Alkaline Hydrolysis of 1,2,3-Trisubstituted Cyclic Amidinium Salts. Kinetic Study of N $\longrightarrow$ N' Acyl Migration in Alkaline Solution in an Ethylenediamine Derivative

By **Beatriz Fernández, Isabel Perillo,** and **Sámuel Lamdan,*** Departamento de Química Orgánica, Facultad de Farmacia y Bioquímica, Universidad Nacional de Buenos Aires, Junín 956, Buenos Aires, República Argentina

The alkaline hydrolysis of 1,2-diphenyl-3-methylimidazolinium iodide (1) affords *N*-benzoyl-*N*-phenyl-*N'*-methylethylenediamine (2). An intermediate of the reaction, probably 1,2-diphenyl-2-hydroxy-3-methylimidazolidine (8), was isolated by thick layer chromatography. Compound (2) in neutral or alkaline media undergoes intramolecular aminolysis affording *N*-benzoyl-*N*-methyl-*N'*-phenylethylenediamine (3) by benzoyl transfer. Kinetic studies were performed on this reaction over the pH range 11.65—12.80. Compound (2) appears to rearrange by a mechanism which involves the formation and catalysed decomposition of a tetrahedral addition intermediate. This intermediate is the same as that isolated by alkaline hydrolysis of (1). Pseudo-first-order rate constants show a first-order dependence on hydroxide ion activity all over the pH range studied indicating that the contribution of the anionic species of the intermediate is negligible under the experimental conditions. The alkaline hydrolysis of the 1,2-diphenyl-1,4,5,6-tetrahydropyrimidinium iodide (9) allowed the isolation of only the rearranged product *N*-benzoyl-*N*-methyl-*N'*-phenyltrimethylenediamine (10).

Alkaline Hydrolysis of 1,2-*Diphenyl*-3-*methylimidazolinium Iodide* (1).—Continuing our study on the reactions of asymmetric imidazolinium compounds with nucleophiles,[1] we have examined the alkaline hydrolysis of 1,2-diphenyl-3-methylimidazolinium iodide (1). Treatment of an aqueous solution of (1) with 5% sodium hydroxide afforded an oil (2) which upon immediate precipitation with aqueous picric acid gave a picrate, $C_{22}H_{19}N_5O_7$, m.p. 163°. The basicity of (2) (pK_a 9.11), the n.m.r. spectrum [with an exchangeable singlet at δ 1.83 (1 H)] suggesting the presence of an aliphatic NH, and the resemblance of the u.v. spectrum with that of the *N*-methyl-*N*-phenylbenzamide,[2] allowed the structure of *N*-benzoyl-*N*-phenyl-*N'*-methylethylenediamine to be assigned to compound (2) (Scheme 1).

Compound (2) is stable under acid conditions. In neutral or alkaline solutions it rearranges giving *N*-benzoyl-*N*-methyl-*N'*-phenylethylenediamine (3), which is identical with that obtained from *N*-(2-bromoethyl)-*N*-methylbenzamide (4) and aniline, and also to material obtained by selective benzoylation of *N*-methyl-*N'*-phenylethylenediamine (5) with phenyl benzoate. Furthermore, the basicity of compound (3) (pK_a 3.93) and its spectroscopic and chemical properties are in line with the proposed structure. The acid hydrolysis of (3) affords *N*-methyl-*N'*-phenylethylenediamine (5) identical with that obtained from 2-bromo-*N*-methylethylamine (6). Likewise, the benzoylation of (3) affords *N*,*N'*-dibenzoyl-*N*-methyl-*N'*-phenylethylenediamine (7), identical with that obtained from (5). Under acid conditions both *N*-benzoyl-*N*-methyl-*N'*-(*p*-nitrophenyl)ethylenediamine [1] and compound (3) do not give the reverse reactions to the original salts. However, unlike the former,[1] (3) rearranges at room temperature again to give (2). This is accounted for by an N $\longrightarrow$ N' acyl migration in acid medium. Since this type of rearrangement has not been reported thus far the kinetics of the reaction were studied as described in the following paper.

Compound (3) gives a negative reaction with the Karl Fischer reagent [3] proving the absence of an equilibrium with the tautomeric pseudo-base 2-hydroxy-1,2-diphenyl-3-methylimidazolidine (8). However, (8) may be the intermediate detected in the alkaline hydrolysis of (1) (Scheme 2). An aqueous 1M solution

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[1] I. Perillo and S. Lamdan, *J.C.S. Perkin I*, 1975, 894.

[2] P. Grammaticakis, *Compt. Rend.*, 1959, **248**, 244.

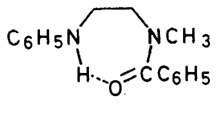
[3] D. Beke, Cs. Czántay, and M. B. Bárczai, *Periodica Polytech.*, 1960, **4**, 329.

of (1) was treated with cooled 1M-sodium hydroxide solution and immediately extracted with chloroform. The chloroform solution chromatographed on non-activated silica gel $HF_{254+366}$ plates using methanol as developing solvent showed a single spot (R_F *ca.* 0). 2—3 Min afterwards a portion of a second extraction was run showing that another spot (R_F *ca.* 0.1) corresponding to (2) began to appear. *Ca.* 1 h afterwards the appearance of the spot corresponding to (3) (R_F *ca.* 0.8) could be detected. Finally, after 22—24 h at room temperature only (3) could be observed by chromatography.

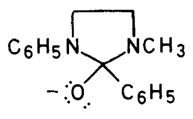
A compound with R_F *ca.* 0 acting as an intermediate of the reaction was isolated by thick layer chromatography using silica $HF_{254+366}$ plates (1 mm) activated at 120° for 1 h with methanol as developing solvent. The portion of silica gel containing this product was separated and extracted with chloroform at room temperature. The u.v. spectrum in this solvent was immediately performed showing absorption at $\lambda_{max.}$ 242 nm. Taking into account the results reported by Robinson *et al.* on the hydrolysis of 1,3-diphenyl-2-imidazolinium chloride (DPIC),[4-6] it may be inferred that the spot with R_F *ca.* 0 corresponds to the pseudo-base (8). This product cannot be detected if the aqueous solution of (1) is made strongly alkaline (pH 13). Consistent with the mechanism proposed by Robinson for the hydrolysis of DPIC,[4-6] the formation of (2) from (1) can be explained by considering the conjugate base of (8) to undergo the electrophilic attack of water on its most basic nitrogen to give the open product (2) (Scheme 3). As will be shown below, (8) also proved to be the intermediate in the intramolecular aminolysis (2) ⟶ (3) (Scheme 2). The appearance of (2) as initial product in the alkaline hydrolysis of (1) can be considered to be the kinetically controlled step due to the different rates of decomposition of (8) to give (2) and (3). Finally (3) accumulates due to its greater thermodynamic stability (Scheme 2).

Alkaline Hydrolysis of 1,2-*Diphenyl*-3-*methyl*-1,4,5,6-*tetrahydropyrimidinium Iodide* (9).—The study on the alkaline hydrolysis of (1) was extended to the tetrahydropyrimidinium homologue (9). Unlike the results obtained with (1), when compound (9) was treated with sodium hydroxide the expected first product *N*-benzoyl-*N*-phenyl-*N'*-methyltrimethylenediamine could not be isolated. When (9) was dissolved in hot water, immediately cooled, and made alkaline with dilute sodium hydroxide, it was observed that the anionic exchange was not rapidly achieved as occurred with compound (1). This exchange was proved to be slow when the alkaline solution was immediately extracted with chloroform. Under these conditions (9) was quantitatively recovered. In *ca.* 45 min the exchange of the iodide ion was achieved and the solution became turbid due to the precipitation of the *N*-benzoyl-*N*-methyl-*N'*-phenyltrimethylenediamine (10) (Scheme 4). A chloroform extraction was performed at this moment and the organic solution was chromatographed on non-activated silica gel $HF_{254+366}$ plates using methanol–chloroform (4 : 1) as developing solvent. Three spots were observed. That of highest R_F (*ca.* 0.93) was identified as compound (10). Two other spots (R_F *ca.* 0.25 and 0.10) were probably those corresponding to the *N*-benzoyl-*N*-phenyl-*N'*-methyltrimethylenediamine and the tetrahedral addition intermediate, since their size and intensity vanished while that of (10) increased.

The structure of (10) was confirmed by elemental analysis, spectroscopic properties, and the basicity (pK_a 4.26). It is interesting to point out that in the n.m.r. spectrum, unlike that of its homologue (3), the aromatic NH appears as a sharp singlet and at a lower δ value. This difference may be probably accounted for by considering that (3) would be able to form an intramolecular hydrogen bond (I). This hydrogen bond might be less probable in compound (10) because it would imply the formation of an eight-membered ring.



(I)



(II)

Intramolecular Aminolysis of N-*Benzoyl*-N-*phenyl*-N'-*Methylethylenediamine* (2).—As mentioned above, compound (2) rearranges in alkaline solutions to give (3). The reaction involves the N ⟶ N' migration of an acyl group and it is interpreted as a base-catalysed nucleophilic reaction involving intramolecular aminolysis which proceeds through the formation and catalysed decomposition of a tetrahedral addition intermediate (Scheme 5). Though there are some previous reports on this type of reaction,[7,8] no kinetic studies have been done thus far.

Kinetic experiments were performed over the pH range 11.65—12.80. The disappearance of (2) was followed by u.v. spectrophotometry in aqueous sodium hydroxide–sodium hydrochloride solutions at 25° and ionic strength 1.0M.

Reactions performed at constant pH while varying the concentration of (2) from 2×10^{-2} to 4×10^{-3}M showed a first-order dependence on the substrate. A plot of the $-\log k_{obs}$ as a function of pOH gave a slope of 1.06 (s 0.168) showing first-order dependence of the reaction on a_{OH^-} under these experimental conditions. From the same plot a second order-rate constant k of 0.14 l mol^{-1} min^{-1} could be calculated. Thus, over this pH range the rearrangement of (2) follows the rate law $v = k[(2)][OH^-]$. The pseudo-first-order rate constants $k_{obs} = k_2k_1/(k_{-1} + k_2)$ increase on increasing the alkali concentration corresponding to a base catalysed

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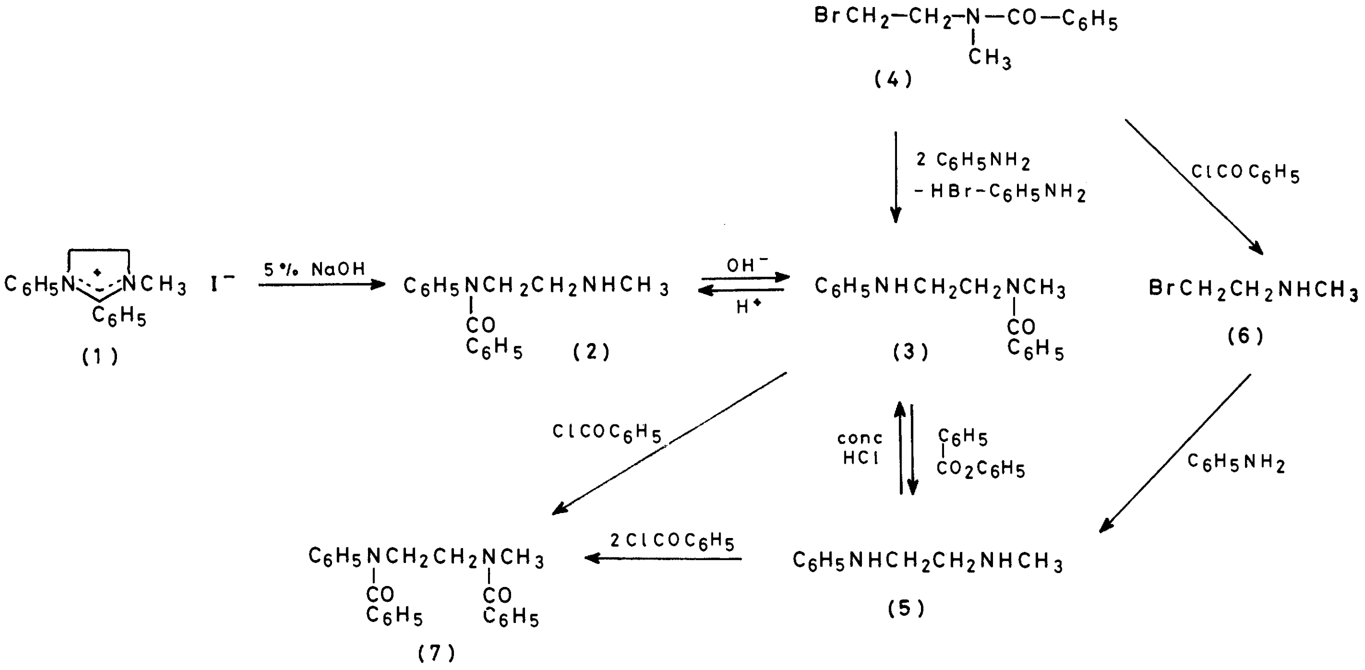
[4] D. R. Robinson and W. P. Jencks, *J. Amer. Chem. Soc.*, 1967, **89**, 7088.

[5] D. R. Robinson, *Tetrahedron Letters*, 1968, 5007.

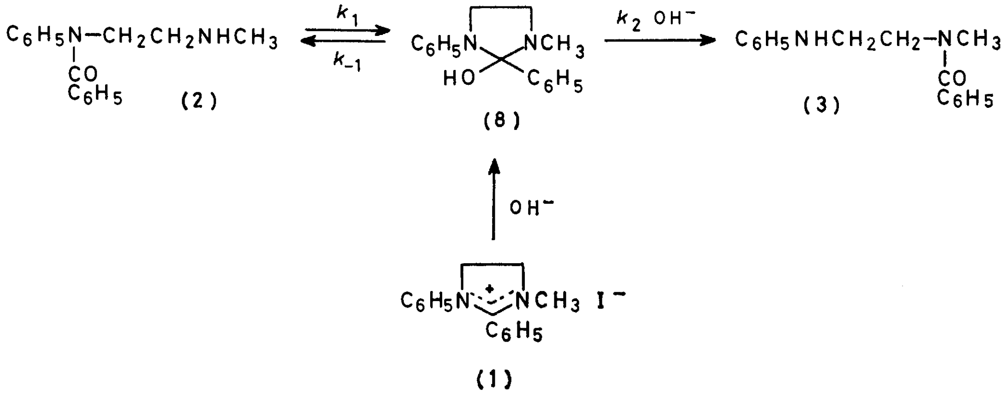
[6] D. R. Robinson, *J. Amer. Chem. Soc.*, 1970, **92**, 3138.

[7] C. J. M. Stirling, *J. Chem. Soc.*, 1958, 4531.

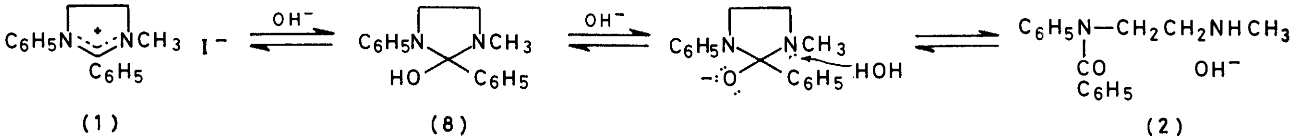
[8] W. B. Wright, H. J. Brabander, and R. A. Hardy, *J. Org. Chem.*, 1961, **26**, 2120.



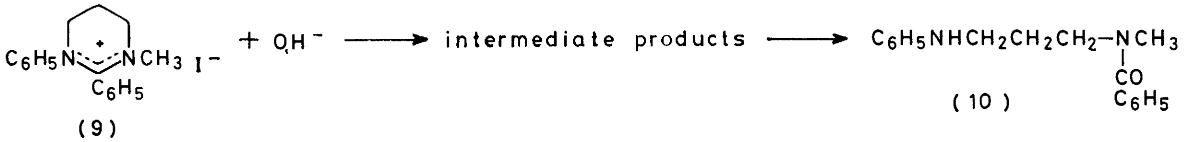
Scheme 1



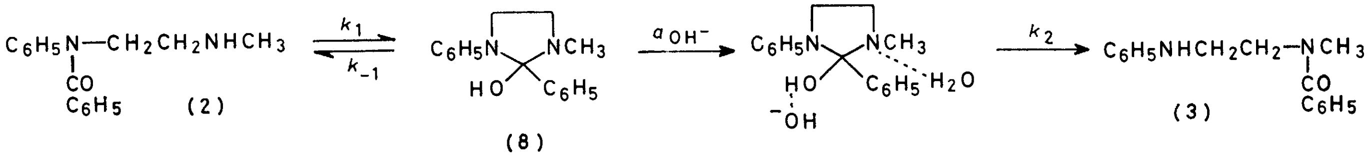
Scheme 2



Scheme 3



Scheme 4



Scheme 5

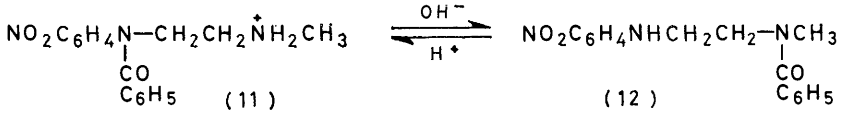
reaction (Table), k_1 and k_{-1} being true constants and k_2 a function of hydroxide ion activity.

Rate constants and half-lives for the N $\longrightarrow$ N′ benzoyl migration in *N*-benzoyl-*N*-phenyl-*N*′-methylenediamine in sodium hydroxide solutions at 25 °C

pH	pOH	$-\log k_{obs}$	k_{obs}/min^{-1} *	$t_{1/2}$/h
11.65	2.35	3.05	8.92×10^{-4}	12.95
11.90	2.10	2.82	1.50×10^{-3}	7.70
12.15	1.85	2.60	2.51×10^{-3}	4.60
12.45	1.55	2.30	5.02×10^{-3}	2.30
12.80	1.20	1.97	1.07×10^{-2}	1.08

* Accuracy of rate constants obtained from duplicate experiments was ±0.05.

An intermediate of this reaction was detected by t.l.c. when a solution of (2) in 1N-hydrochloric acid was neutralized with 1N cooled sodium hydroxide, extracted with chloroform, and chromatographed. This intermediate showed, after isolation by thick layer chromatography, the same chromatographic behaviour and u.v. spectrum as those of the pseudo-base (8).



$$\underset{\substack{|\\ CO\\ C_6H_5}}{NO_2C_6H_4N}{-}CH_2CH_2\overset{+}{N}H_2CH_3 \ \ (11) \quad \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} \quad (12) \ \ NO_2C_6H_4NHCH_2CH_2{-}\underset{\substack{|\\ CO\\ C_6H_5}}{N}CH_3$$

SCHEME 6

From the pOH dependence of the slower phase of the reaction it was observed that deviations from this general trend did not occur (*s* 0.168). Therefore, it may be assumed that the contribution of the anionic species (II) is negligible even at pH values where the main part of the intermediate is expected to be in the anionic form.[6,*] Thus, the simplest interpretation for this reaction under steady-state conditions is the one-encounter mechanism in which a single catalyst molecule both removes and donates a proton during a single encounter with the intermediate (8) (Scheme 5) avoiding the formation of the anionic species (II) as a free intermediate. Then, the open product (3) is obtained during the subsequent slower phase.

As expected, the rates of rearrangement depend on the different nucleophilicities of the nitrogen atoms. This is proved when *N*-benzoyl-*N*-(*p*-nitrophenyl)-*N*′-methylethylenediamine (11) dissolved in 30—35% sulphuric acid [†] is made alkaline. In fact, when the acid solution of (11) is made alkaline, extracted, and immediately chromatographed, only the rearranged product (12) is detected (Scheme 6). The instantaneous migration of the acyl group due to the marked differences in the nucleophilicity of the nitrogen atoms accounts for the appearance of compound (12) as the sole product in the alkaline hydrolysis of the 1-methyl-2-phenyl-3-(*p*-nitrophenyl)imidazolinium iodide.[1]

EXPERIMENTAL

M.p.s are uncorrected and were taken on a Buchi capillary apparatus. I.r. spectra were recorded with a Beckman 20 A instrument for potassium bromide pellets. U.v. spectra in ethanol 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 R 12 (60 MHz) spectrometer in deuteriochloroform, with tetramethylsilane as internal reference. The presence of exchangeable protons was confirmed by use of deuterium oxide.

1,2-*Diphenyl*-3-*methylimidazolinium Iodide* (1).—A solution of 1,2-diphenyl-2-imidazoline [9] (2.22 g) in methylene chloride (15 ml) was refluxed with methyl iodide (14.2 g) for 75 min. The solvent and the excess of methyl iodide were removed *in vacuo*. The residue crystallized affording the *iodide* (1) (90%), m.p. 208° (from absolute ethanol or propan-2-ol) (Found: C, 52.8; H, 4.79; N, 7.75; I^-, 35.2. $C_{16}H_{17}IN_2$ requires C, 52.8; H, 4.65; N, 7.7; I^-, 34.9%); $\lambda_{max.}$ 206 (ε 25 000), 220 (25 300), and 270 nm (12 000); $\nu_{max.}$ 1 640, 1 610, 1 565, 1 480, 1 310, 775, and 704 cm^{-1}; δ 3.27 (3 H, s, CH_3), 4.70 (4 H, s, CH_2CH_2), 7.20—7.72 (8 H, m, ArH), and 7.80—8.00 (2 H, m, *ortho* to N-1); the *picrate* had m.p. 139° (from ethanol) (Found: C, 56.7; H, 4.15; N, 15.15. $C_{22}H_{19}N_5O_7$ requires C, 56.7; H, 4.1; N, 15.05%).

N-*Benzoyl*-N-*phenyl*-N′-*methylethylenediamine* (2).—(*a*) After dissolving (1) in water with the aid of heating, the resulting solution was rapidly cooled and made alkaline with 5% sodium hydroxide separating an oil. The oil was rapidly extracted with chloroform and the organic layer was washed, dried, and concentrated affording compound (2) (70%), δ 1.83 (1 H, s, exchangeable, NH), 2.45 (3 H, s, CH_3), 2.88 (2 H, t, $HNCH_2$), 4.13 (2 H, t, $OCNCH_2$), and 7.04—7.70 (10 H, m, ArH); pK_a 9.11; R_F (methanol) 0.12; the *picrate* had m.p. 163° (from ethanol) (Found: C, 54.7; H, 4.65; N, 14.4. $C_{22}H_{21}N_5O_8$ requires C, 54.7; H, 4.35; N, 14.5%). The detection of an intermediate, presumably the pseudo-base (8), was achieved as follows. An aqueous solution of (1) was neutralized with sodium hydroxide and extracted with chloroform. The organic solution was chromatographed on 10 × 20 cm glass plates coated with Merk silica $HF_{254+366}$ (0.25 mm) dried at 100° for 10 min and methanol was used as running solvent.

(*b*) An acid solution of compound (2) is obtained by the rearrangement of (3) in aqueous acid solutions. For example, a 4×10^{-2}M solution of compound (3) in N-hydrochloric acid, undergoes practically complete rearrangement in 48 h.

N-*Benzoyl*-N-*methyl*-N′-*phenylethylenediamine* (3).—(*a*) Compound (2) in neutral or alkaline media, spontaneously rearranges affording compound (3), m.p. 90° (from cyclohexane or benzene–light petroleum) (Found: C, 75.3; H, 7.1; N, 11.0. $C_{16}H_{18}N_2O$ requires C, 75.6; H, 7.1; N, 11.05%); $\lambda_{max.}$ 206 (ε 26 900) and 246 nm (14 500)

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[*] A pK_a value of 12.75 was found by Robinson for the intermediate in alkaline hydrolysis of DPIC.[6]

[†] Compound (11) is obtained by rearrangement of *N*-benzoyl-*N*-methyl-*N*′-(*p*-nitrophenyl)ethylenediamine (12) in concentrated sulphuric acid (Scheme 6). A 4×10^{-2} solution of (12) in 35% sulphuric acid is completely rearranged in *ca.* 36 h. This type of rearrangement in acid media is described in the following paper.

[9] I. Perillo and S. Lamdan, *J. Heterocyclic Chem.*, 1970, **7**, 791.

$\nu_{max.}$ 3 336, 1 615, 1 400, 1 320, 750, and 692 cm^{-1}; δ 3.00 (3 H, s, CH_3), 3.20—3.80 (4 H, m, CH_2CH_2), 3.80 (1 H, exchangeable, NH), 6.35—6.80 (3 H, m, *o*- and *p*-H), and 6.85—7.45 (7 H, m, ArH); pK_a 3.93; R_F (methanol) 0.70. Compound (3) gives a negative reaction with the Karl Fischer reagent. By dissolving compound (3) in 10% hydrochloric acid and immediately precipitating with aqueous picric acid, the *picrate* was obtained, m.p. 132° (from ethanol) (Found: C, 54.5; H, 4.35; N, 14.45. $C_{22}H_{21}N_5O_8$ requires C, 54.7; H, 4.35; N, 14.5%).

(*b*) Benzoyl chloride (1.54 ml) was added to a solution of 2-bromo-*N*-methylethylamine hydrobromide [10] (2.19 g) in cold 1N-sodium hydroxide (23 ml). The mixture was vigorously shaken until the odour of benzoyl chloride had disappeared. The emulsion was extracted with chloroform and the extract was washed with 5% sodium hydroxide, 10% hydrochloric acid, and water. The resulting organic solution was dried and concentrated *in vacuo* affording *N*-(2-bromoethyl)-*N*-methylbenzamide (4). An intimate mixture of the crude amide (4) (2.42 g) and aniline (1.86 g) was heated in a water-bath at 100° for 1 h. The crude product was washed three times with boiling water and the oil dissolved in 10% hydrochloric acid. The acid solution was extracted with a little chloroform to remove non-basic impurities. The resulting aqueous solution was cooled and made alkaline affording (3) as an oil that solidified on standing (68%).

(*c*) A mixture of *N*-methyl-*N*′-phenylethylenediamine (5) (1.5 g) and phenyl benzoate (3.96 g) in anhydrous dioxan (20 ml), was allowed to react at room temperature for seven days. After removing the solvent *in vacuo*, the residue was dissolved in 10% hydrochloric acid and the resulting acid solution was filtered and made alkaline affording (3) (50%).

N-*Methyl*-N′-*phenylethylenediamine* (5).—This compound was synthesized by Wright *et al.* by catalytic debenzylation of *N*-benzyl-*N*-methyl-*N*′-phenylethylenediamine,[8] and by Fourneau and Lestrange from *N*-(2-chloroethyl)aniline.[11] We synthesized it in two different ways. (*a*) A mixture of 2-bromo-*N*-methylethylamine hydrobromide (6) [10] (21.9 g), aniline (9.3 g), and anhydrous sodium carbonate (21.2 g) in toluene (50 ml) was refluxed for 16 h. The mixture was shaken with 5% sodium hydroxide and the organic layer was separated. This solution was washed with water, dried, and concentrated *in vacuo*. The residue was distilled under reduced pressure in a Vigreux–Claissen apparatus affording (5) (50%), b.p. 118—120° at 5 mmHg; δ 1.88 (1 H, s, exchangeable, aliphatic NH), 2.46 (3 H, s, CH_3), 2.70—3.00 (2 H, m, CH_2 bonding to aliphatic amine), 3.10—3.40 (2 H, m, CH_2 bonding to aromatic amine), 3.50 (1 H, s, exchangeable, aromatic NH), 6.50—6.95 (3 H, m, *o*- and *p*-H), and 7.00—7.40 (2 H, m, ArH); the *picrate* had m.p. 172° (from ethanol) (Found: C, 41.7; H, 3.5; N, 18.5. $C_{21}H_{20}N_8O_{14}$ requires C, 41.45; H, 3.3; N, 18.4%).

(*b*) Compound (3) (0.5 g) in concentrated hydrochloric acid (5 ml) was refluxed for 8 h. After cooling and diluting with water, benzoic acid was filtered off. The acid solution was treated with aqueous picric acid affording the picrate of (5) (62%), identical with the sample obtained from 2-bromo-*N*-methylethylamine.

NN′-*Dibenzoyl*-N-*methyl*-N′-*phenylethylenediamine* (7).—(*a*) A mixture of compound (5) (1.50 g), benzoyl chloride (3.37 g), and triethylamine (4.40 g) was dissolved in anhydrous chloroform (30 ml) and refluxed for 2 h. The chloroform solution was washed with 10% hydrochloric acid, three times with 40% sodium hydroxide, and water, dried, and concentrated. The residue crystallized affording (7) (83%), m.p. 99° (from cyclohexane or methanol–water) (Found: C, 77.1; H, 6.45; N, 7.8. $C_{23}H_{22}N_2O_2$ requires C, 77.1; H, 6.15; N, 7.8%); $\nu_{max.}$ 1 640, 1 500, 1 402, 1 392, 1 286, 1 080, 708, and 695 cm^{-1}; δ 3.10 (3 H, s, CH_3), 3.67—4.35 (4 H, m, CH_2CH_2), and 7.00—7.48 (15 H, m, ArH).

(*b*) Benzoylation of compound (3) was performed according to the above procedure, using compound (3) (2.54 g), benzoyl chloride (2.11 g), and triethylamine (1.98 g) affording compound (7) (85%).

1,2-*Diphenyl*-3-*methyl*-1,4,5,6-*tetrahydropyrimidinium Iodide* (9).—The same procedure used for the synthesis of compound (1) was followed for the reaction of 1,2-diphenyl-1,4,5,6-tetrahydropyrimidine [12] (2.36 g) with methyl iodide (14.2 g) affording compound (9) (82%), m.p. 195° (from absolute ethanol) (Found: C, 53.9; H, 4.9; N, 7.55; I^-, 33.8. $C_{17}H_{19}IN_2$ requires C, 54.0; H, 5.05; N, 7.4; I^-, 33.6%); $\lambda_{max.}$ 220 nm (ε 24 700); $\nu_{max.}$ 1 620, 1 595, 1 490, 1 320, 770, and 704 cm^{-1}; δ 2.60 (2 H, quintuplet, $C{\cdot}CH_2{\cdot}C$), 3.10 (3 H, s, CH_3), 4.15 (4 H, quartet, CH_2N), 7.00—7.50 (8 H, m, ArH), and 7.60—7.80 (2 H, m, H *ortho* to N-1); the *picrate* had m.p. 110° (from ethanol) (Found: C, 57.5; H, 4.6; N, 14.5. $C_{23}H_{21}N_5O_7$ requires C, 57.6; H, 4.4; N, 14.6%).

N-*Benzoyl*-N-*methyl*-N′-*phenyltrimethlyenediamine* (10).—After dissolving compound (9) in water with the aid of heating, the resulting solution was rapidly cooled and made alkaline with 5% sodium hydroxide. The solution slowly became turbid separating an oil. After about two days the oil solidified affording compound (10) (88%), m.p. 73° (from cyclohexane) (Found: C, 76.2; H, 7.45; N, 10.7. $C_{17}H_{20}N_2O$ requires C, 76.1; H, 7.45; N, 10.45%); $\lambda_{max.}$ 206 (ε 31 500) and 244 nm (16 700); $\nu_{max.}$ 3 350, 1 620, 1 600, 1 478, 1 400, 1 270, 740, and 692 cm^{-1}; δ 1.96 (2 H, quintuplet, $C{\cdot}CH_2{\cdot}C$), 3.08 (3 H, s, CH_3), 3.44 (1 H, s, exchangeable, NH), 3.10—3.90 (4 H, m, CH_2N), 6.52—6.92 (3 H, m, *o*- and *p*-H), and 7.00—7.60 (7 H, m, ArH).

Kinetic Measurements.—Samples of (2) were obtained from a benzoyl transfer reaction. A 4 × 10^{-2}M solution of (3) in 1N-hydrochloric acid was allowed to react at infinite time. This type of rearrangement in acid media is described in another paper. Complete transformation was checked by the u.v. absorption at 270 nm ($\varepsilon_{max.}$ 3 700) and by potentiometric titration.

Reactions were performed at 25° using NaOH–NaCl solutions over the pH range 11.65—12.80. Ionic strength was maintained at 1.0M with added sodium chloride. Measurements of pH were performed in a Beckman Zeromatic II pH-meter using a standardized glass electrode. The meters were standardized at pH 6.86, 9.18, and 12.45 at 25° with Beckman standard buffers. Hydroxide ion activity was defined by the relation $-\log a_{OH^-} = 14 - pH$ where pH is the meter reading. Activity coefficients of hydroxide ion calculated from known hydroxide concentrations and activity measurements varied by ±0.03. Thus, pH-meter readings were estimated to be proportional to hydroxide ion activity in these solutions.

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[10] L. Knorr and G. Meyer, *Ber.*, 1905, **38**, 3133.

[11] J. P. Fourneau and Y. de Lestrange, *Bull. Soc. chim. France*, 1947, 827.

[12] I. Perillo and S. Lamdan, *J. Heterocyclic Chem.*, 1973, **10**, 915.

Kinetic experiments were performed with initial concentrations of (2) of 4 × 10^{-3}M. All reactions were followed spectrophotometrically in a Beckman DB-G grating spectrophotometer at 270 nm where (3) has little absorption ($\varepsilon_{\text{max.}}$ 660).

Plots of the log ($A - A_\infty$) against time on semilogarithmic graph paper were linear for at least 90% of the reactions and pseudo-first-order rate constants were calculated from the relationship k_{obs} ln $2/t_{1/2}$.

General Kinetic Procedure.—A portion (5 ml) of 4 × 10^{-2}M solution of (2) in 1N-hydrochloric acid was potentiometrically neutralized to pH 7.0 with 1N-sodium hydroxide and immediately transferred to a volumetric flask (50 ml) containing the buffer solution at 25 °C. Calculated concentrations of NaCl previously added to the buffer solution allowed a final ionic strength of 1.0M. The pH values of all the buffer mixtures were measured before and after each run and were found to remain constant.

Solutions were thermostatted at 25 ± 0.1°. At known intervals samples (1 ml) were transferred to a volumetric flask (50 ml) containing dilute hydrochloric acid to give a final pH value of *ca.* 3.0—4.0. Solutions were made up to volume with distilled water. This acid pH range was selected to avoid the reverse reaction (3) $\longrightarrow$ (2) which occurs at pH values below 2.70.* The same procedure was followed with the buffer without (2) to prepare the blanks. Final solutions (8 × 10^{-5}M) were read at 270 nm and the absorbance at time zero was estimated by extrapolation.

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* This value arises from results obtained when the rearrangement of (3) under acid conditions was studied.