Synthesis and Properties of 1,2-Diaryl-4,5,6,7-tetrahydro-1*H*-1,3-diazepines and 1,2-Diaryl-1,4,5,6,7,8-hexahydro-1,3-diazocines. Comparison with the Five- and Six-membered Homologues

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The cyclization of *N*-aroyl-*N'*-aryl-tetra- and -penta-methylenediamines with ethyl polyphosphate afforded 1,2-diaryl derivatives of 4,5,6,7-tetrahydro-1*H*-1,3-diazepines and 1,4,5,6,7,8-hexahydro-1,3-diazocines respectively. To compare the basicity of these compounds with that of the five- and six-membered homologues, their pK_a values were determined. The pK_a values decrease in the order: tetrahydropyrimidines > tetrahydrodiazepines > hexahydrodiazocines > imidazolines. Rate constants for the hydrolysis of a series of homologues were determined in boiling alkaline 95% ethanol. It was observed that stability to alkaline hydrolysis increases in the order: imidazolines < tetrahydropyrimidines ≪ tetrahydrodiazepines < hexahydrodiazocines. With these and other data, some conformational aspects were analysed.

THIS is an extension of our work on the synthesis and properties of 1,2-diaryl derivatives of 2-imidazolines [1,2] and 1,4,5,6-tetrahydropyrimidines.[3,4] We have now synthesized and studied the seven- and eight-membered homologues, in order to observe the influence of ring size upon the ease of cyclization and on basicity and stability to alkaline hydrolysis.

Synthesis of 1,2-*Diaryl*-4,5,6,7-*tetrahydro*-1H-1,3-*diazepines and* 1,2-*Diaryl*-1,4,5,6,7,8-*hexahydro*-1,3-*diazocines*.—The principal methods used to prepare imidazolines and tetrahydropyrimidines do not always give good results for the synthesis of 4,5,6,7-tetrahydro-1*H*-1,3-diazepines,[5-7] and often fail to give the eight- and nine-membered homologues.[5-8]

Cyclization of the 1,4-diaminobutane derivatives was successfully achieved using ethyl polyphosphate (PPE) in chloroform solution, or phosphorus oxychloride in some cases. On the other hand, when polyphosphoric acid (PPA) was used, either in the presence or absence of solvent, cyclization failed and resinous products and low yields were obtained.

Difficulties were greater when the synthesis of hexahydrodiazocines was attempted. Abundant resinous products were obtained, the starting material was partially recovered, and yields were very low. Experiments performed with various reagents under varying experimental conditions proved PPE to be the best cyclization agent, for a reaction time of 2 h at 120°. Yields were lower when either time or temperature were increased, indicating that the product is probably destroyed under energic experimental conditions.

Tetrahydrodiazepines and hexahydrodiazocines were isolated as bases, and characterized as picrates or chloroplatinates. M.p.s, crystallization solvents, elemental analyses, and yields are given in Table 2. The corresponding data for the salts are listed in Table 3.

Basicity.—The pK_a values for the synthesized compounds (1)—(6), and for a series of homologues, were determined (Table 4). Comparing the pK_a values of compounds (1) and (5) with those of the corresponding homologues (7) and (11), it can be seen that basicity decreases in the order: tetrahydropyrimidines > tetra-

TABLE 1

N-Aroyl-*N'*-aryl-tetra- and -penta-methylenediamines $Ar^1NH[CH_2]_nNHCOAr^2$

Ar^1	Ar^2	*n*	Yield (%)	M.p. (°C)	Recryst. solvent	Formula		Analysis C (%)	H (%)	N (%)
4-$NO_2C_6H_4$	Ph	4	98	145	Methanol	$C_{17}H_{19}N_3O_3$	Reqd.:	65.2	6.05	13.4
							Found:	65.2	6.3	13.45
4-$NO_2C_6H_4$	4-$NO_2C_6H_4$	4	95	156	Ethanol	$C_{17}H_{18}N_4O_5$	Reqd.:	57.0	5.05	15.65
							Found:	57.2	5.35	15.85
2-$NO_2C_6H_4$	Ph	4	82	94	Benzene	$C_{17}H_{19}N_3O_3$	Reqd.:	65.2	6.05	13.4
							Found:	65.2	6.3	13.5
2-$NO_2C_6H_4$	4-$NO_2C_6H_4$	4	77	143	Ethanol	$C_{17}H_{18}N_4O_5$	Reqd.:	57.0	5.05	15.65
							Found:	56.8	5.15	15.65
4-$NO_2C_6H_4$	Ph	5	80	125	Methanol	$C_{18}H_{21}N_3O_3$	Reqd.:	66.1	6.45	12.85
							Found:	66.0	6.7	12.9
4-$NO_2C_6H_4$	4-$NO_2C_6H_4$	5	67	116	Chloroform	$C_{18}H_{20}N_4O_5$	Reqd.:	58.1	5.4	15.05
							Found:	58.2	5.5	14.95

[1] I. Perillo and S. Lamdan, *J. Heterocyclic Chem.*, 1970, **7**, 791.
[2] B. Fernández, I. Perillo, and S. Lamdan, *J.C.S. Perkin II*, 1973, 1371.
[3] I. Perillo and S. Lamdan, *J. Heterocyclic Chem.*, 1973, **10**, 915.
[4] B. Fernández, I. Perillo, and S. Lamdan, *J.C.S. Perkin II*, 1974, 1416.
[5] R. N. Johnson and H. M. Woodburn, *J. Org. Chem.*, 1962, **27**, 3958.
[6] H. M. Woodburn and J. R. Fisher, *J. Org. Chem.*, 1957, **22**, 895.
[7] C. Grundmann and A. Kreutzberger, *J. Polymer Sci.*, 1959, **38**, 425.
[8] P. Oxley and W. F. Short, *J. Chem. Soc.*, 1947, 497.

hydrodiazepines > hexahydrodiazocines > imidazolines. The same results are observed when the pK_a values of the 1,2-bis-(*p*-nitrophenyl) derivatives (2), (6), (8), and (12) are compared. The resulting decrease in planarity of the N–C–N system is maintained. The model corresponding to the tetrahydropyrimidinic ring (II), shows a half-chair conformation in which the planarity of the N–C–N system remains unaffected.

TABLE 2

1,2-Diaryl-4,5,6,7-tetrahydro-1*H*-1,3-diazepines and 1,2-diaryl-1,4,5,6,7,8-hexahydro-1,3-diazocines

Compound	Yields (%) PPA	PPE	$POCl_3$	M.p. (°C)	Recryst. solvent	Formula		Analysis C (%)	H (%)	N (%)
(1)	7 [a]	92	76	139	Cyclohexane	$C_{17}H_{17}N_3O_2$	Reqd.:	69.2	5.75	14.25
							Found:	68.9	6.0	14.4
(2)		89	65	161	Cyclohexane	$C_{17}H_{16}N_4O_4$	Reqd.:	60.0	4.7	16.45
							Found:	59.9	5.0	16.25
(3)		80	62	126	n-Heptane	$C_{17}H_{17}N_3O_2$	Reqd.:	69.2	5.75	14.25
							Found:	69.2	6.05	14.15
(4)		75	59	131	Cyclohexane	$C_{17}H_{16}N_4O_4$	Reqd.:	60.0	4.7	16.45
							Found:	60.0	4.9	16.65
(5)		39 [b]	24	119	n-Hexane	$C_{18}H_{19}N_3O_2$	Reqd.:	69.9	6.15	13.6
							Found:	69.8	6.15	13.8
(6)	0 [a]	42 [b]	30	165	Ethanol	$C_{18}H_{18}N_4O_4$	Reqd.:	61.0	5.05	15.8
							Found:	61.3	4.9	15.55

[a] Abundant resinous products are obtained and the starting material is recovered. [b] Without solvent, 2 h at 120°.

TABLE 3

Salts of 1,2-diaryl-4,5,6,7-tetrahydro-1*H*-1,3-diazepines and 1,2-diaryl-1,4,5,6,7,8-hexahydro-1,3-diazocines

Compound	Salt	Recryst. solvent	M.p. (°C)	Formula		Analysis C (%)	H (%)	N (%)	Cl (%)
(1)	Picrate	Ethanol	226	$C_{23}H_{20}N_6O_9$	Reqd.:	52.7	3.8	16.05	
					Found:	52.4	4.0	16.1	
(2)	Picrate	Ethanol	200	$C_{23}H_{19}N_7O_{11}$	Reqd.:	48.5	3.35	17.2	
					Found:	48.8	3.4	17.1	
(3)	Picrate	Methanol	163	$C_{23}H_{20}N_6O_9$	Reqd.:	52.7	3.8	16.05	
					Found:	52.9	4.1	15.9	
(3)	Chloroplatinate		228	$C_{34}H_{36}Cl_6N_6O_4Pt$	Reqd.:	40.8	3.6	8.4	21.3
					Found:	40.6	3.9	8.6	21.0
(4)	Chloroplatinate		234	$C_{34}H_{34}Cl_6N_8H_8Pt$	Reqd.:	37.4	3.1	10.3	19.55
					Found:	37.6	3.3	10.1	19.25
(5)	Chloroplatinate		216—219	$C_{36}H_{40}Cl_6N_6O_4Pt$	Reqd.:	42.0	3.9	8.15	20.7
					Found:	41.8	3.5	8.2	20.55
(6)	Chloroplatinate		228	$C_{36}H_{38}Cl_6N_8O_8Pt$	Reqd.:	38.6	3.4	10.0	19.05
					Found:	38.5	3.7	9.95	10.05

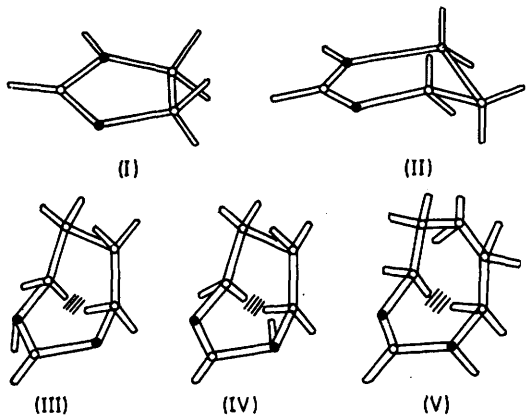
the basicity may be accounted for by any factor capable of affecting the planarity of the N–C–N system, which is necessary for the delocalization of the positive charge of the amidinium ion. Molecular models are shown in the Figure for the different cyclic amidines in which the This would account for the high basicity of these compounds. The tetrahydrodiazepine ring has two theoretical conformations (III) and (IV), but they are of low probability, not only due to the eclipsed conformation of

TABLE 4

Basicity of homologous cyclic amidines

Compound	pK_a	K_a
(1)	8.43 [a]	3.71×10^{-9}
(2)	7.38 [b]	4.17×10^{-8}
(3)	10.39 [a]	4.07×10^{-11}
(4)	9.15 [a]	7.08×10^{-10}
(5)	7.78 [b]	1.66×10^{-8}
(6)	6.75 [b]	1.78×10^{-7}
(7)	7.65 [c]	2.24×10^{-8}
(8)	6.74 [c]	1.82×10^{-7}
(9)	7.51 [c]	3.09×10^{-8}
(10)	6.61 [a]	2.45×10^{-7}
(11)	10.51 [d]	3.09×10^{-11}
(12)	9.16 [d]	6.92×10^{-10}
(13)	10.55 [d]	2.82×10^{-11}
(14)	9.23 [d]	5.89×10^{-10}

[a] Determined by the u.v. method. Selected $\lambda_{max.}$ for (1): 310 and 390 nm; for (3): 255 and 295 nm; for (4): 300 nm and for (10): 255 and 295 nm. [b] Determined by potentiometry. [c] Values taken from ref. 2. [d] Values taken from ref. 4.



Conformational models of 2-imidazolines and homologues. (I), 2-Imidazoline; (II), 1,4,5,6-tetrahydropyrimidine; (III) and (IV), 4,5,6,7-tetrahydro-1*H*-1,3-diazepine; (V), 1,4,5,6,7,8-hexahydro-1,3-diazocine. Schematic drawings were taken from Büchi molecular models. ● Nitrogen atoms; ○ carbon atoms

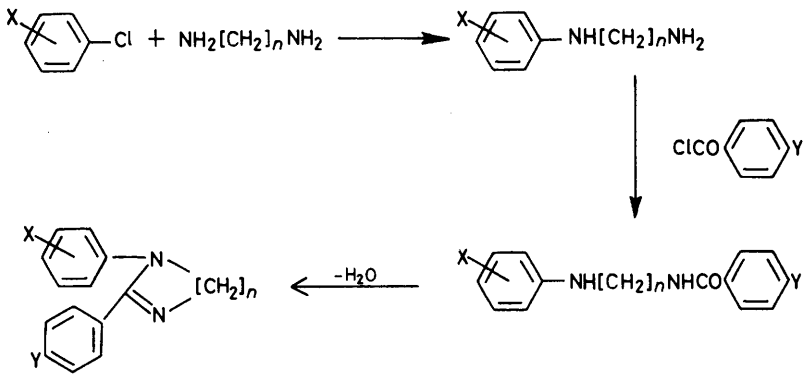
5- and 6-methylene groups, but also because of the interaction of 4- and 7-H_2. In the hexahydrodiazocines (V), the latter effect must be still more pronounced due to the enhanced proximity of 4- and 8-H_2. Thus, possible torsion of the seven- and eight-membered rings may result in less favoured delocalization of the amidinium charge, and consequently in a decrease in basicity.

Imidazolines (I) are the least basic compounds. They are rigid molecules,[9,10] in which the N–C–N system cannot remain planar due to the high repulsion determined by the eclipsed conformation of the methylene groups. The observed pK_a values for the 1-(*o*-nitrophenyl)-2-phenyl homologues (3), (9), and (13) were compared with those of the 1-(*p*-nitrophenyl) isomers (1), (7), and (11). If inductive and mesomeric effects from the 1-(*o*- and *p*-nitrophenyl) groups are considered to affect the electronic density at N-1, we might expect a higher decrease in the basicity caused by the *o*- than by the *p*-nitro-group, as occurs in *o*- and *p*-nitroanilines (pK_a −0.26 and 1.00 respectively [11]). However, in the imidazolines and tetrahydropyrimidines the effect of the *o*-nitro-group on the basicity is similar to that caused by the *p*-nitro-group. Furthermore, in the tetrahydrodiazepines, we noted that the 1-(*o*-nitrophenyl) derivative (3) is rather more basic than the *p*-nitrophenyl isomer (1). The same results are observed when the pK_a values of (4), (10), and (14) and (2), (8), and (12) are compared in the same way.

The absence of absorption for all the *o*-nitro-derivatives in the visible region, as opposed to the situations for *o*-nitroanilines,[12] suggests that the lack of coplanarity in the *o*-$NO_2C_6H_4\dot{N}<$ system may account for our experimental pK_a values.

The resemblance between the u.v. spectra of (9), $\lambda_{max.}$ 206 (ε 21 400) and 225 nm (13 500), and (13), $\lambda_{max.}$ 206 (ε 19 300) and 225 nm (13 800), which are different from that of (3), $\lambda_{max.}$ 206 (ε 20 250) and 241 nm (14 000), suggests that the principal influence on the seven-membered ring may be somewhat different from that for the other heterocycles. The pK_a value of tetrahydrodiazepine (3) (10.39) is higher than the approximate value calculated for the 1,2-diphenyl derivative (9.5—9.9), and rather lower than the approximate value calculated for 2-phenyl-4,5,6,7-tetrahydro-1*H*-1,3-diazepine.* Therefore, an explanation for the experimental results is found if it is considered that in the tetrahydrodiazepines, the *o*-nitrophenyl group has no mesomeric interaction with the N-1 due to rotation of the C–N-1 bond. Thus, only the inductive effect of the *o*-nitrophenyl group would cause the decrease in basicity.

On the other hand, the greater influence of the *o*-nitrophenyl group on imidazolines and tetrahydropyrimidines may mean that a displacement of the nitro-group from the aromatic ring plane could occur, as observed for other aromatic compounds.[13–16] In these



(1) X = *p*-NO_2, Y = H, *n* = 4
(2) X = *p*-NO_2, Y = NO_2, *n* = 4
(3) X = *o*-NO_2, Y = H, *n* = 4
(4) X = *o*-NO_2, Y = NO_2, *n* = 4
(5) X = *p*-NO_2, Y = H, *n* = 5
(6) X = *p*-NO_2, Y = NO_2, *n* = 5
(7) X = *p*-NO_2, Y = H, *n* = 2
(8) X = *p*-NO_2, Y = NO_2, *n* = 2
(9) X = *o*-NO_2, Y = H, *n* = 2
(10) X = *o*-NO_2, Y = NO_2, *n* = 2
(11) X = *p*-NO_2, Y = H, *n* = 3
(12) X = *p*-NO_2, Y = NO_2, *n* = 3
(13) X = *o*-NO_2, Y = H, *n* = 3
(14) X = *o*-NO_2, Y = NO_2, *n* = 3

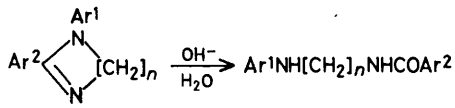
SCHEME 1

* The difference between the pK_a values of compounds (1) and (11), and between those for compounds (2) and (12) (Table 4), is about two units. Therefore, we can expect, on the basis of the electronic delocalization between the aryl group and N-1, a pK_a value for 1,2-diphenyl-4,5,6,7-tetrahydro-1*H*-1,3-diazepine of 9.5—9.9, and an approximate value of 10.7—11.0 for the 2-phenyltetrahydrodiazepine.

[9] J. Elguero, E. González, J.-L. Imbach, and R. Jacquier, *Bull. Soc. chim. France*, 1969, 4075.
[10] L. Villa, V. Ferri, and E. Grana, *Il Farmaco, Ed. Sci.*, 1967, **22**, 491.
[11] D. D. Perrin, 'Dissociation Constants of Organic Bases in Aqueous Solution,' Butterworths, London, 1965.
[12] M. J. Kamlet, H. G. Adolph, and J. C. Hoffsommer, *J. Amer. Chem. Soc.*, 1964, **86**, 4018.
[13] R. W. Franck and M. A. Williamson, *J. Org. Chem.*, 1966, **31**, 2420.
[14] I. D. Rae, *Austral. J. Chem.*, 1965, **18**, 1807.
[15] I. D. Rae, *Austral. J. Chem.*, 1967, **20**, 1173.
[16] P. R. Wells, *Austral. J. Chem.*, 1964, **17**, 967.

cases the mesomeric interaction between the aryl group and the heterocyclic ring would remain.

Alkaline Hydrolysis.—Tetrahydrodiazepines and hexahydrodiazocines, due to their nature as amidines, are hydrolysed in alkaline solutions to afford *N*-acyl derivatives of the corresponding tetra- and penta-methylenediamines (Scheme 2). In an attempt to determine the



SCHEME 2

influence of ring size upon the stability to alkaline hydrolysis, rate constants were determined for compounds (1) and (5), and for the homologous imidazoline (7).

Pseudo-first order rate constants and half-lives for the homologous cyclic amidines are given in Table 5. A

TABLE 5

Rate constants and half-lives for the alkaline hydrolysis of homologous cyclic amidines

Compound	Selected λ/nm	10^6 k/s^{-1}	$t_{1/2}$/h
(7)	307 and 390	5.60	34.0
(11)	280	4.53[4]	42.5[4]
(1)	300 and 390	0.45	~430
(5)	285 and 390	0.42	~460

comparison of half-lives shows that the stability to the alkaline hydrolysis is in the order: imidazolines < tetrahydropyrimidines ≪ tetrahydrodiazepines < hexahydrodiazocines.

The steric strain of the imidazoline ring may easily account for its lower stability compared with that of the six-membered ring. In contrast, it is difficult to find a simple explanation for the high stability of the seven- and eight-membered rings. Molecular models indicate that they are flexible. Presumably, conformational factors influencing the stability of the compound and preventing the attack of the nucleophile OH^- on C-2, may account for the results.

EXPERIMENTAL

M.p.s were taken with a Büchi capillary apparatus. I.r. spectra were recorded with a Beckman 20A instrument for potassium bromide pellets. U.v. spectra were recorded with a Perkin-Elmer 202 spectrophotometer and extinction coefficients were calculated from readings on a Beckman DB-G grating spectrophotometer. N.m.r. spectra were obtained with a Perkin-Elmer R12 60 MHz spectrometer in deuteriochloroform, with tetramethylsilane as internal reference. The presence of exchangeable protons was confirmed by use of deuterium oxide.

N-(p-*Nitrophenyl*)*tetramethylenediamine*. *p*-Chloronitrobenzene (15 g) and 1,4-diaminobutane (88 g) were heated in an oil-bath at 135—140° for 1 h. The excess of diamine was removed *in vacuo*. The residue was dissolved in boiling 10% hydrochloric acid and filtered to remove *NN'*-bis-(*p*-nitrophenyl)tetramethylenediamine. The solution was made alkaline with concentrated sodium hydroxide and filtered. Crystallization afforded the product (81%), m.p. 101° (from benzene–cyclohexane) (Found: C, 57.2; H, 7.35; N, 19.95. $C_{10}H_{15}N_3O_2$ requires C, 57.4; H, 7.2; N, 20.1%); $\nu_{max.}$ 1 605, 1 460, 1 308, 1 116, and 943 cm^{-1}; the *picrate* had m.p. 150° (from methanol) (Found: C, 44.0; H, 4.22; N, 18.95. $C_{16}H_{18}N_6O_9$ requires C, 43.8; H, 4.1; N, 19.2%).

N-(o-*Nitrophenyl*)*tetramethylenediamine hydrochloride*. *o*-Chloronitrobenzene and 1,4-diaminobutane were used as starting materials. The procedure used for the former synthesis was followed, but heating was performed in a boiling water-bath at 100°. After removal of the bis-derivative, the solution was made alkaline and the *N*-(*o*-nitrophenyl)tetramethylenediamine separated as an oil that was extracted with chloroform. The organic solution was washed, dried, and treated with ethereal hydrogen chloride solution, affording the hydrochloride of the product (78%), m.p. 170° (from anhydrous ethanol) (Found: C, 49.1; H, 6.6; N, 17.05. $C_{10}H_{16}ClN_3O_2$ requires C, 48.9; H, 6.5; N, 17.1%); $\nu_{max.}$ 3 000—3 150, 1 620, 1 525, 1 260, 1 235, and 1 163 cm^{-1}; the *picrate* had m.p. 158° (from ethanol).

N-(p-*Nitrophenyl*)*pentamethylenediamine*. *p*-Chloronitrobenzene and 1,5-diaminopentane were used as starting materials. The procedure used for the synthesis of *N*-(*p*-nitrophenyl)tetramethylenediamine was followed affording the product (70%), m.p. 97° (from n-hexane) (Found: C, 58.9; H, 7.8; N, 19.0. $C_{11}H_{17}N_3O_2$ requires C, 59.2; H, 7.6; N, 18.85%); the *picrate* had m.p. 139° (from methanol) (Found: C, 45.3; H, 4.7; N, 18.6. $C_{17}H_{20}N_6O_9$ requires C, 45.1; H, 4.4; N, 18.6%).

N-Aroyl-N'-arylpolymethylenediamines. These compounds were prepared by acylation of the *N*-nitrophenylpolymethylenediamines with benzoyl chlorides in the presence of triethylamine, by the following procedure. A mixture of *N*-nitrophenylpolymethylenediamine (0.01 mol), aroyl chloride (0.013 mol), and triethylamine (0.02 mol) was refluxed in chloroform (60—100 ml) for 1.5 h. The solvent was removed *in vacuo* and the residue triturated with 10% hydrochloric acid and filtered. The resulting solid was washed with water, 5% sodium hydroxide, and water. Then it was dried and crystallized. Crystallization solvents, m.p.s, elemental analyses, and yields for the products obtained are given in Table 1.

1,2-Diaryl-4,5,6,7-tetrahydro-1H-1,3-diazepines. These compounds were prepared by cyclization of *N*-aroyl-*N'*-aryltetramethylenediamines with PPE in chloroform solution, by the following procedure. *N*-Aroyl-*N'*-aryltetramethylenediamine (1 g) was refluxed for 2 h with a chloroform solution (20 ml) of PPE.[17] The organic layer was extracted with dilute hydrochloric acid (×4); the acid extract was made alkaline with 20% sodium hydroxide. If the tetrahydrodiazepine precipitated, it was collected and crystallized. If this failed to occur, the suspension was extracted with methylene chloride (4 × 30 ml). The organic solution was washed with water, dried, evaporated *in vacuo*, and the residue crystallized.

Cyclization with phosphorus oxychloride was performed as follows. *N*-Aroyl-*N'*-aryltetramethylenediamine (1 g) was refluxed for 2 h with phosphorus oxychloride (15 ml). The excess of reagent was removed *in vacuo*, keeping the reaction flask in a water-bath at 100°. The residue was

[17] W. Pollmann and G. Schramm, *Biochim. Biophys. Acta*, 1964, **80**, 1.

dissolved in ice–water (100 ml) and the resulting aqueous solution was treated as indicated.

Cyclization was also attempted by heating an intimate mixture of *N*-aroyl-*N'*-aryltetramethylenediamine (1 g) with polyphosphoric acid (83% phosphorus pentaoxide) in an oil-bath at 150° for 2 h. After cooling, the mixture was dissolved in ice–water and the resulting aqueous solution was treated as indicated for the cyclization with PPE. Crystallization solvents, m.p.s, elemental analyses, and yields for the bases are given in Table 2.*

Picrates were obtained dissolving the bases in dilute hydrochloric acid and precipitating with an aqueous solution of picric acid (Table 3). Chloroplatinates were obtained by addition of 10% aqueous chloroplatinic acid to a boiling solution of the base in ethanol. After cooling, the precipitate was filtered and washed with warm ethanol (Table 3).

1,2-*Diaryl*-1,4,5,6,7,8-*hexahydro*-1,3-*diazocines*. These compounds were prepared by cyclization of *N*-aroyl-*N'*-arylpentamethylenediamines with PPE, following the procedure used for the synthesis of tetrahydrodiazepines, but PPE (10 g) was used without solvent, and heating was performed in an oil-bath at 120° for 2 h. As above, products were isolated as bases (Table 2) or salts (Table 3).*

1-(o-*Nitrophenyl*)-2-(p-*nitrophenyl*)-2-*imidazoline*.—Following the general procedure used for the synthesis of *N*-aroyl-*N'*-arylpolymethylenediamines, the acylation of the *N*-(*o*-nitrophenyl)ethylenediamine [1] with *p*-nitrobenzoyl chloride in chloroform solution, afforded the *N*-(*p*-nitrobenzoyl)-*N'*-(*o*-nitrophenyl)ethylenediamine (72%), m.p. 163° (from methanol) (Found: C, 54.5; H, 4.4; N, 16.7. $C_{15}H_{14}N_4O_5$ requires C, 54.5; H, 4.25; N, 16.95%). Cyclization of this compound with PPE, in a similar way as for the synthesis of 1,2-diaryl-4,5,6,7-tetrahydro-1*H*-1,3-diazepines, afforded 1-*o*-(nitrophenyl)-2-(*p*-nitrophenyl)-2-imidazoline (85%), m.p. 188° (from methanol) (Found: C, 57.5; H, 4.15; N, 17.9. $C_{15}H_{12}N_4O_4$ requires C, 57.7; H, 3.85; N, 17.95%).

Basicity.—pK_a Values for compounds (1)—(6) were determined by u.v. spectrophotometry [4] or potentiometrically in methylcellosolve–water by the extrapolation method to 0% organic solvent.[2]

Alkaline Hydrolysis.—Kinetic runs were performed in boiling alkaline 95% ethanol following the general procedure used in the hydrolysis of the 1,2-diaryl-1,4,5,6-tetrahydropyrimidines.[4] The reactions were followed at two different wavelengths providing concordant results. At constant pH the rates of disappearance of compounds were found to be first order. Plots of log (absorbance) against time showed that linearity held up to 60—70% of the reactions.

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* Tables of spectroscopic properties of these compounds are given in Supplementary Publication No. SUP 22127 (4 pp.). 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.