complex (11) but the neutral form (13) of a tautomer of (4d). In this case the hydrolysis of (4d) at high pH follows the mechanism shown in Scheme 3 and the pH



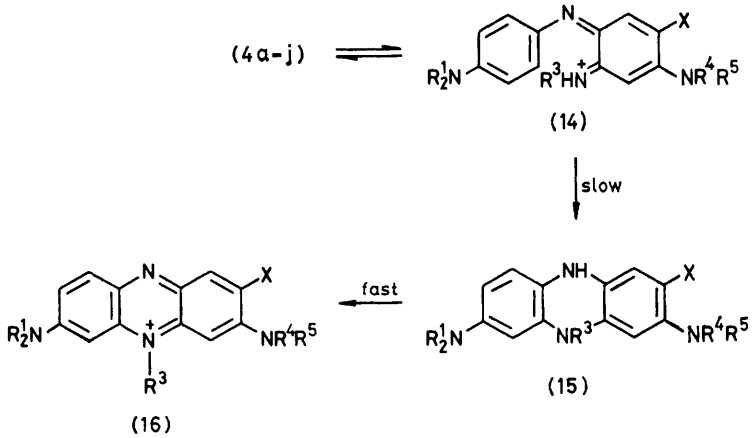
(4d) (13)

dependence (SUP 22013), in particular the attainment of a limiting rate above pH 12.5, is due to depletion of the species (4d) by formation of the neutral form (13). From data in SUP 22013, the values of k_a at 30 °C are in the range 0.042—0.66 l mol^{-1} s^{-1}. It is evident that successive *N*-methylation of the imino-group of 2-aminoindamines reduces the rate of attack by hydroxide ions and/or increases the rate of reversion of the intermediate complex (11) to the constituent ions. In this connection it should be noted that the rate of hydrolysis of attack by the iminium group of the tautomeric form (14) of (4) on the benzenoid carbon *ortho* to the nitrogen bridge, to give the diaminodihydrophenazine (15). This

$$-\mathrm{d[In]}/\mathrm{d}t = k_2[\mathrm{In}^+] \qquad \text{(iii)}$$

is followed by rapid oxidation of (15) to the phenazine or phenazinium ion (16), as shown in Scheme 4.

Rate data for the intramolecular cyclization and spectral and pK_a data for the resulting phenazines are given in Table 2. It can be seen that, in general, *NN*-dimethylation of the imino-group decreases the rate by a factor of 3 [(4h) *cf.* (4f)] while *NN*-dimethylation of R^1 of indamine (4) increases the rate of cyclization by a factor of 2—3 [(4h) *cf.* (4e); (4i) *cf.* (4d); (4g) *cf.* (4d)]. The 5-methyl group [(4g) *cf.* (4f)] slightly decreases the rate except when the adjacent imino-group is dimethylated. In this case the 5-methyl group increases the rate by a factor of 5—6 [(4i) *cf.* (4h); (4d) *cf.* (4e)]. This can be explained in terms of steric overcrowding



SCHEME 4 Mechanism of cyclisation of 2-amino- (R^3 = H) and 2-methylamino-indamines (R^3 = Me)

NN-dimethyl-*p*-benzoquinone di-imine is lower than that of the parent di-imine by a factor of 20 [*cf.* a factor of 16 for (4d) over (4b)] and that these hydrolyses are believed to occur by a similar mechanism to that given above.[1]

Intramolecular Cyclization of 2-Aminoindamines.—The intramolecular cyclizations to 2,8-diaminophenazines (16) are very slow at room temperature ($t_{1/2}$ *ca.* 5 h) and it was found more convenient to study the kinetics at 67 °C. The reactions, which were followed spectrophotometrically, gave first-order rate plots and the rates were independent of pH over the range 6—9. In this region the 2-aminoindamines exist as the monocation (4) and this is evidently the reactive species. The rate of cyclization is given by equation (iii), where k_2 is the specific first-order rate constant.

It is suggested that the reaction involves electrophilic between the dimethyliminium group and the *o*-methyl group which would facilitate the formation of the active tautomer (14). It is also of interest to note that a single methyl group on the imino nitrogen causes a 10-fold decrease in the rate of cyclization [(4c) *cf.* (4b)] suggesting that the three-fold decrease for *NN*-dimethylation [(4h) *cf.* (4f)] may even be moderated by steric effects with the *ortho* hydrogen atoms.

N-Monomethylation of the 2-amino-group of the indamine (4) increases the rate of cyclization as might be expected. This effect is essentially equal and opposite to the effect of *N*-monomethylation of the imino-group which is understandable on comparing the relationship of the tautomers (4) and (14) in Scheme 4.

Most surprising is the behaviour of 2-dimethylamino-5-methylindamine (4k) which might, at first sight, be expected not to undergo cyclization. However, when

this indamine is dissolved in an aqueous buffer at pH 5—9, the indamine colour rapidly disappears and is not immediately replaced by another coloured species. However, on longer storing the absorption due to the 2,8-diamino-10-methylphenazinium ion (18) appears.

TABLE 2

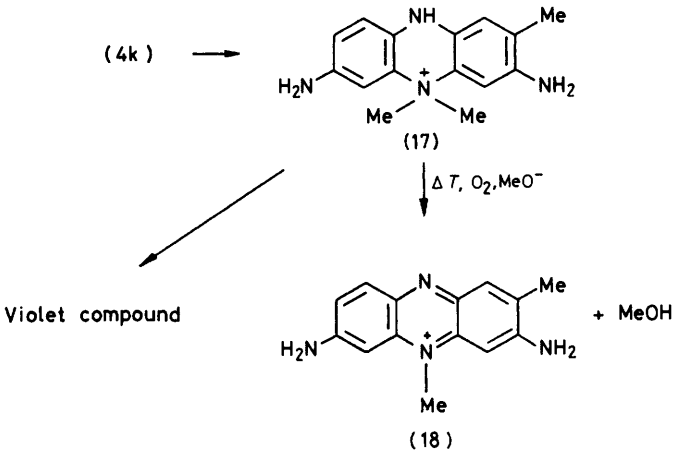
Rate data for the cyclization of 2-aminoindamines at 67 °C and spectral data and pK_a for the resulting diaminophenazines

Indamine (4)	k_2/s^{-1}	Diaminophenazine (16) Cation $\lambda_{max.}$/nm (log ε)	pK_a	Neutral $\lambda_{max.}$/nm (log ε)
a		502 (4.46)	6.6	431 (4.28)
b	1.5×10^{-4}	506 (4.30)	6.5	438 (4.13)
c	1.5×10^{-5}	514 (4.19)	6.6	445 (4.02)
d	3.3×10^{-4}	526 (4.21)	5.6	426 (4.09)
e	5.7×10^{-5}	524 (4.33)	6.7	452 (4.09)
f	5.1×10^{-4}	524 (4.33)	6.7	452 (4.09)
g	4.0×10^{-4}	518 (4.50)	6.3	452 (4.23)
h	1.5×10^{-4}	554 (4.34)	6.8	478 (4.14)
i	1.0×10^{-4}	554 (4.40)	5.7	470 (4.11)
j	1.0×10^{-3}	511 (4.37)		*
k	$\sim 10^{-2}$ †	511 (4.37)		*

* This is a 10-methylphenazinium salt and has no neutral form. † This indamine gives a colourless relatively stable compound (17); k_2 is for the formation of this compound.

Structure (18) was confirmed by comparison with the product obtained from the 2-monomethyl analogue (4j). When the reaction is carried out at room temperature on a preparative scale, a colourless solid separates having a molecular weight, and n.m.r. spectrum compatible with structure (17) (Scheme 5).

Demethylation during the intramolecular cyclization of 2-dimethylaminoindamines has been reported previously. Thus Cohen and Crabtree [5] obtain a 2-amino-8-dimethylamino-3,5,7-trimethylphenazinium salt on



SCHEME 5 Mechanism of cyclisation of 2-dimethylamino-5-methylindamine (4k)

oxidation of a mixture of 4-dimethylamino-3-methylaniline and 5-dimethylamino-2-methylaniline with acid dichromate. It is interesting that they were unable to prepare the analogous phenazines using 2,4-diaminotoluene or *m*-phenylenediamine. It is now evident that these reactions fail because the slower cyclizing 2-aminoindamine intermediates undergo hydrolysis under the acidic conditions employed by Cohen and Crabtree. Similar demethylations during the cyclization of 2-dimethylaminoindamines have been observed in the formation of 2,8-diamino-10-methylphenazinium salts from the condensation of 4-nitrosodimethylaniline [5,6] or 4-nitrosomethylaniline [5,7] with 5-dimethylamino-2-methylaniline.

Using the isolated sample of the colourless intermediate (17) we have been able to study its conversion into phenazine derivatives. While the major product is the phenazinium compound (18) having $\lambda_{max.}$ 511 nm, a significant amount of a second product $\lambda_{max.}$ 576 nm is formed. The conversion of (17) into products in-

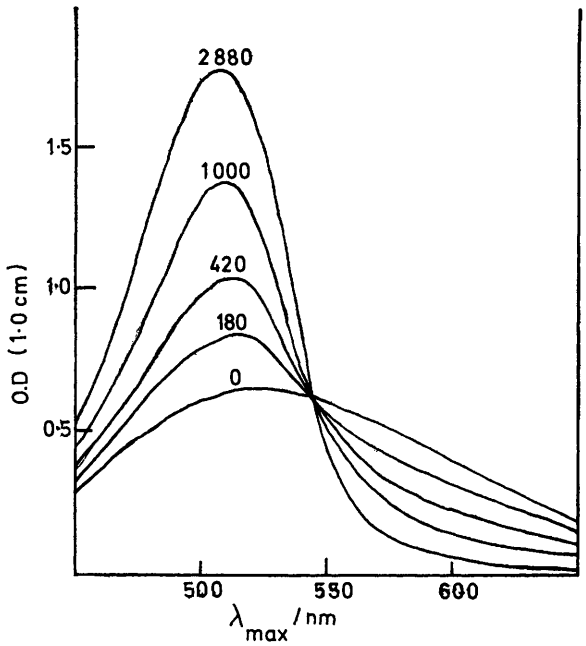


FIGURE 3 Spectrophotometric course of the cyclization of 5-methyl-2-methylaminoindamine (5.2×10^{-5}M) at pH 5.1 and 30 °C (time in min)

volves attack on (17) by hydroxide ion followed by rapid elimination of a methyl group as methanol. The latter was detected in a reaction mixture by g.l.c. Such elimination would give dihydro-derivative of the methylphenazinium ion (18), to which it would be converted by rapid oxidation.

Reactions of 5-Methyl-2-methylaminoindamine (4j).—Most indamines studied showed a wide variation in rate of reaction over the pH range 1—13 and it was not convenient to determine the rates at a single temperature over the whole pH range. The indamine (4j) is an exception and the rate of reaction was determined over the whole pH range at 30 °C.

Assuming the three contributing reactions, *i.e.* acid catalysed hydrolysis of the dicationic species, intramolecular cyclization of the monocation, and hydroxide

[5] J. B. Cohen and H. G. Crabtree, *J. Chem. Soc.*, 1921, **119**, 2055.

[6] D.R.P. 80,758; *Friedlander*, IV, 376.

[7] D.R.P. 69,188; *Friedlander*, III, 397.

ion catalysed hydrolysis of the monocation, the experimental rate for the disappearance of the indamine at any particular pH should be given by equation (iv) where

$$-d[In]/dt = k[In]$$
$$= \{k_1(1 - \alpha)[H^+] + k_2\alpha + k_a\alpha[OH^-]\}[In] \quad (iv)$$

k is the experimental rate constant, k_1, k_2, and k_a are the specific rate constants as defined above, α is the fraction of the indamine present as its conjugate acid, and [In] is the total indamine concentration, regardless of ionic species. From rate determinations in the pH range 1—2.5, 5.5—8.0, and 11.5—12.6 respectively the rate constants were evaluated as k_1 1.4×10^{-2} l mol^{-1} s^{-1}, k_2 1.40×10^{-5} s^{-1}, and k_a 1.2×10^{-1} l mol^{-1} s^{-1}.

Using these values, the experimental rate data were found to fit a theoretical plot of log k *versus* pH except that, in the region pH 2.5—4.5 the experimental rate constants were considerably higher than predicted. It can be seen from Figure 4 that the three contributing

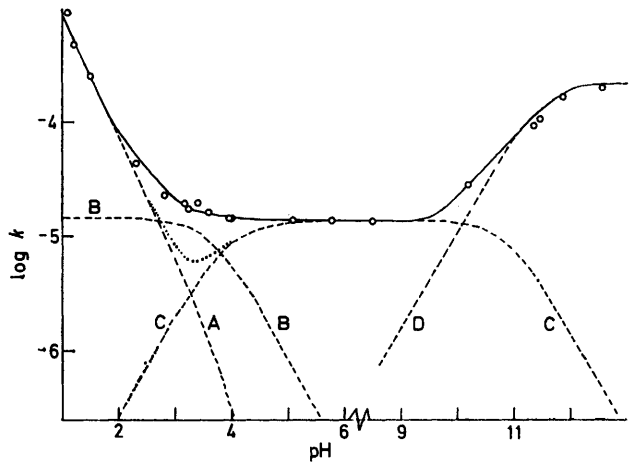


FIGURE 4 Plot of log k *versus* pH for the reactions of 5-methyl-2-methylaminoindamine (4j) showing the contributions of acid catalysed (A) and uncatalysed (B) hydrolysis of the dication of the indamine at the azomethine link, the intramolecular cyclization (C), and hydrolysis of the terminal imino-group (D) as broken lines, to the total rate (full line). The dotted line shows values of log k if only A and C contributed to the total rate

reactions give a log k *versus* pH curve as shown by the full line in the pH ranges 1—2 and 5—13 and by the dotted line in the pH range 2—5. It is thus evident that an additional reaction contributes to the observed rate in the pH range 2—5. Examination of the final spectra of the reaction mixtures showed that the yield of phenazine (16; $R^1 = R^2 = R^4 = R^5 = H$, $R^3 = X = Me$) was lower than expected, while the yield of 5-methyl-2-methylaminobenzoquinone 1-imine was higher. Evidently the uncatalysed hydrolysis of the dication, at the azomethine link, is a significant reaction over the pH range 2—5. The contribution of this reaction to the total rate was evaluated as $k' = k$(expt.) $- k$(calc.), where k(calc.) was obtained from equation (iv). It was found that the higher rate could be ascribed to the uncatalysed hydrolysis of the dication species of the indamine (4j) and that k' is given by equation (v) where k'_1 is the specific first-order rate

$$k' = k'_1(1 - \alpha) \quad (v)$$

constant for the reaction and α is the fraction of the indamine present as the monocation. From the data $k'_1 = 1.2 \times 10^{-5}$ s^{-1}. Using this value, k was evaluated from equation (vi) and the plot of log k *versus* pH is

$$k = k_1(1 - \alpha)[H^+] + k'_1(1 - \alpha) + k_2\alpha + k_a\alpha[OH^-] \quad (vi)$$

given by the full line in Figure 4. It can be seen that the experimental points give a good fit to the theoretical curve, over the whole pH range.

As a further check on this hypothesis, the yield of the phenazinium salt (16; $R^1 = R^2 = R^4 = R^5$, $R^3 = X =$ Me) was calculated from the final spectra and compared with the calculated yield obtained from equation (vii).

$$\% \text{ Phenazinium salt} = 100\, k_2\, \alpha/k \quad (vii)$$

The results supported the proposed mechanism.

Oxidative Coupling to 3-Dimethylaminoaniline.—There have been a number of contradictory statements in the literature concerning the phenazine product of the oxidative coupling reaction of *p*-dimethylaminoaniline with its *m*-isomer. Karrer [8] reported that oxidation of the mixture with acid potassium dichromate gave 2,8-bisdimethylaminophenazine. He later revised his opinion,[4] which was also criticized by Kehrmann and Falconnier,[9] in favour of the product being the 3-amino-8-dimethylamino-10-methylphenazinium salt, *i.e.* the initial coupling occurring *para* to the amino-group rather than *para* to the dimethylamino-group of the *m*-diamine. Cohen and Crabtree [5] further confounded the issue by reportedly making both phenazines by the same method. We have now prepared the intermediate indamine by oxidative coupling of *NN*-dimethyl-*p*-phenylenediamine with 3-dimethylaminoaniline. The product was isolated as its perchlorate and was cyclized to give 2,8-bisdimethylaminophenazine having pK_a 6.8, which would not be the case for the 10-methylphenazinium salt of the alternative product.

We have also prepared an authentic sample of the *NN*-dimethylindaminium salt (4e) by condensing 4-dimethylamino-2-nitro-1-fluorobenzene with *p*-phenylenediamine, reducing the nitro-group, and oxidising the resulting triaminodiphenylamine. The product (4e) is identical with that obtained by oxidative coupling of *p*-phenylenediamine with 3-dimethylaminoaniline, and undergoes cyclization to give 2-dimethylamino-8-aminophenazine, identical with that formed by cyclization of the indamine (4h) obtained by oxidative coupling of *NN*-dimethyl-*p*-phenylenediamine with *m*-phenylenediamine. It can therefore be concluded that coupling to 3-dimethylaminoaniline occurs exclusively *para* to the dimethylamino-group.

[8] P. Karrer, *Ber.*, 1916, **49**, 1643.

[9] F. Kehrmann and G. Falconnier, *Ber.*, 1917, **50**, 421.

EXPERIMENTAL

Diaminobenzenes.—The diaminobenzenes were either commercial samples or prepared by standard techniques from the appropriate *o*- or *p*-toluidine. The compounds were stored as bishydrochlorides.

4-Amino-4'-dimethylamino-2-nitrodiphenylamine.—A mixture of *NN*-dimethyl-*p*-phenylenediamine (136.2 g), 4-fluoro-3-nitroaniline (39.05 g), and anhydrous sodium carbonate (18.5 g) in water (750 ml) was refluxed for 5 h. After cooling to room temperature the aqueous layer was decanted. The crude product was boiled with water (700 ml), cooled, and the aqueous layer again decanted. The sticky, crystalline product was crystallized from 95% ethanol to dark crystals (15.7 g) of the *diphenylamine*, m.p. 185—187° (Found: C, 61.65; H, 5.85; N, 20.75. $C_{14}H_{16}N_4O_2$ requires C, 61.75; H, 5.9; N, 20.55%).

4'-Amino-4-dimethylamino-2-nitrodiphenylamine.—By a similar procedure *4'-amino-4-dimethylamino-2-nitrodiphenylamine*, m.p. 130—132° (Found: C, 62.05; H, 5.9; N, 20.75. $C_{14}H_{16}N_4O_2$ requires C, 61.75; H, 5.9; N, 20.55%) was prepared from 4-fluoro-3-nitro-*NN*-dimethylaniline [3] and *p*-phenylenediamine.

Indamines.—The various indamines were prepared by literature methods [10,11] or, for spectra and kinetic experiments, *in situ* by air oxidation of the triaminodiphenylamine or oxidative coupling of the *p*- and *m*-diamines with ferricyanide.

2,8-Diaminophenazines.—The indamine was dissolved in pH 7 buffer at a concentration *ca.* 10^{-2}M, and stored at 60° until complete conversion to phenazine was shown by t.l.c. By this time the phenazine had usually precipitated. In some cases, however, sodium hydroxide was added to precipitate the phenazine. Because a variety of indamine salts were used, and base was sometimes necessary to precipitate the phenazine, the exact compositions of the phenazine precipitates were not known. In addition the phenazines were difficult to recrystallize. Therefore, the C, H, and N analytical data for the phenazines were normalized to 100% to compensate for these problems and the derived data are presented in SUP 22013. The n.m.r. spectrum of phenazinium salt (16; $R^1 = R^2 = R^4 = R^5 =$ H, $R^3 =$ X = Me) showed τ 7.68 (3 H, CMe) and 5.03 (3 H, NMe), thus confirming its structure.

Indoanilines.—The indamine (100 mg) was dissolved in pH 12.6 buffer (50 ml) and heated at 60° for 12 h. The precipitate was collected and recrystallized from ethanol–water. Analytical data for the indoanilines so produced are collected in SUP 22013.

Acid Hydrolysis Products.—It was not possible to isolate products from acid hydrolysis of the indamines. However, *p*-diamine (7) was detected in reaction mixtures by t.l.c., and the quinone imine (8; R^2—R^5 = H, X = Me) could be compared on t.l.c. with an authentic sample. The structure of the other quinone imines was assumed by analogy and, in some cases, by recovery of 2-hydroxybenzoquinones (10) from steam distilled, acid hydrolysis reactions. These compounds are readily recognized by their spectra.[12]

2,8-Diamino-3,10,10-trimethyl-5,10-dihydrophenazinium Salt (17).—A solution of potassium ferricyanide (16 g) in water (20 ml) was added to a mixture of *p*-phenylenediamine bishydrochloride (2.3 g) and 2-amino-4-dimethylaminotoluene bishydrochloride (3.0 g) in pH 5.9 buffer (50 ml). The solution immediately turned violet. After stirring for 60 min, an almost colourless precipitate (5.0 g) was collected. The solid, m.p. 170° (decomp.), turned red-violet over a period of days. I.r. peaks at 2 045 and 2 080 cm^{-1} suggest that it is a ferri- or ferro-cyanide salt. The mass spectrum had *m/e* 255 (4.02%), 254 (20.1), 240 (42.8), 239 (42.4), 225 (46.0), 224 (39.4), and 210 (26.0) and the n.m.r. spectrum had τ 7.9 (3 H, CMe), 5.9 (6 H, 2 × NMe), 5.4br (4 H, 2 × NH_2), and 0.5 (1 H, NH). These results are indicative of the proposed structure (17).

Reaction of the Dihydrophenazinium Salt (17).—The reaction mixture resulting from storing a solution of the indamine (4k) at 30° and pH for two days, was analysed on an Aerograph A700 gas chromatograph using a 6 ft × 1/4 in 15% Carbowax 1540 on Chromosorb column. The methyl fragment was readily identified as methanol by retention time and peak enhancement. By chromatography, the reaction mixture was shown to contain the phenazinium salt (16; $R^1 = R^2 = R^4 = R^5 =$ H, $R^3 =$ X = Me) and an unidentified violet material.

Kinetics.—The reaction rates were determined spectrophotometrically, using a Unicam SP 800A spectrophotometer, by repetitive scanning of the visible spectra (for slow reactions) or recording optical density at constant wavelength (for fast reactions). Typical data for the reactions of the indamine (4j) are given in SUP 22013.

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[10] U.S.P. 3,876,368/1975.

[11] A. Bernthesen and H. Schweitzer, *Annalen*, 1886, **236**, 343.

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