Reduction of Substituted 1*H*-4,5-Dihydroimidazolium Salts [1]

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Reactions of several substituted 1*H*-4,5-dihydroimidazolium salts **1** with nucleophilic and electrophilic reducing agents acting *via* hydride transfer were explored. Reaction of compounds **1** with lithium aluminum hydride in THF afforded the corresponding imidazolidines **2**. When alkaline borohydrides (sodium borohydride, potassium borohydride, sodium cyanoborohydride) in ethanol at room temperature were used, partial or total over-reduction of compounds **2** leading to *N,N,N'*-trisubstituted ethylenediamines took place on occasion. Results may be explained taking into account that reductive cleavage of **2** proceeds *via* a stabilized iminium ion present in protic solvents. Treatment of compounds **1** with an excess of borane in THF afforded the corresponding imidazolidines **2** or their borane complexes, according to the substituent type.

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Introduction.

Isolated instances of reduction of the 1*H*-4,5-dihydroimidazolium salts **1** have been reported in the literature, giving rise to imidazolidines **2** [2-5] or their over-reduction products, that is, *N,N,N'*-trisubstituted ethylenediamines **3** [6] (Scheme I). However, there has been no systematic study on the influence of substituent type or on conditions affecting the course of the reaction.

In order to examine the potential reactive capacity of salts **1** as precursors of imidazolidines **2** [7] and to determine the scope of application of the reaction, we studied the reaction of compounds **1a-m** (Scheme I) with both nucleophilic and electrophilic reducing agents acting by means of hydride ion transfer.

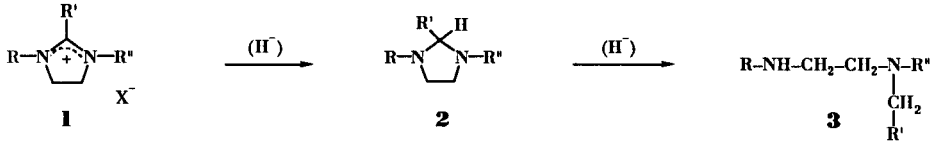
Results and Discussion.

The reaction of equimolecular amounts of compounds **1a-g** and **1i-m** with lithium aluminum hydride in tetrahydrofurane (THF) by refluxing for 1 hour led without exception to the corresponding imidazolidines **2** in excellent yields.

The structural assignments of compounds **2** were based on microanalyses, spectroscopic properties (Table I), and, in some cases, by comparison with authentic samples [17].

When salts **1** were treated with alkaline borohydrides (sodium borohydride, potassium borohydride, sodium cyanoborohydride) in ethanol at room temperature, imidazolidines **2** were invariably the first product obtained. However, in certain cases such as the **1a-e,g** compounds,

Scheme I

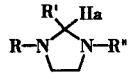


1 **2** **3**

1,2,3	R	R'	R"	X⁻
a	C_6H_5	C_6H_5	CH_3	I^-
b	*p*-CH_3-OC_6H_4	C_6H_5	CH_3	I^-
c	*p*-ClC_6H_4	C_6H_5	CH_3	I^-
d	*p*-$CH_3C_6H_4$	C_6H_5	CH_3	I^-
e	β-$C_{10}H_7$	C_6H_5	CH_3	I^-
f	C_6H_5	*p*-ClC_6H_4	CH_3	I^-
g	C_6H_5	p-$CH_3OC_6H_4$	CH_3	I^-
h	C_6H_5	*p*-$NO_2C_6H_4$	CH_3	I^-
i	C_6H_5	C_6H_5	C_6H_5	I^-
j	C_6H_5	H	C_6H_5	Cl^- or ClO_4^-
k	CH_3	C_6H_5	CH_3	I^-
l	*i*-C_3H_7	C_6H_5	CH_3	I^-
m	C_6H_5	CH_3	CH_3	I^-

Table I

Substituted Imidazolidines **2a-m**



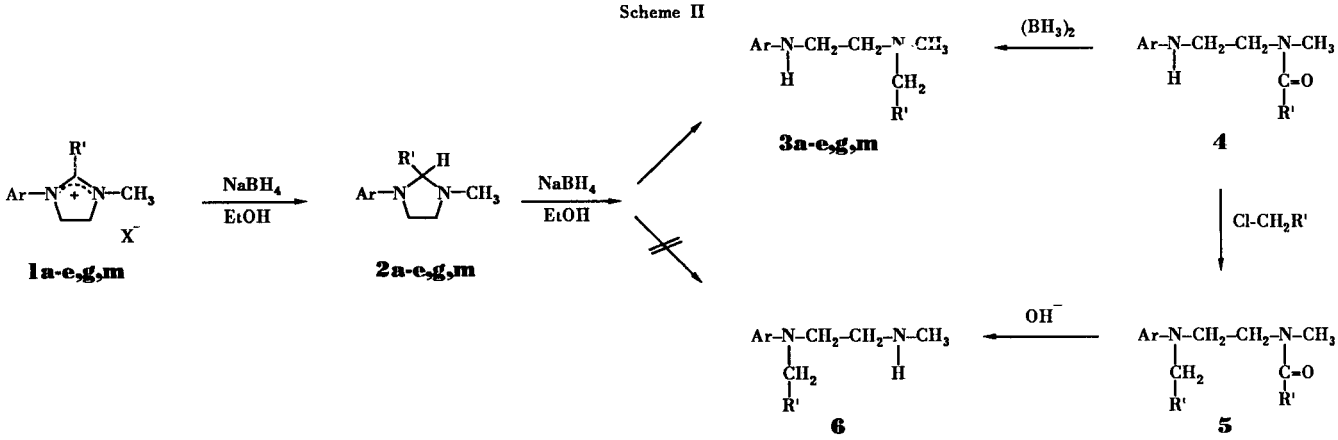
Compound No.	Mp (°C)	Recrystallization solvent	Previous Reference	Formula	Analyses Calcd./Found %C	%H	%N	IR ν (cm^{-1})		^{1}H NMR δ (ppm)	Multiplicity	Assignment
2a	64	ethanol		$C_{16}H_{18}N_2$	80.67	7.56	11.76	2930	(C-H)	7.42-6.40	m	aromatics
					80.62	7.65	11.73	2840	(C-H)	4.60	s	Ha
								1610	(C=C)	4.00-2.50	m	CH_2-CH_2
								1580	(C=C)	2.25	s	N-CH_3
								1330	(C-N)			
								940	imidazolidine			
								920	imidazolidine			
								750	(C_6H_5)			
2b	70	methanol		$C_{17}H_{20}N_2O$	76.12	7.46	10.45	2910		7.50-7.35	m	C_6H_5
					76.10	7.50	10.40	2830	(C-H)	6.90	d	CH_3O-C_6H_4-
								1610	(C-H)			(2 *ortho* H)
								1320	(C=C)	6.60	d	CH_3-C_6H_4-
								940	(C-N)			(2 *meta* H)
								935	imidazolidine			
									imidazolidine	4.62	s	Ha
										3.10-4.05	m	CH_2-CH_2
										2.50	s	N-CH_3
2c	89	methanol		$C_{16}H_{17}N_2Cl$	70.46	6.24	10.27	2900	(C-H)	7.25	s	C_6H_5
					76.54	6.29	10.21	2750	(C-H)	6.90	d	Cl-C_6H_4
								1600	(C=C)			(2 *ortho* H)
								1310	(C-N)	6.25	d	Cl-C_6H_4
								970	imidazolidine			(2 *meta* H)
								910	imidazolidine	4.45	s	Ha
								750	(C_6H_5)			
								790	(C-Cl)	4.00-2.50	m	CH_2CH_2
								720	(C_6H_5)	2.25	s	N-CH_3
2d	77	ethanol		$C_{17}H_{20}N_2$	80.95	7.93	11.21	2880	(C-H)	7.50	s	C_6H_5
					80.90	7.98	11.14	2720	(C-H)	7.20	d	CH_3-C_6H_4
								1620	(C=C)			(2 *ortho* H)
								1570	(C=C)	6.52	d	CH_3-C_6H_4
								1305	(C-N)			(2 *meta* H)
								940	imidazolidine	4.50	s	Ha
								910	imidazolidine	4.00-2.50	m	CH_2-CH_2
										2.20	s	N-CH_3
										2.10	s	Ar-CH_3
2e	134	methanol		$C_{20}H_{20}N_2$	83.33	6.94	9.72	2930	(C-H)	8.00-7.20	m	aromatics
					83.28	6.99	9.70	2850	(C-H)	4.83	s	Ha
								2770	(C-H)	4.03-2.72	m	CH_2-CH_2
								1620	(C=C)	2.45	s	N-CH_3
								1590	(C=C)			
								1325	(C-N)			
								940	imidazolidine			
								920	imidazolidine			
								740	(C_6H_5)			
2f	99			$C_{16}H_{17}N_2Cl$	70.46	6.24	10.27	2900	(C-H)	7.60-7.20	m	aromatics
					70.40	6.32	10.20	2750	(C-H)	6.61	dd	Cl-C_6H_4
								1610	(C=C)	4.70	s	Ha
								1600	(C=C)	4.00-2.60	m	CH_2-CH_2
								1330	(C-N)	2.25	s	N-CH_3
								910	imidazolidine			
								790	(C-Cl)			
								740	(C_6H_5)			

Table I(continued)

Compound No.	Mp (°C)	Recrystallization solvent	Previous Reference	Formula	Analyses Calcd./Found %C	%C	%N	IR ν (cm^{-1})		^{1}H NMR δ (ppm)	Multiplicity	Assignment
2g	[a]			$C_{17}H_{20}N_2O$	76.12	7.46	10.45	2910	(C-H)	7.60-6.10	m	aromatics
					76.00	7.53	10.40	2700	(C-H)	4.50	s	Ha
								1620	(C=C)	3.70	s	O-CH_3
								1590	(C=C)	3.80-2.30	m	CH_2-CH_2
								1300	(C-N)	2.20	s	N-CH_3
								930	imidazolidine			
								915	imidazolidine			
								720	(C_6H_5)			
2h	hygroscopic			$C_{16}H_{17}N_3O_2$	67.84	6.00	14.84	2950	(C-H)	8.00-6.70	m	aromatics
	[a]				67.70	6.20	14.70	2830	(C-H)	3.70	s	Ha
								1620	(C=C)	3.40-2.60	m	CH_2-CH_2
								1325	(C-N)	2.30	s	N-CH_3
								910	imidazolidine			
								920	imidazolidine			
								720	(C_6H_5)			
2i	137	ethanol	[13]					2940	(C-H)	7.50-6.50	m	aromatics
								2830	(C-H)	6.00	s	Ha
								1630	(C=C)	3.5-4.00	m	CH_2-CH_2
								1320	(C-N)			
								920	imidazolidine			
								910	imidazolidine			
								740	(C_6H_5)			
2j	125	methanol + water	[2] [14] [15]					2750	(C-H)	7.50-6.50	m	aromatics
								1620	(C=C)	4.70	s	N-CH_2-N
								1600	(C=C)	3.50	s	CH_2-CH_2
								1330	(C-N)			
								940	imidazolidine			
								910	imidazolidine			
								720	(C_6H_5)			
2k	oil		[16]					2800	(C-H)	7.40-7.20	m	aromatics
								2720	(C-H)	3.60-3.20	m	CH_2-CH_2
								1635	(C=C)	3.25	s	Ha
								1315	(C-N)	2.20	s	N-CH_3
								940	imidazolidine			
								925	imidazolidine			
								730	(C_6H_5)			
2l	oil			$C_{13}H_{20}N_2$	76.47	9.80	13.72	2800	(C-H)	6.70-6.25	m	C_6H_5
	[b]				76.40	9.90	13.80	2750	(C-H)	3.80	s	Ha
								1620	(C=C)	3.50-2.35	m	CH_2-CH_2 and
								1330	(C-N)			$HC(CH_3)_2$
								930	imidazolidine	2.20	s	N-CH_3
								920	imidazolidine	1.05	dd	$HC(CH_3)_2$
								720	(C_6H_5)			
2m	oil			$C_{11}H_{16}N_2$	75.00	9.03	15.91	2800	(C-H)	7.20-6.80	m	C_6H_5-N=
	[c]				75.20	9.15	15.98	2750	(C-H)			(2 *meta* H)
								1590	(C=C)	6.60-6.25	m	C_6H_5-N=
								1320	(C-N)			(*para* and 2
								1050	imidazolidine			*ortho* H)
								970	imidazolidine	4.20-3.00	m	CH_2-CH_2 and Ha
								710	(C_6H_5)	2.40	s	N-CH_3
										1.10	d	C-CH_3

[a] This compound could not be obtained as a solid sample. A pure sample was isolated by plc (benzene/methanol 9:1). [b] Bp 130-132° (760 mm) [17]. [c] Bp 143-145° (10 mm).

Scheme II

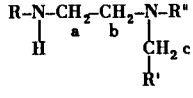


the alkaline borohydride cleaved the imidazolidine ring between C_2 and the N bearing the aryl radical, giving rise to a mixture consisting mainly of 1,2-diaryl-3-methylimidazolidines **2a-e,g** and *N'*-aryl-*N*-benzyl-*N*-methylethylenediamines **3a-e,g** (Scheme II). Over-reduction was completed in roughly 36 hours and the rate increases by heating.

Compounds **3** were characterized as picrates and their structure demonstrated on the basis of their spectroscopic properties (Table II), as well as by comparison with standard samples, obtained by reduction of the corresponding *N'*-aryl-*N*-benzoyl-*N*-methylethylenediamines **4** with borane in THF (Scheme II).

Table II

N,N,N'-Trisubstituted-ethylenediamines **3**



Compound No	Previous Reference	IR ν (cm^{-1})		δ (ppm)	^{1}H NMR Multiplicity	Assignment	Mp (°C) (ethanol)	Picrates Formula	Analyses Calcd./Found % C	%H	%N
3 a	[19]	3250	(C-H)	7.52-6.51	m	aromatics	116	$C_{28}H_{26}N_8O_{14}$	48.13	3.72	16.04
		2930	(C-H)	4.25	bs [a]	NH			48.30	3.85	16.20
		2830	(C-H)	3.60	s	CH_2 c					
		1620	(C=C)	3.25	t	CH_2 a					
		1305	(N-C)	2.72	t	CH_2 b					
		720	(C_6H_5)	2.30	s	CH_3					
3 b	[20]	3300	(N-H)	8.03	s	C_6H_5	140	$C_{29}H_{28}N_8O_{15}$	47.80	3.85	15.38
		2920	(C-H)	7.10	d	CH_3O-C_6H_5			47.75	3.55	15.20
		2820	(C-H)			(2 *ortho* H)					
		1620	(C=C)	6.90	d	CH_3 O-C_6H_5					
		1315	(C-N)			(2 *meta* H)					
		1210	(Ar-O-C)	4.35	bs [a]	NH					
		730	(C_6H_5)	3.92	s	O-CH_3					
				3.75	s	CH_2 c					
				3.32	t	CH_2 a					
				2.74	t	CH_2 b					
				2.3	s	N-CH_3					
3 c	[20]	3350	(N-H)	7.40	d	Cl-C_6H_4	158	$C_{28}H_{25}N_8O_{14}Cl$	45.87	3.41	15.29
		2820	(C-H)			(2 *ortho* H)			45.75	3.39	15.30
		2790	(C-H)	6.80	d	Cl-C_6H_4					
		1610	(C=C)			(2 *meta* H)					
		1305	(C-N)	4.50	bs [a]	NH					
		780	(C-Cl)	3.75	s	CH_2 c					
				3.32	t	CH_2a					
		720	(C_6H_5)	2.75	t	CH_2 b					
				2.30	s	N-CH_3					

Table II(continued)

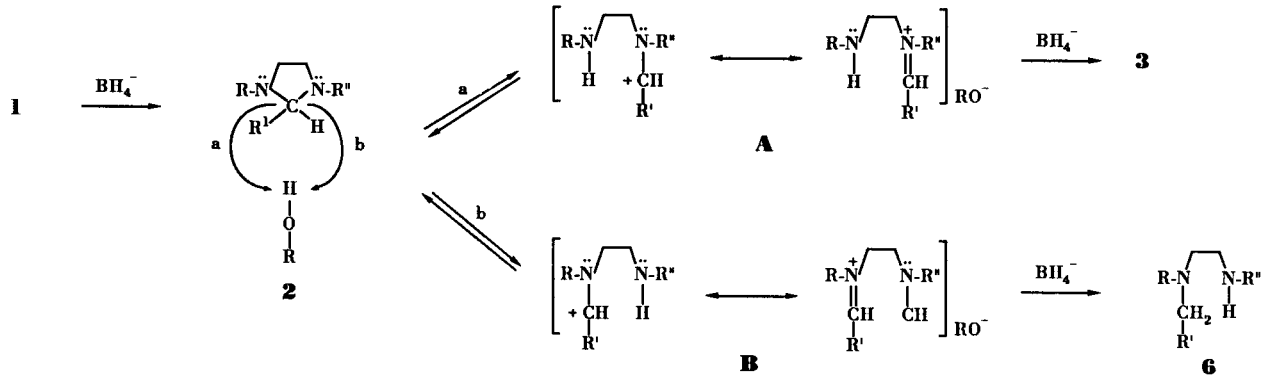
Compound No	Previous Reference	IR ν (cm^{-1})		^1H NMR δ (ppm)	Multiplicity	Assignment	Mp (°C) (ethanol)	Picrates Formula	Analyses Calcd./Found % C	%H	%N
3d		3400	(N-H)	7.62	s	aromatics	142	$C_{29}H_{28}N_8O_{14}$	48.88	3.93	15.73
		2920	(C-H)	7.30	d	CH_3-C_6H_4-			48.95	3.95	15.87
		2810	(C-H)			(2 *ortho* H)					
		1630	(C=C)	6.90	d	CH_3-C_6H_4					
		1315	(C-N)			(2 *meta* H)					
		760	(C_6H_5)	3.72	s	CH_2 c					
				3.50	bs [a] [b]	NH					
				3.33	t	CH_2 a					
				2.75	t	CH_2 b					
				2.32	s	N-CH_3					
				2.20	s	Ar-CH_3					
3e		3300	(N-H)	8.15-7.01	m	aromatics	168	$C_{32}H_{28}N_8O_{14}$	51.33	3.74	14.97
		2910	(C-H)	3.75	s	CH_2 c			51.47	3.89	15.05
		2850	(C-H)	3.41	t	CH_2 a					
		1620	(C=C)	3.30	bs [a] [b]	NH					
		1310	(C-N)	2.84	t	CH_2 b					
		720	(C_6H_5)	2.32	s	N-CH_3					
3g		3330	(N-H)	7.25-6.72	m	aromatics	147	$C_{29}H_{28}N_8O_{15}$	47.80	3.85	15.38
		2900	(C-H)	4.10	bs [a]	NH			47.90	3.93	15.22
		2830	(C-H)	3.82	s	O-CH_3					
		1620	(C=C)	3.51	s	CH_2c					
		1320	(C-N)	3.21	t	CH_2a					
		1215	(Ar-O-C)	2.60	t	CH_2b					
		725	(C_6H_5)	2.22	s	N-CH_3					
3k		3220	(N-H)	7.20	s	C_6H_5	155	$C_{23}H_{24}N_8O_{14}$	43.40	3.77	17.61
		2930	(C-H)	3.40	s	CH_2 c			43.30	3.85	17.77
		2850	(C-H)	2.80-2.52	m	CH_2a and					
		1610	(C=C)			CH_2 b					
		1320	(C-N)	2.30	s	N-CH_3 (ter-					
		730	(C_6H_5)			tiary amine)					
				2.10	s	N-CH_3 (secon-					
						dary amine)					
				2.08	s [a]	NH					
3m	[21,22]	3260	(N-H)	2.80-2.40	m	CH_2a, CH_2 b	127				[22]
		2930	(C-H)			and CH_2 c					
		2840	(C-H)	2.20	s	N-CH_3(ter-					
		1610	(C=C)			tiary amine)					
		1330	(C-N)	2.05	s	N-CH_3 (secon-					
		720	(C_6H_5)			dary amine)					
				1.95	s	NH					
				1.1	t	CH_3-C					

[a] Exchangeable. [b] Partially overlapped with the triplet.

Reductive cleavage of 1,2-diaryl-3-methylimidazolidines in no case led to *N*-aryl-*N*-benzyl-*N'*-methylethylenediamines **6**. In order to confirm the latter finding, *N*-benzyl-*N'*-methyl-*N*-phenylethylenediamine **6** (Ar = R' = C_6H_5) was synthesized by an unambiguous route starting from **4** (Scheme II).

When reaction of **1k** and **1m** with alkaline borohydrides were performed, the reaction products, **2k** and **2m**, could only be detected by tlc. Due to the fact that reductive cleavage of the imidazolidine ring took place rapidly, the only products isolated were **3k** and **3m** respectively. Likewise, compound **11** gave rise to a mixture of two isomers in roughly the same yield, presumably **31** and *N*-benzyl-*N*-isopropyl-*N'*-methylethylenediamine **6** (R = *i*-C_3H_7, R' = C_6H_5, R'' = CH_3, Scheme III).

Scheme III



Taken together, these results may be explained bearing in mind the mechanism advanced for reductive cleavage of imidazolidines and other cyclic aminals [23-25]. Thus, in analogy with other compounds having the =N-C(R)H-N= structural unit [26], reductive cleavage proceeds *via* a stabilized iminium ion (Scheme III), so that electron availability at the nitrogen atoms and the substituent type at C-2 should influence the ease of over-reduction and therefore the nature of the products obtained. Accordingly, the low electron density at the nitrogen atoms when R and/or R'' is Ar, explains the following facts: (a) over-reduction of 1,2-diaryl-3-methylimidazolidines **2a-e,g** and 1-aryl-2,3-dimethylimidazolidine **2m** (R = Ar, R'' = alkyl) led solely to the corresponding compounds **3**, indicating that the reaction proceeds by preferential elimination of the less basic amine and the formation of the more stable iminium cation **A** (Scheme III) [26,27]. Similar results are observed in the borohydride reduction of 5,10-methylenetetrahydrofolic acid [29] and of compounds employed as its models [30]. Destabilization of the iminium ion in the presence of an electron-aceptor group at the C-2 aryl radical, such as *p*-NO_2 or *p*-Cl, explains why imidazolidines **2f** and **2h** fail to undergo ring cleavage under such experimental conditions. (b) 1,2-Diarylimidazolidines **2i** and **2j** (R = R'' = Ar) proved stable in the reducing medium.

In contrast, the high electron density at the two nitrogen atoms, when R and R'' are alkyl radicals, explains why compounds **2k** and **2l** were rapidly over-reduced, and that **2l** yielded a mixture of two isomeric *N,N,N'*-trisubstituted ethylenediamines [31], presumably *via* the iminium ions **A** and **B**, similar in stability (Scheme III).

Since in the proposed mechanism (Scheme III) the hydroxylic solvent plays a leading role in the heterocyclic cleavage of the C-N linkage, the nature of the solvent must by essential for the reaction. Therefore, in order to avoid reductive cleavage of compounds **2a-e,g**, reduction of salts **1a-e,g** was carried out employing sodium borohydride supported on silica gel [33] in a non-hydroxylic solvent such as chloroform or dichloromethane, allowing cyclic aminals **2** to be obtained in good yields. However, when sodium borohydride/aluminum oxide is used [34], a mixture of compounds **2** and **3** was again obtained.

Treatment of the 1,3-diaryl-1*H*-4,5-dihydroimidazolium salts **2i,j** with an excess of borane led to the corresponding imidazolidines in excellent yields. The remainder of the salts gave rise mainly to boron hydride/imidazolidine complexes, with only small amounts of the over-reduction product. These results contrast with those described by Northrop and Russ [35], who reported that imidazolidine cleavage with borane in a 1:1-1.75 molar ratio took place readily. Most likely the formation of imidazolidine complexes on employing an excess of borane in our present work prevented over-reduction [36]. Attempts to destroy such complexes by traditional methods resulted in total hydrolytic or partial reductive cleavage of the imidazolidines.

EXPERIMENTAL

Melting points were taken on a Büchi capillary apparatus and are uncorrected. The ir spectra were recorded on a Beckman 180 A spectrometer. Samples were run as potassium bromide pellets for solids and films for oils. The ^1H nmr spectra were obtained on a Varian FT 80 A spectrometer using deuteriochloroform as 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), m (multiplet) and bs (broad signal). The presence of exchangeable protons was confirmed by use of deuterium oxide. 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} using benzene-methanol (9:1) as the solvent. Column chromatography was carried out on Silica Gel 60 (70-325 mesh). Reagents, solvents and starting materials were purchased from standard sources and purified according to literature procedures.

N-Acyl-*N'*-arylethylenediamines.

The title compounds used as precursors of 1,2-disubstituted 1*H*-4,5-dihydroimidazoles, were prepared from the appropriated

N-(2-bromoethyl)carboxamide and arylamines by the method of Perillo *et al.* [40]. The physical data and elemental analyses of new compounds are as follows:

N-Benzoyl-*N'*-(*p*-tolyl)ethylenediamine.

This compound had mp 130° (ethanol); ^{1}H nmr: δ 8.15-6.50 (m, 10H, aromatics and CO-NH), 4.05-3.20 (m, 5H, CH_2-CH_2-NH) and 2.3 (s, 3H, CH_3).

Anal. Calcd. for $C_{16}H_{18}N_2O$: C, 75.59; H, 7.08; N, 11.02. Found: C, 75.43; H, 7.20; N, 11.10.

N-*p*-(Chlorobenzoyl)-*N'*-phenylethylenediamine.

This compound had mp 140° (methanol); ^{1}H nmr: δ 8.20-6.45 (m, 10H, aromatics and CONH) and 4.10-3.35 (m, 5H, CH_2-CH_2-NH).

Anal. Calcd. for $C_{15}H_{15}N_2OCl$: C, 65.57; H, 5.46; N, 10.20; Cl, 12.93. Found: C, 65.49; H, 5.60; N, 10.25; Cl, 12.99.

N-Acetyl-*N'*-phenylethylenediamine.

This compound was obtained as an oil and was purified by column chromatography eluting with chloroform-methanol (9:1); ^{1}H nmr: δ 8.05 (bs, 1H, exchangeable, CONH), 7.15-6.90 (m, 2H, C_6H_5-NH, 2 *meta* H), 6.65-6.45 (m, 3H, C_6H_5-NH, 2 *ortho* H and *para* H), 4.10-3.55 (m, 5H, CH_2-CH_2-NH) and 2.10 (s, 3H, CH_3).

Anal. Calcd. for $C_{10}H_{14}N_2O$: C, 67.41; H, 7.86; N, 15.73. Found: C, 67.53; H, 7.98; N, 15.80.

1,2-Disubstituted 1*H*-4,5-Dihydroimidazoles.

The title compounds were used as precursors of 1*H*-4,5-dihydroimidazolium salts **1d**, **1f**, **1e** and **1m**.

2-Phenyl-1-(*p*-tolyl)-1*H*-4,5-dihydroimidazole (lit [41]).

This compound was prepared by ring closure of *N*-benzoyl-*N'*-(*p*-tolyl)ethylenediamine with PPE following the method of Perillo *et al.* [40]. It was used without further purification. An analytical sample was obtained by column chromatography; ^{1}H nmr: δ 7.35-6.75 (m, 9H, aromatics), 4.00-3.50 (m, 4H, CH_2-CH_2) and 3.20 (s, 3H, CH_3).

Anal. Calcd. for $C_{16}H_{16}N_2$: C, 81.35; H, 6.78; N, 11.86. Found: C, 81.44; H, 6.85; N, 11.86.

2-(*p*-Chlorophenyl)-1-phenyl-1*H*-4,5-dihydroimidazole.

This compound was prepared by ring closure of *N*-(*p*-chlorobenzoyl)-*N'*-phenylethylenediamine with PPE following the method of Perillo *et al.* [40]. This compound was obtained as an oil; ^{1}H nmr: δ 7.70-7.30 (dd, 4H, Cl-C_6H_4), 7.10-6.90 (m, 2H, C_6H_5-N=, 2 *meta* H), 6.75-6.50 (m, 3H, C_6H_5-N=, 2 *ortho* and *para* H) and 3.75-3.25 (m, 4H, CH_2-CH_2); ms: m/z 256 (M+). The base was analyzed as picrate, mp 140° (ethanol).

Anal. Calcd. for $C_{21}H_{16}N_5O_7Cl$: C, 51.90; H, 3.29; N, 14.42; Cl, 7.31. Found: C, 51.80; H, 3.40; N, 14.37; Cl, 7.38.

1-Isopropyl-2-phenyl-1*H*-4,5-dihydroimidazole.

This compound was synthesized from *N*-isopropylethylenediamine [18] and benzimidic acid methyl ester hydrochloride according to Hill's method [42]. The crude product was purified by column chromatography eluting with benzene-methanol (9:1). Appropriate fractions were pooled and evaporated to dryness to afford 40% of pure oily material; ^{1}H nmr: δ 7.50-7.20 (m, 5H, C_6H_5), 4.00-3.25 (m, 5H, CH_2-CH_2 and CH) and 1.02 (d, 6H, CH_3); ms: m/z 188 (M+).

Anal. Calcd. for $C_{12}H_{16}N_2$: C, 76.59; H, 8.51; N, 14.89. Found: C, 76.68; H, 8.64; N, 14.95.

1-Phenyl-2-methyl-1*H*-4,5-dihydroimidazole (lit [43,44]).

This compound was prepared by ring closure of *N*-acetyl-*N'*-phenylethylenediamine with PPE following the method of Perillo *et al.* [40]. It was obtained as an oil and was purified as the preceding compound; ^{1}H nmr: δ 7.40-7.10 (m, 2H, C_6H_5-N=, 2 *meta* H), 6.90-6.45 (m, 3H, C_6H_5-N=, 2 *ortho* and *para* H), 3.90 (s, 4H, CH_2-CH_2) and 2.15 (s, 3H, CH_3); ms: m/z 160 (M+).

Anal. Calcd. for $C_{10}H_{12}N_2$: C, 75.00; H, 7.50; N, 17.50. Found: C, 75.10; H, 7.62; N, 17.41.

1*H*-4,5-Dihydroimidazolium Salts **1**.

Compounds **1a** [45], **1b,c,e,g,h** [1], **1i** [46], **1j** [47] and **1k** [48] were prepared following literature methods.

Compounds **1d**, **1f**, **1e** and **1m** were obtained by treatment of the corresponding 1,2-disubstituted 1*H*-4,5-dihydroimidazole with methyl iodide according to our method [1]. The physical data and elemental analyses of new compounds are as follows:

1-Methyl-2-phenyl-3-(*p*-tolyl)-1*H*-4,5-dihydroimidazolium Iodide (**1d**).

This compound had mp 148° (2-propanol); ^{1}H nmr: δ 7.60-6.75 (m, 9H, aromatics), 4.4 (s, 4H, CH_2-CH_2), 3.15 (s, 3H, N-CH_3) and 2.10 (s, 3H, CH_3-Ar).

Anal. Calcd. for $C_{17}H_{19}N_2I$: C, 53.97; H, 5.02; N, 7.40. Found: C, 54.08; H, 5.15; N, 7.50.

2-(*p*-Chlorophenyl)-1-methyl-3-phenyl-1*H*-4,5-dihydroimidazolium Iodide (**1f**).

This compound had mp 198° (2-propanol); ^{1}H nmr: δ 7.70-7.10 (m, 9H, aromatics), 4.60-4.30 (m, 4H, CH_2-CH_2) and 3.25 (s, 3H, CH_3).

Anal. Calcd. for $C_{16}H_{16}N_2ClI$: C, 48.18; H, 4.01; N, 7.02; Cl, 8.90. Found: C, 48.10; H, 4.19; N, 7.12; Cl, 8.96.

1-Isopropyl-3-methyl-2-phenyl-1*H*-4,5-dihydroimidazolium Iodide (**1l**).

This compound had mp 75° (2-propanol); ^{1}H nmr: δ 7.50-7.20 (m, 5H, C_6H_5), 4.40-4.15 (m, 4H, CH_2-CH_2), 3.60 (symmetric m, 1H, CH), 2.80 (s, 3H, CH_3-N) and 1.25 (d, 6H, CH_3-C).

Anal. Calcd. for $C_{13}H_{19}N_2I$: C, 47.27; H, 5.76; N, 8.48. Found: C, 47.36; H, 5.86; N, 8.53.

1,2-Dimethyl-3-phenyl-1*H*-4,5-dihydroimidazolium Iodide (**1m**).

This compound had mp 68° (anhydrous 2-propanol); ^{1}H nmr: δ 7.60-7.20 (m, 5H, C_6H_5), 4.30 (s, 4H, CH_2-CH_2), 3.25 (s, 3H, CH_3-N) and 2.25 (s, 3H, CH_3-C).

Anal. Calcd. for $C_{11}H_{15}N_2I$: C, 43.70; H, 4.96; N, 9.27. Found: C, 43.78; H, 5.05; N, 9.37.

Reaction of 1*H*-4,5-Dihydroimidazolium Salts **1** with Lithium Aluminum Hydride. General Procedure.

To a suspension of 1*H*-4,5-dihydroimidazolium salts **1a-g,i-m** (0.03 mole) in dry THF (40 ml), lithium aluminum hydride (0.03 mole) was added. The mixture was refluxed for 1 hour and then filtered. The organic solution was concentrated *in vacuo* affording imidazolidines **2a-g**, **i-m**. Melting points, recrystallization solvents, elemental analyses and spectroscopic data of the compounds are given in Table I. Structures were confirmed by comparison with authentic samples [17].

N'-Aryl-*N*-benzyl-*N*-methylethylenediamines **3a-e,g**.

These compounds were obtained by reduction of the corresponding *N'*-aryl-*N*-benzoyl-*N*-methylethylenediamines **4** [1] with diborane according to the procedure described by Brown and Heim [49]. The ir and ^{1}H nmr of the bases, melting points and elemental analyses of the picrates are given in Table II.

N-Benzyl-*N'*-methyl-*N*-phenylethylenediamine **6** (Ar = R' = C_6H_5).

A mixture of *N*-benzoyl-*N*-methyl-*N'*-phenylethylenediamine **4** (Ar = R' = C_6H_5) [50] (0.01 mole) and benzyl chloride (0.011 mole) in ethanol (30 ml) was refluxed and the reaction monitored by tlc. When reactants were no longer detectable (*ca.* within 4 hours), the solvent was removed *in vacuo* and the crude product purified by column chromatography using chloroform:methanol (9:1) as the eluent. Removal solvent of the main fraction furnished *N*-benzoyl-*N'*-benzyl-*N*-methyl-*N'*-phenylethylenediamine **5** (Ar = R' = C_6H_5) (35% yield); ^{1}H nmr: δ 7.70-6.75 (m, 15H, aromatics), 4.00-3.25 (m, 6H, CH_2-CH_2 and Ar-CH_2) and 2.90 (s, 3H, CH_3); ms: m/z 344 (M+).

A mixture of **5** (Ar = R' = C_6H_5) (400 mg) in ethanol (10 ml) and 10% sodium hydroxide (5 ml) was refluxed for 4 hours. After cooling, the mixture was extracted with methylene chloride and the organic layer washed with water, dried and concentrated *in vacuo*. The residue was purified by chromatography and eluted with benzene-methanol (7:3) to give *N*-benzyl-*N'*-methyl-*N*-phenylethylenediamine **6** (Ar = R' = C_6H_5) (28% yield) as a colorless oil; Rf 0.24 (chloroform-methanol, 9:1); ^{1}H nmr: δ 7.30-6.55 (m, 10H, aromatics), 3.75-3.55 (m, 4H, CH_2-N-CH_2), 2.6 (t, 2H, CH_2-NH), 2.10 (s, 3H, CH_3) and 1.5 (s, 1H, exchangeable, NH); ms: m/z 240 (M+).

Reaction of 1*H*-4,5-Dihydroimidazolium Salts **1** with Alkaline Borohydrides.

Alkaline borohydride (sodium borohydride, potassium borohydride or sodium cyanoborohydride) (0.05 mole) was added during 5 minutes to a solution of the respective 1*H*-4,5-dihydroimidazolium salt **1a-m** (0.01 mole) in ethanol (20 ml) keeping the mixture at room temperature for one hour. The solvent was then removed *in vacuo* and water (50 ml) added to the residue. The suspension was extracted with three 10 ml portions of chloroform. The organic layer was decanted, washed, dried and then examined by tlc using chloroform-methanol (9:1) as solvent.

Solutions obtained from compounds **1f,h-j** showed a single spot which was identified as the corresponding imidazolidine [17]. Solvent removal afforded compounds **2f,h-j** (Table I).

The organic solutions obtained from compounds **1k** and **1m** showed single low Rf spots. Reaction product of compound **1k** failed to absorb at 254 nm and was developed by iodine vapours. Solvent removal afforded **3k** and **3m** which were isolated as bases and characterized as picrates (Table II). Likewise, compound **1l** rendered an oil which on being developed with iodine proved to be a mixture of two low Rf components whose separation was achieved by column chromatography using 7:3 benzene-methanol as the eluent; ms: m/z 206 (M+) for both compounds. Immediately after completing borohydride addition, organic solutions from compounds **1k-m** yielded detectable amounts of the corresponding imidazolidines **2k-m** [17] which rapidly evolved into the final reaction products.

Organic solutions from borohydride reaction with compounds **1a-e,g** showed the presence of three spots identified by comparison with standard samples: the one of greatest Rf (*ca.* 0.9) as the imidazolidene/boron hydride complex [51,52]; the one of least Rf (*ca.* 0.6) as *N'*-aryl-*N*-benzyl-*N*-methylethylenediamine **3a-e,g** (Table II); and the one of intermediate Rf (*ca.* 0.8) as the corresponding imidazolidine [17] (Table I).

In the case of the reaction involving compounds **1c**, the boron hydride/**2c** complex was isolated after evaporating the solvent and treating the residue with a small volume of methanol; its melting point was 145°; ir: 2910 (C-H), 2830 (C-H), 2320 (B-H), 1600 (C=C), 1320 (C-N), 970 (imidazolidine) and 930 cm^{-1} (imidazolidine).

Anal. Calcd. for $C_{16}H_{20}N_2BCl$: C, 67.13; H, 6.99; N, 9.79. Found: C, 67.35; H, 7.20; N, 9.95.

In the solution obtained from compound **1a** there were no traces of *N*-benzyl-*N'*-methyl-*N*-phenylethylenediamine **6** (Ar = R' = C_6H_5) (Rf 0.24), chloroform-methanol (9:1). In solutions from remaining compounds no further spot attributable to compounds **6** could be detected.

Treatment of compounds **1a-e,g** with alkaline borohydrides for 36 hours at room temperature or refluxing for 3 hours rendered solely compounds **3a-e,g**, which were isolated as bases and characterized as picrates (Table II).

Reaction of 1*H*-4,5-Dihydroimidazolium Salts **1** with Sodium Borohydride Supported on Silica Gel. General Procedure.

In a stirred solution of compounds **1a-e,g** (0.01 mole) in anhydrous methylene chloride (30 ml), sodium borohydride supported on silica gel (3 g) [33] was added in two portions at 10 minute intervals. Stirring was continued at room temperature for several hours and the reaction followed by tlc. When transformation **1** → **2** was achieved the reagent was filtered, washed with methylene chloride and the filtrate evaporated to dryness, affording imidazolidines **2**.

When the reaction was performed with sodium borohydride supported on alumina [34] a mixture of compounds **2** and **3** was obtained.

Reaction of 1*H*-4,5-Dihydroimidazolium Salts **1** with Borane.

1*H*-4,5-Dihydroimidazolium salts **2a-g,i-m** (0.001 mole) was rapidly added as a solid, to a 2.15 *M* solution of borane in THF (10 ml) [56] magnetically stirred at 0° under a dry nitrogen atmosphere. The cooling bath was then removed and stirring continued for 3 hours. The solution mixture was examined by tlc.

Solutions obtained from compounds **1i** and **1j** showed the sole presence of the corresponding imidazolidines **2i** and **2j**, which were isolated by solvent removal in a 90-95% yield.

Solutions from remaining salts showed the presence of the corresponding imidazolidine borane complex [51] as the main product. Evaporating the solvent and heating the residue with methanol or water to destroy the complex rendered a mixture of roughly equal amounts of the corresponding compounds **2** and **3**. Alternatively, the residue obtained from reduction with borane was treated with an excess of aqueous hydrochloric acid and extracted with a small volume of chloroform to eliminate non-basic products. The resulting acid solution was alkalinized and extracted with chloroform. The organic solution was washed, dried and examined by tlc, showing the presence of the corresponding *N,N'*-disubstituted ethylenediamine as the main product, together with small amounts of compounds **3** [57].

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Anal. Calcd. for $C_6H_{16}N_2$: C, 62.07; H, 13.79; N, 24.14. Found: C, 62.25; H, 13.92; N, 24.01.

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