Ring Opening Reaction of 1,2-Diaryl-3-methyl-1,4,5,6-tetrahydropyrimidinium Salts with Metal Hydride Complexes [1]

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The reaction of a series of 1,2-diaryl-3-methyl-1,4,5,6-tetrahydropyrimidinium iodides **1** with reducing agents acting by hydride ion transfer was studied. With excellent yields alkaline borohydrides readily reacted to form *N'*-aryl-*N*-benzyl-*N*-methyltrimethylenediamines **3** by reductive cleavage of the intermediate hexahydropyrimidine **2**. Ring opening is explained by the formation of a stabilized iminium ion, which also accounts for the cyclic aminal **2** hydrolysis observed in alcoholic solution after gradual addition of borohydride. Reactions with lithium aluminum hydride or with borane failed to render satisfactory results due to insolubility of the salt in solvents commonly employed. Comparisons are made with the behaviour of 1*H*-4,5-dihydroimidazolium salts which were studied in an earlier paper.

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Pursuing our studies on the reduction of cyclic amidinium salts as synthetic precursors of cyclic aminals and substituted alkylene-diamines [2], we attempted the reduction of a series of 1,2-diaryl-3-methyl-1,4,5,6-tetrahydropyrimidinium iodides **1a-h** (Scheme I) with agents acting by hydride ion transfer.

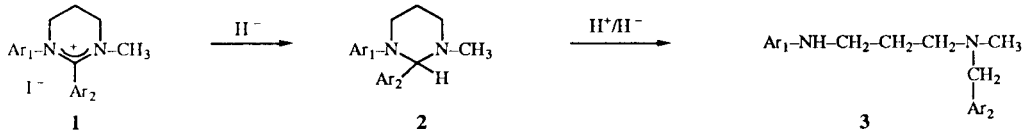
The reduction of tetrahydropyrimidinium salts **1a-h** with an excess of alkaline borohydrides (sodium borohydride, potassium borohydride, sodium cyanoborohydride) in alcoholic solution invariably led to the corresponding *N'*-aryl-*N*-benzyl-*N*-methyltrimethylenediamine **3** as the only product (95-100% yield) (Scheme II). In contrast to observations on the reduction of homologous 1*H*-4,5-dihydroimidazolium salts under similar conditions [2], no intermediate products such as the expected hexahydropyrimidines **2** could be detected in any case.

N,N,N'-Trisubstituted trimethylenediamines **3** were characterized as dihydrochlorides (Table I) and their structure confirmed by comparison with authentic samples obtained by reduction of *N*-aroyl-*N'*-aryl-*N*-methyltrimethylenediamines **4** [1] with borane (Scheme II) in tetrahydrofuran (THF). Spectroscopic data are given in Table I. Features of ir and ^{1}H-nmr spectra are as expected [4] and the fragmentation observed in ms by electron impact is typical of alkylamines (Scheme III).

In an attempt to obtain hexahydropyrimidines **2**, reduction of the salts **1f** and **1h** [6] was carried out by gradually adding a slight excess of alkaline borohydride in order to maintain minimal reagent concentration during most of the reaction time. A mixture was obtained mainly consisting of three products: the aldehyde corresponding to the C-2 aryl group, *N*-aryl-*N'*-methyltrimethylenediamine **5** and a third product that could be isolated in the case of reaction of **1f**, and whose uv, ir and mass spectra was consistent with the hexahydropyrimidine **2f**. In confirmation, the latter product disappeared on treating the reaction mixture with an excess of borohydride giving rise to the concomitant appearance of the corresponding compound **3**.

It may be speculated from a strictly mechanistic viewpoint that the unsymmetrical hexahydropyrimidine **2** obtained as the first reduction product from salts **1** undergoes in alcoholic medium selective cleavage of the bond between C-2 and the nitrogen bearing the aryl radical, with the elimination of the less basic amine and the formation of the more stable iminium ion **A** (Scheme II) [8].

Scheme I

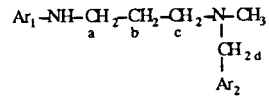


1 **2** **3**

1,2,3	Ar_1	Ar_2
a	C_6H_5	C_6H_5
b	*p*-ClC_6H_4	C_6H_5
c	*p*-$CH_3OC_6H_4$	C_6H_5
d	*p*-$CH_3C_6H_4$	C_6H_5
e	β-$C_{10}H_7$	C_6H_5
f	*p*-$NO_2C_6H_4$	C_6H_5
g	C_6H_5	*p*-ClC_6H_4
h	C_6H_5	*p*-$NO_2C_6H_4$

Table I

N'-Aryl-*N*-benzyl-*N*-methyltrimethylenediamines **3a-h**



Compound No.	IR ν (cm^{-1})	^{1}H-NMR δ (ppm)	Multiplicity	Assignment	Mass m/z	%	Mp (°C)	Dihydrochlorides Formula	Analyses Calcd./Found %C	%H	%N	%Cl
3a [a]	3300 (N-H)	7.35	s	C-C_6H_5	58	85.6	173	$C_{17}H_{24}N_2Cl_2$	62.39	7.34	8.56	21.71
	2900 (C-H)	7.35-7.00	m	*N*-C_6H_5	91	38.1			62.44	7.39	8.69	21.80
	2820 (C-H)			(2 meta H)	106	27.6						
	1610 (C=C)	6.70-6.42	m	*N*-C_6H_5	120	53.7						
	1310 (C-N)			(3 *ortho* and	132	24.5						
	730 (C_6H_5)			*para* H)	133	28.8						
	720 (C_6H_5)	4.00	bs [b]	N-H	134	52.0						
		3.65	s	CH_2 d	160	27.6						
		3.25	t	CH_2 a	162	25.0						
		2.60	t	CH_2 c	254	100.0						
		2.30	s	CH_3	(M$^+$)							
		1.90	q	CH_2 b								
3b	3280 (N-H)	7.35	s	C_6H_5	58	47.9	181	$C_{17}H_{23}N_2Cl_3$	56.43	6.36	7.75	29.46
	2910 (C-H)	7.05	d	Cl-C_6H_4	91	100.0			56.50	6.48	7.60	29.35
	2830 (C-H)			(2, *ortho* H)	120	30.6						
	1615 (C=C)	6.40	d	Cl-C_6H_4	134	34.8						
	1320 (C-N)			(2, *meta* H)	140	19.9						
	820 (*p*-C_6H_4)	4.35	bs [b]	N-H	289	25.3						
	780 (C-Cl)	3.45	s	CH_2 d	(M$^+$)							
	730 (C_6H_5)	3.10	t	CH_2 a								
	700 (C_6H_5)	2.45	t	CH_2 c								
		2.25	s	CH_3								
		1.64	q	CH_2 b								
3c	3320 (N-H)	7.35	s	C_6H_5	58	27.0	162	$C_{18}H_{26}N_2OCl_2$	60.50	7.28	7.84	19.89
	2930 (C-H)	6.80	d	CH_3O-C_6H_4	91	34.9			60.60	7.39	7.90	19.69
	2840 (C-H)			(2 *ortho* H)	120	49.6						
	1610 (C=C)	6.52	d	CH_3O-C_6H_4	121	24.8						
	1330 (C-N)			(2 *meta* H)	134	43.2						
	1210 (Ar-O-C)	3.90	bs [b]	NH	136	25.8						
	820 (*p*-C_6H_4)	3.85	s	O-CH_3	163	37.4						
	730 (C_6H_5)	3.55	s	CH_2 d	284	100.0						
	705 (C_6H_5)	3.25	t	CH_2 a	(M$^+$)							
		2.55	t	CH_2 c								
		2.20	s	N-CH_3								
		1.90	q	CH_2 b								
3d	3310 (N-H)	7.40	s	C_6H_5	58	24.4	159	$C_{18}H_{26}N_2Cl_2$	63.34	7.62	8.21	20.82
	2940 (C-H)	7.05	d	CH_3-C_6H_4	91	100.0			63.42	7.69	8.28	20.95
	2825 (C-H)			(2 *ortho* H)	120	60.3						
	1620 (C=C)	6.60	d	CH_3-C_6H_4	132	21.0						
				(2 *meta* H)								
	1325 (C-N)	3.90	bs [b]	N-H	134	36.9						
	825 (*p*-C_6H_4)	3.64	s	CH_2 d	146	21.0						
	720 (C_6H_5)	3.30	t	CH_2 a	268	34.6						
	710 (C_6H_5)	2.65	t	CH_2 c	(M$^+$)							
		2.35	s	CH_3								
		2.30	s	CH_3								
		1.95	q	CH_2 b								
3e	3340 (N-H)	7.35	s	C_6H_5	58	28.0	188	$C_{21}H_{26}N_2Cl_2$	66.84	6.90	7.43	18.83
	2920 (C-H)	7.65-7.10	m	β-naphthyl	83	32.4			66.97	7.02	7.45	18.70
	1615 (C=C)			(H-4 to H-8)	85	23.4						
	1335 (C-N)	6.80-6.60	m	β-naphthyl	91	100.0						
	725 (C_6H_5)			(H-1 and H-3)	120	38.7						
	690 (C_6H_5)	4.00	bs [b]	N-H	127	34.0						
		3.40	s	CH_2 d	134	36.8						
		3.20	t	CH_2 a	148	26.4						
		2.40	t	CH_2 c	149	20.6						
		2.15	s	CH_3	156	38.4						
		1.75	q	CH_2 b	157	39.6						
					304	51.2						
					(M$^+$)							

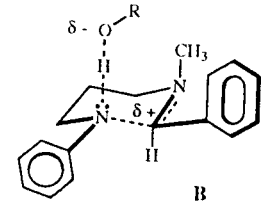
Table I (continued)

Compound No.	IR ν (cm^{-1})	^{1}H-NMR δ (ppm)	Multiplicity	Assignment	Mass m/z	Mass %	Mp (°C)	Dihydrochlorides Formula	Analyses Calcd./Found %C	%H	%N	%Cl
3f	3325 (N-H)	7.90	d	NO_2-C_6H_4	58	96.7	138	$C_{17}H_{23}N_3O_2Cl_2$	54.84	6.18	11.29	19.09
	2930 (C-H)			(2 *ortho* H)	91	69.3			54.95	6.28	11.20	19.00
	2850 (C-H)	7.20	s	C_6H_5	120	82.8						
	1620 (C=C)	6.35	d	NO_2-C_6H_4	134	100.0						
	1560 (C-NO_2)			(2 *meta* H)	151	5.5						
	1330 (C-N)	5.80	bs [b]	N-H	208	36.0						
	810 (*p*-C_6H_4)	3.35	s	CH_2 d	299	44.0						
	730 (C_6H_5)	3.10	t	CH_2 a	(M$^+$)							
	700 (C_6H_5)	2.40	t	CH_2 c								
		2.15	s	CH_3								
		1.65	q	CH_2 b								
3g	3315 (N-H)	7.30	s	Cl-C_6H_4	58	100.0	214	$C_{17}H_{23}N_2Cl_3$	56.43	6.36	7.75	29.46
	2920 (C-H)	7.25-7.05	m	C_6H_5-N	70	23.1			56.50	6.49	7.70	29.40
	2870 (C-H)			(2 *meta* H)	106	51.9						
	1610 (C=C)	6.85-6.55	m	C_6H_5-N	125	34.7						
	1340 (C-N)			(2 *ortho*	132	31.1						
	830 (*p*-C_6H_4)			and *para* H)	133	45.8						
	730 (C_6H_5)	4.00	bs [b]	N-H	154	27.6						
	690 (C_6H_5)	3.55	s	CH_2 d	168	24.3						
		3.25	t	CH_2 a	169	25.5						
		2.65	t	CH_2 c	194	20.0						
		2.30	s	CH_3	195	21.4						
		1.90	q	CH_2 b	289	47.6						
					(M$^+$)							
3h	3310 (N-H)	8.15	d	NO_2-C_6H_4	58	100.0	156	$C_{17}H_{23}N_3O_2Cl_2$	54.84	6.18	11.29	19.09
	2930 (C-H)			(2 *ortho* H)	106	60.8			54.92	6.15	11.18	19.15
	2835 (C-H)	7.50	d	NO_2-C_6H_4	132	20.9						
	1610 (C=C)			(2 *meta* H)	133	28.1						
	1550 (C-NO_2)	7.15	t	C_6H_5-N	136	35.1						
	1330 (C-N)			(2 *meta* H)	165	23.4						
	825 (*p*-C_6H_4)	6.60	m	C_6H_5-N	178	26.0						
	720 (C_6H_5)			(2 *ortho* and	179	28.1						
	690 (C_6H_5)			*para* H)	299	46.3						
		3.70	bs [b]	N-H	(M$^+$)							
		3.60	s	CH_2 d								
		3.20	t	CH_2 a								
		2.50	t	CH_2 c								
		2.25	s	CH_3								
		1.80	q	CH_2 b								

[a] This compound was synthesized previously by alkylation of aniline with 3-(*N*-benzyl-*N*-methyl)aminopropyl halide [3]. [b] Exchangeable.

With an excess of borohydride, the ion is rapidly reduced to give rise to compounds **3**. However, with minimal reducing agent concentration, the newly-formed ion is captured by water naturally present in the reaction medium leading to hydrolysis products [17].

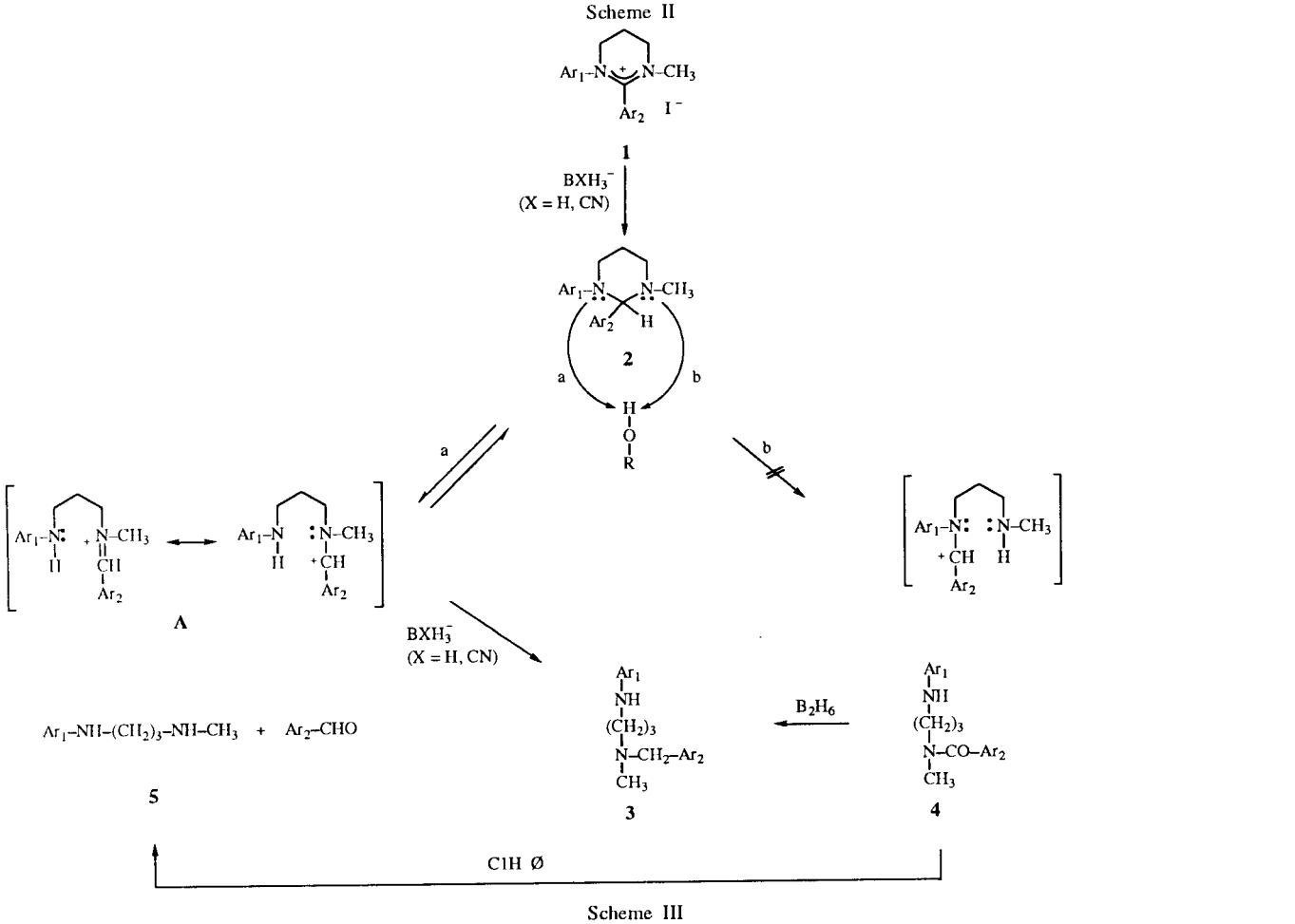
Although the overreduction of hexahydropyrimidines **2** with borohydride in alcoholic solution was not unexpected, since the ion is strongly stabilized through the aliphatic amine electrons and those of the benzene ring, the greater reactivity of such compounds as compared with homologous imidazolidines under similar conditions, is nonetheless striking. An explanation for this peculiarity cannot be found in the greater distance of the arylamino group, an electron acceptor, *versus* the iminium group of this trimethylene series, because the seven-membered homologue of compound **2f** (1-methyl-3-(*p*-nitrophenyl)-2-phenyl-1*H*-4,5,6,7-tetrahydro-1,3-diazepine) has been shown to be considerably stable in the same reducing medium [22]. Energy factors related to the stability of transition stage **B** which leads to the intermediate iminium ion **A**, or steric features allowing a better approach of the alcohol molecule to the nitrogen atom bearing the aryl group, may explain the prompt reductive cleavage of compounds **2**.



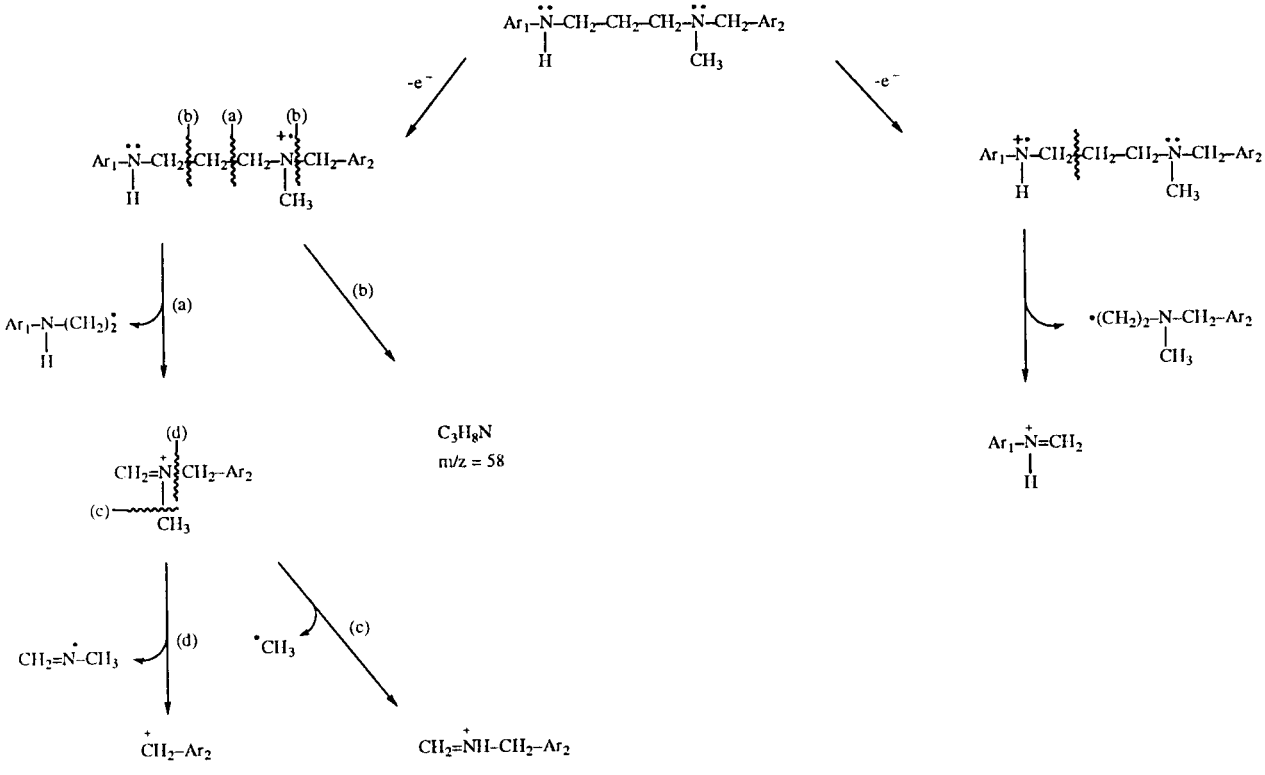
B

At variance with observations on dihydroimidazolium salts reduction [2], overreduction of cyclic aminal **2** could neither be avoided nor decreased by resorting to aprotic

Scheme II



Scheme III



solvents and a silica gel [23] or aluminum oxide support [24] for the reagent. The presence of hydroxy groups in the employed support (Si-OH or Al-OH) [25], explains the ability of the reagent to transfer H^+/H^- to a suitable acceptor [23], compound **2** in this case.

Reductions with lithium aluminum hydride and borane rendered poor results due to insolubility of salts **1** in commonly employed solvents. Thus, on reducing salt **1a** with either reagent in THF, hexahydropyrimidine **2a** was obtained as the first reaction product in both cases and readily identified by the presence of methyne hydrogen on C-2 in the ^{1}H-nmr spectrum. Although in such reducing media ring stability was higher than that observed with alkaline borohydrides in ethanol, protracted heating required for complete salt transformation again led to reductive ring cleavage in the case of lithium aluminum hydride and to ill-defined mixture of products in the case of borane.

EXPERIMENTAL

Melting points were taken on a Büchi capillary apparatus and are uncorrected. The ir spectra were recorded on a Beckman 180A spectrometer. Samples were run as potassium bromide pellets for solids and films for oils. The ^{1}H-nmr spectra were obtained on a Varian FT 80 A spectrometer using deuteriochloroform as the solvent. Chemical shifts are reported in parts per million (δ) downfield from an internal TMS reference. Signals are quoted as: s (singlet), d (doublet), t (triplet), q (quintuplet), m (multiplet) and bs (broad signal). The presence of exchangeable protons was confirmed by use of deuterium oxide. The uv spectra were recorded on a Jasco 7850 spectrophotometer. Mass spectra were recorded on a MS Shimadzu QP-1000 instrument at 20 eV. Analytical tlc was carried out on aluminium sheets Silica Gel 60 F_{254} and neutral Aluminium Oxide 60 F_{254} using benzene-methanol (9:1), chloroform-methanol (95:5), chloroform-diethylamine (9:1) and methanol-acetone-triethanolamine (10:10:0.3) as solvents. Column chromatography was carried out on Silica Gel 60 (70-325 mesh). Preparative thin layers separations (plc) were performed on Silica Gel PF_{254}, neutral Aluminium Oxide PF_{254} or Cellulose on 20 x 20 x 0.25 cm layers. Reagents, solvents and starting materials were purchased from standard sources and purified according to literature procedures.

1,2-Diaryl-3-methyl-1,4,5,6-tetrahydropyrimidinium Iodides **1a-h**.

These compounds were obtained by treatment of the corresponding 1,2-diaryl-1,4,5,6-tetrahydropyrimidine with methyl iodide according to our method [1].

N-Methyl-*N'*-(*p*-nitrophenyl)trimethylenediamine **5** (Ar_1 = *p*-$NO_2C_6H_4$).

A mixture of *N*-benzoyl-*N*-methyl-*N'*-(*p*-nitrophenyl)trimethylenediamine **4** (Ar_1 = *p*-$NO_2C_6H_4$, Ar_2 = C_6H_5) [1] (0.5 g) and concentrated hydrochloric acid (5 ml) was refluxed for 3 hours. The solution was cooled and water (20 ml) added. The crystallized precipitate (benzoic acid) was filtered off and the acid solution was brought to *p*H 6 with solid sodium carbonate and extracted with chloroform (2 ml) to remove impurities. The resulting aqueous solution was made strongly alkaline with 20% sodium hydroxide and extracted with methylene chloride. The organic solution was washed, dried and concentrated *in vacuo* affording *N*-methyl-*N'*-(*p*-nitrophenyl)trimethylenediamine **5** (Ar_1 = *p*-$NO_2C_6H_4$) (85% yield), mp 84-86° (ethanol-water); ir: ν 3340 (NH), 3250 (NH), 2940 (CH), 1600 (C=C), 1360 (C-N) and 800 (*p*-C_6H_4) cm^{-1}; uv: (ethanol): λ max 210 and 384 nm; ^{1}H nmr: δ 8.00 (d, 2H, *p*-$NO_2C_6H_4$, 2 *ortho* H), 6.45 (d, 2H, *p*-$NO_2C_6H_4$, 2 *meta* H), 5.80 (bs, 1H, exchangeable, ArN*H*), 3.10 (t, 2H, ArNH-C*H*$_2$), 2.45 (t, 2H, CH_3NH-C*H*$_2$), 2.10 (s, 3H, CH_3), 1.85 (q, 2H, C-CH_2-C) and 1.60 (3, 1H, exchangeable, CH_3N*H*); ms: m/z 209 (M^+).

Anal. Calcd. for $C_{10}H_{15}N_3O_2$: C, 57.42; H, 7.18; N, 20.09. Found: C, 57.32; H, 7.29; N, 20.17.

N-Methyl-*N'*-phenyltrimethylenediamine **5** (Ar_1 = C_6H_5).

This compound was obtained by acid hydrolysis of **4** (Ar_1 = Ar_2 = C_6H_5) [1] according to the procedure described for the preparation of **5** (Ar_1 = *p*-$NO_2C_6H_4$). It was obtained as an oil (70% yield) and purified by column chromatography using chloroform-methanol (7:3) for elution; ir : ν 2340 (NH), 2270 (NH), 2890 (CH), 1610 (C=C), 1370 (C-N), 1310 (C-N) and 695 (C_6H_5) cm^{-1}; ^{1}H-nmr: δ 7.30-7.10 (m, 2H, N-C_6H_5, 2 *meta* H), 6.80-6.50 (m, 3H, N-C_6H_5, 2 *ortho* H and *para* H), 4.20 (bs, 1H, exchangeable, Ar-N*H*), 3.20 (t, 2H, ArNH-C*H*$_2$), 2.65 (t, 2H, CH_3NH-C*H*$_2$), 2.15 (s, 3H, CH_3) and 1.85 (m, 3H, 1H exchangeable, C-CH_2-C and N*H*-CH_3); ms: m/z 164 (M^+).

Anal. Calcd. for $C_{10}H_{16}N_2$: C, 73.17; H, 9.76; N, 17.07. Found: C, 73.06; H, 9.90; N, 17.20.

Reaction of 1,2-Diaryl-3-methyl-1,4,5,6-tetrahydropyrimidinium Iodides **1** with Alkaline Borohydrides.

Alkaline borohydride (sodium borohydride, potassium borohydride or sodium cyanoborohydride) (0.025 mole) was added during 5 minutes to a solution of the respective 1,4,5,6-tetrahydropyrimidinium salt **1a-h** (0.005 mole) in ethanol (40 ml) keeping the mixture at 0° for 30 minutes. When the evolution of gas had ceased (*ca.* 45-60 minutes), the solvent was removed *in vacuo* and water (40 ml) added to the residue. The suspension was extracted with three 10 ml portions of methylene chloride. The organic solution was washed with water, dried with anhydrous sodium sulfate and examined by tlc showing a single spot. The organic solvent was removed to give compounds **3a-h**, which were isolated as bases (95-100% yield) and characterized as dihydrochlorides. These salts were obtained dissolving the bases in anhydrous ethanol and precipitating with ethereal hydrogen chloride solution. The resulting solids (hygroscopic) were washed with anhydrous ether, crystallized from absolute ethanol-ether and dried under heated vacuum desiccator. Spectroscopic data of the bases, and melting points formula and elementary analyses of the hydrochlorides are given in Table I.

The structure of compounds **3** was confirmed by comparison with authentic samples obtained by reduction of the corresponding *N*-aroyl-*N'*-aryl-*N*-methyltrimethylenediamines **4** [1] with diborane, according to the procedure described by Brown and Heim [26].

When reaction of compounds **1** with an excess of alkaline borohydride as indicated above, was monitored at different times by tlc, only compounds **1** and **3** were detected. No further spot attributable to compounds **2** could be detected. Similar results were obtained when compounds **1** were treated with sodium borohydride supported on silica gel [23] or aluminum oxide [24] in chlo-

roform or methylene chloride, following the procedure described for the reduction of 1*H*-4,5-dihydroimidazolium salts [2].

Attempts to Obtain Hexahydropyrimidines **2f** and **2h** [6].

A.

Alkaline borohydride (sodium borohydride or cyanoborohydride) (0.0011 mole, fractionated in eight portions), was added during one hour to a solution of the salt **1f** (0.001 mole) in ethanol (10 ml), keeping the reaction mixture at −10°. The reaction was monitored by tlc on aluminum oxide (benzene-methanol, 9:1) [27]. When disappearance of **1f** (Rf *ca.* 0.6) was observed, the solvent was removed. Water was added to the residue and the suspension extracted with chloroform. The organic solution was washed, dried and the solvent evaporated *in vacuo* to give an oily residue with a noticeable odor of benzaldehyde. Analytical tlc showed the presence of three spots at Rf *ca.* 0.95, 0.10 and 0.0. The ^{1}H-nmr spectrum of the crude product showed characteristic signals at δ 10 (s, CHO), 5.80 (bs, exchangeable, NH) and 4.55 (s, CH). Separation of the three components was accomplished according to the following procedure: an aliquot of the crude product (40 mg) was chromatographed on neutral aluminum oxide preparative plates using benzene-methanol (9:1) as the developing solvent. Two bands were separated and eluted with methanol-dioxane (1:1). That of higher Rf afforded benzaldehyde. The other proved to be a mixture of two low Rf components that were separated by plc on cellulose plates using benzene-methanol (8:2) as the eluent. The slower moving band afforded 6 mg of a product that was identified as *N*-methyl-*N'*-(*p*-nitrophenyl)trimethylenediamine **5** (Ar_1 = p-$NO_2C_6H_4$) by comparison with an authentic sample obtained by hydrolysis of **4** (Ar_1 = p-$NO_2C_6H_4$, Ar_2 = C_6H_5). The second band afforded 4 mg of a product, presumably **2f**; ν 2940 (CH), 2860 (CH), 1600 (C=C), 1560 (C-NO_2), 1320 (C-N), 820 (p-C_6H_4) and 700 (C_6H_5) cm^{-1}; uv (ethanol): λ max 206 and 382 nm; ms: m/z 297 (M^+).

When the crude product obtained from **1f** as indicated above, was treated with an excess of sodium borohydride, the spot attributed to compound **2f** rapidly disappeared with the simultaneous detection of **3f**.

B.

Reaction of compound **1h** (0.001 mole) with sodium borohydride (0.0011 mole) following the same procedure as for compound **1f**, rendered a mixture of *p*-nitrobenzaldehyde, *N*-methyl-*N'*-phenyltrimethylenediamine **5** (Ar_1 = C_6H_5) and a third product **2h** which rapidly evolved into **3h**.

C.

Reaction of compound **1h** (0.005 mole) with sodium borohydride (0.006 mole) supported on silica gel [23] or aluminum oxide [24] rendered a mixture of roughly equal amounts of compounds **1h** and **3h** together with small amounts of a third product. Attempts to isolate this compound (presumably the hexahydropyrimidine **2h**) by plc were unsuccessful.

Reaction of 1,2-Diaryl-3-methyl-1,4,5,6-tetrahydropyrimidinium Iodides **1** with Lithium Aluminum Hydride.

Because of the low solubility of compounds **1** in THF (or other ethereal solvents) the reductions were carried out by means of a Soxhlet extractor arranged between the reaction flask, in which was placed the lithium aluminum hydride, and the reflux condenser [28]. Typical experiments are described:

A.

A suspension of lithium aluminum hydride (0.0012 mole) in dry THF (20 ml) was placed in the reaction flask and powdered compound **1a** (0.0010 mole) in the extractor thimble. The hydride solution was maintained at a moderate rate of boiling for 4 hours. The mixture was filtered, the organic solution concentrated *in vacuo* and the residue chromatographed on cellulose preparative plates using benzene-methanol (8:2) as developing solvent. The slower moving band afforded 7 mg of pure oily material, presumably **2a**; ir: ν 2920 (CH), 2830 (CH), 1605 (C=C), 1580 (C=C), 1380 (C-N), 1305 (C-N), and 705 (C_6H_5) cm^{-1}; ^{1}H-nmr: δ 7.60-7.00 (m, 7H, aromatics), 6.80-6.55 (m, 3H, C_6H_5-N, 2 *ortho* and *para* H), 5.25 (s, 1H, CH), 3.25-2.80 (m, 4H, CH_2-N), 2.55 (s, 3H, CH_3) and 2.10 (m, 2H, C-CH_2-C).

B.

The reaction was performed as described for the previous experiment, except that heating was prolonged until all the substance in the thimble had been carried into the reaction vessel (*ca.* 24 hours). Gentle refluxing was continued for 4 hours. The reaction mixture was cooled and cautiously treated with water, 10% sodium hydroxide and water, in succession [28]. The hydrolyzed material was concentrated *in vacuo* in dryness. An aliquot of the residue was analyzed by tlc showing the presence of compound **3a** as the main product. No traces of the assumed compound **2a** were detected. The crude product was purified by column chromatography affording **3a** (35% yield).

Reaction of 1,2-Diaryl-3-methyl-1,4,5,6-tetrahydropyrimidinium Iodides **1** with Borane.

Typical procedures are described:

A.

A suspension of powdered compound **1a** (0.001 mole) in THF (10 ml) constantly stirred under a dry nitrogen atmosphere, was treated with 1M solution of borane in THF (1.5 ml). The mixture was refluxed for 4 hours. During that lapse of time borane solution aliquots (0.75 ml) were added every 30 minutes in order to maintain a suitable concentration of reducing agent [29]. The reaction mixture was filtered to remove unchanged iodide. Evaporating of the solvent and heating the residue with a small volume of methanol to destroy borane complexes rendered a solution which showed the presence of three components. That of lower Rf value was isolated by plc on cellulose plates and showed chromatographic and spectroscopic (ir, ms) properties similar to those of the assumed compound **2a**.

B.

The reaction was performed as described for the previous experiment, except that heating was prolonged to ensure complete transformation of the salt (*ca.* 20 hours). The solution was worked up as was indicated above rendering a mixture of unidentifiable products.

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