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1*H*-4,5-Dihydroimidazolium salts **1** react readily with nucleophilic reagents originating cyclic products which may be stable or become transformed into acyclic compounds maintaining the structural ethylenediamine unit. With methylmagnesium iodide compound **1e** affords the expected imidazolidine, but in the case of substituted 1-aryl-3-methyl-2-phenyl salts **1b-d** the *N*-aryl-*N'*-methylethylenediamines **3b-d** and acetophenone (**4**) were isolated, the process representing the transfer of the C-2 unit to a nucleophilic carbon. With alkaline cyanides salts **1** react efficiently affording α,α -diaminonitriles **5**. In these compounds the cyano group may be readily substituted by nucleophiles (hydroxyl anion, species with nucleophilic carbon and reagents that act by hydride ion transfer), in a way similar to the salts but with better yields.

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The reaction of compounds **1** with aliphatic or arylalkyl amines probably involves decomposition of an intermediate orthoamide to yield, through the expulsion of the more basic amine, a benzimidoyl derivative (presumably *N*-aryl-*N*-(*N*-alkylbenzimidoyl)-*N'*-methylethylenediamines resulting from kinetic control detected by chromatography and spectroscopy. They then isomerize to the thermodynamically more stable *N*-(*N*-alkylbenzimidoyl)-*N'*-aryl-*N*-methylethylenediamines **9**.

Introduction.

1*H*-4,5-Dihydroimidazolium salts with different types of substitution have been used as suitable models of the coenzyme *N*⁵,*N*¹⁰-methenyltetrahydrofolic acid promoting biochemical transfer of one carbon unit at the oxidation level of formic acid [1-3]. Thus, in attempts to mimic the biological process chemically reproducing the transfer of C-2, the reactions of various models with suitable nucleophilic reagents have been studied [4-13]. By analogy with the natural cofactor, in which the transferable carbon is linked to two nitrogen atoms with dissimilar electronic features [14], the results on asymmetrically *N*-substituted salts are noteworthy, particularly the reports of Pandit on 1-methyl-3-tosyl or acetyl derivatives [4,5], those of Saunders on 1-benzyl-3-methyl derivatives [6,7] and those of Benkovic on a complex imidazolinium salt derived from a tetrahydroquinoxaline analog model of the natural cofactor [8-10].

Furthermore, the value of 1*H*-4,5-dihydroimidazolium salts as synthetic precursors has been demonstrated [6,7,15-18]. In this connection, as part of our studies on substituted 1,2-diaryl-3-methyl salts we have reported that alkaline hydrolysis under conditions of kinetic control leads to *N*-aroyl-*N*-aryl-*N'*-methylethylenediamines which in neutral or alkaline media rearrange giving stable *N*-aroyl-*N'*-aryl-*N*-methylethylenediamines, compounds **6** (see below) [15-17]. On the other hand, the reaction with reducing agents acting *via* hydride transfer leads to imidazolidines or

N,N,N'-trisubstituted ethylenediamines, compounds **7** and **8** (see below), depending on the type of reagent and on the substituents on the heterocyclic ring [18].

In order to provide an in depth study on such type of salts and to explore their usefulness as synthetic tools to obtain cyclic and acyclic compounds having the structural ethylenediamine unit (>*N*-CH₂-CH₂-*N*<), we have examined the reactions of a series of asymmetric 1,2-diaryl-3-methyl-1*H*-4,5-dihydroimidazolium salts **1a-d**, as well as the symmetric 1,3-diphenyl counterpart **1e** (Table I) with diverse nucleophilic reagents.

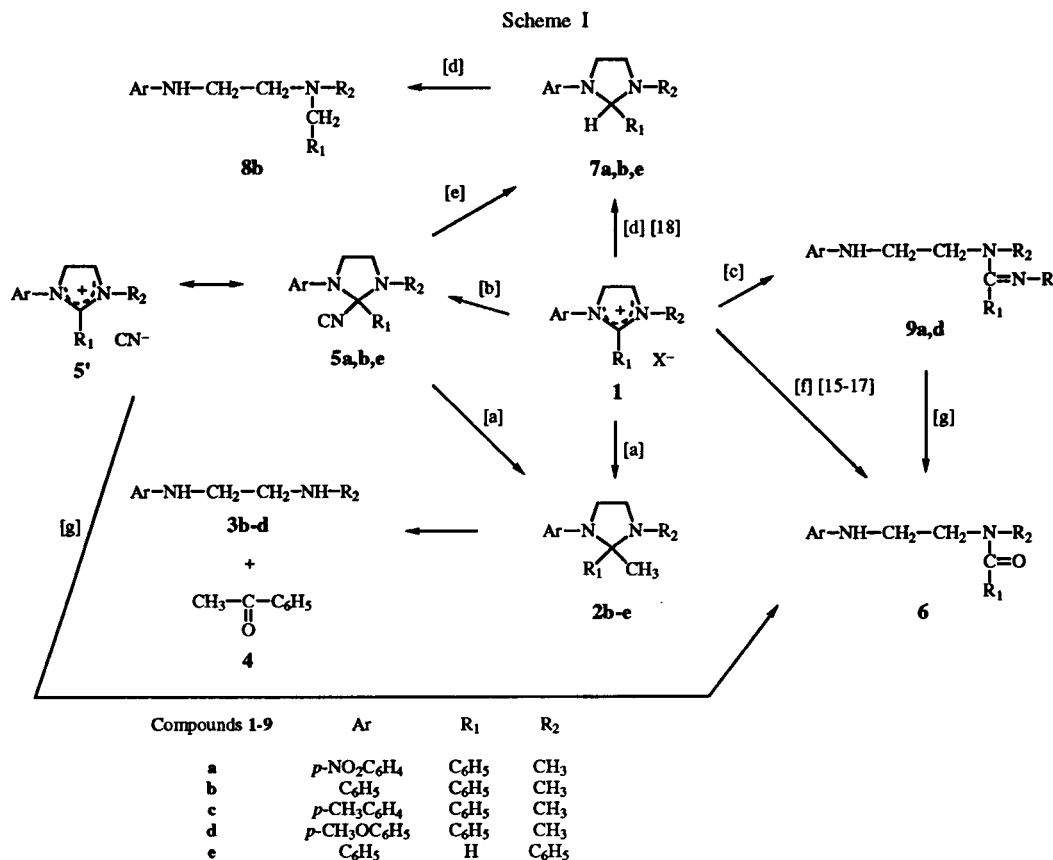
Table I
1*H*-4,5-Dihydroimidazolium Salts

Compound	Ar	R ₁	R ₂	X ⁻
1a	<i>p</i> -NO ₂ C ₆ H ₄	C ₆ H ₅	CH ₃	I ⁻
1b	C ₆ H ₅	C ₆ H ₅	CH ₃	I ⁻
1c	<i>p</i> -CH ₃ C ₆ H ₄	C ₆ H ₅	CH ₃	I ⁻
1d	<i>p</i> -CH ₃ OC ₆ H ₄	C ₆ H ₅	CH ₃	I ⁻
1e	C ₆ H ₅	H	C ₆ H ₅	Cl ⁻

Results and Discussion.

Reactions of salts **1a-e** with Grignard reagents, potassium cyanide and amines are presented in Scheme I.

The reaction of a suspension of salts **1b-d** with methylmagnesium iodide in tetrahydrofuran leads in all cases to a first product presumed to be the 2,2-disubstituted imidazolidines **2b-d**, the one which was detected but could not be isolated. Work-up of the reactions leads with fair yields to *N*-aryl-*N'*-methylethylenediamines **3b-d** and acetophenone (**4**), the process representing the transfer of a phenyl substituted one-carbon unit from the salt to a reagent with a nucleophilic carbon. As secondary products, small quantities of the corresponding 1,2-diaryl-1*H*-4,5-dihydroimidazoles



[a] CH₃MgI/THF; [b] KCN; [c] R-NH₂ (R = *i*-C₃H₇, CH₂-C₆H₅); [d] NaBH₄/EtOH; [e] LiAlH₄/THF or NaBH₄/silica gel (CHCl₃) or EtOH; [f] NaOH/H₂O; [g] H₂O.

(demethylated product) are obtained, resulting from methyl activation in the course of S_N2 displacements. From the reaction of 1e with methylmagnesium iodide, the expected 1,3-diphenyl-2-methylimidazolidine (2e) was isolated.

The behavior of salts 1 with alkaline cyanides was studied using as substrate compounds 1a,b,e. The reaction of nitrophenyl derivative 1a with potassium cyanide in anhydrous ethanol at room temperature afforded a yellow solid that crystallized in the reaction medium and to which the structure of the α,α-diaminonitrile 5a was assigned by elemental analysis and spectroscopic data. On the other hand, in the case of the salts 1b and 1e, *N*-benzoyl-*N*'-methyl-*N*'-phenylethylenediamine (6b) and *N*-formyl-*N*,*N*'-diphenylethylenediamine (6e) alone, respectively, were obtained under the same conditions. These products may have originated by alkaline hydrolysis of the starting salt or else from the expected products 5b,e as a result of the alkaline medium generated by the relatively basic nature of the cyanide and traces of moisture which was difficult to eliminate from the reaction medium. In order to avoid hydrolytic processes, the reaction was carried out using potassium cyanide adsorbed on aluminum oxide [19,20] in a non-hydroxylic solvent (anhydrous methylene chloride). Under these conditions products 5b and 5e

were obtained. Good results were also achieved by rapidly agitating a solution of the salt in a mixture of water and ether, in order to extract the products 5 as soon as they were formed. This would indicate that hydrolysis occurs preferably on the reaction product.

The uv spectral study of 5a indicates that its structure varies according to the nature of the solvent (Table II). In non-polar or poorly polar solvents, the compound appears to have predominantly the covalent structure proposed for 5. Thus, in solvents such as *n*-hexane, carbon tetrachloride, benzene and even chloroform and tetrahydrofuran, absorptions are similar to those of *N*-methyl-*N*'-(*p*-nitrophenyl)-ethylenediamine (3a) and 1-methyl-2-phenyl-3-(*p*-nitrophenyl)imidazolidine (7a), which absorb at a wavelength close to the visible range (λ *ca.* 350 nm) due to the presence of the *p*-nitroaniline moiety (Table II). In protic polar solvents, the presence of a maximum at about 300 nm coincides with salt 1a and discloses its strong ionic character. Since only a single species is detected by chromatography, the cyano product may be considered as a hybrid resonating between limiting covalent 5 and ionic 5' structures. In terms of valence bonds, the contribution of the ionic structure is responsible for the different degree of ionic character of the C-CN bond and would be consistent with the increase in

Table II
UV Spectroscopy Data for Compounds 1a, 3a, 5a and 7a in Different Solvents

Compound	Solvents (Dielectric Constant)													
	<i>n</i> -hexane		carbon tetrachloride		benzene		chloroform		1-butanol		methanol		water	
	(D = 1.89)		(D = 2.24)		(D = 2.28)		(D = 4.80)		(D = 17.80)		(D = 33.0)		(D = 39.0)	
	λ_{max}	log ϵ	λ_{max}	log ϵ	λ_{max}	log ϵ	λ_{max}	log ϵ	λ_{max}	log ϵ	λ_{max}	log ϵ	λ_{max}	log ϵ
	(nm)		(nm)		(nm)		(nm)		(nm)		(nm)		(nm)	
5a	[a]		348	3.95	352	4.17	356	4.30	295	4.03	295	4.03	[b]	
1a	[a]		[a]		[a]		300	4.13	304	4.13	309	3.98	318	4.10
3a [15]	[a]		358	3.94	379	4.07	388	4.09	399	4.12	389	4.11	400	4.08
7a [15]	335	3.88	345	3.90	355	4.22	360	3.99	360	4.24	361	4.29	365	4.25

[a] The insolubility of the species in the solvent do not allow the uv spectrum to be observed. [b] The uv spectrum could not be determined due to the ease of hydrolysis of this compound.

such character upon increasing solvent polarity [21], as shown by the hypsochromic shift observed. In terms of molecular orbital theory, the same finding could be described as the result of an orbital interaction $n \rightarrow \sigma^*$ between the non-linked electron pair of the heteroatom and the vacant σ^* orbital of the C-CN bond [21,22].

The ^1H nmr spectra of 5a and 5b in deuteriochloroform are also compatible with the covalent structure. While as a result of the planar (or almost planar) character of the salts methylene hydrogen atoms in compounds 1 are observed as symmetrical multiplets (AA'BB' system) centered on $\delta = 4.7\text{--}4.9$ ppm [15,16], the signals corresponding to the methylenes of 5a and 5b appear as more shielded complex multiplets (δ ca. 3.2–4.3 ppm). This is typical of the 1,2-diaryl-3-methylimidazolidines where the four hydrogen atoms are dissimilar [18]. Likewise, chemical shifts of N-CH₃ hydrogen atoms of cyanoaminals (δ ca. 2.35 ppm) are similar to those of the corresponding imidazolidines ($\delta = 2.40$) [18] and differ from those of the salts ($\delta = 3.25$) [15–17] in which a marked paramagnetic shift arising from low electron density on the nitrogen atom is observed.

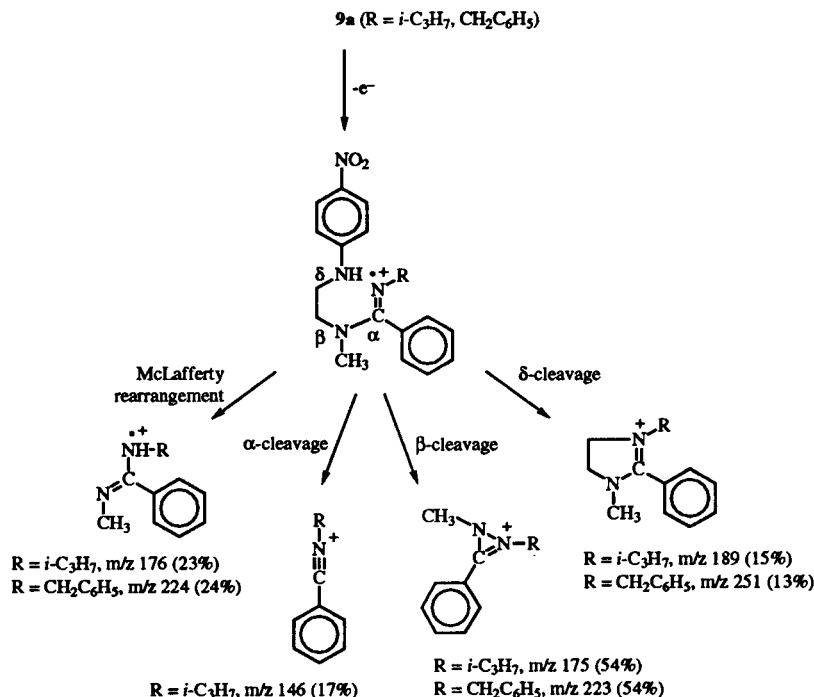
Gaseous and solid state spectra also indicate a covalent structure. The ir spectrum of 5a in potassium bromide fails to present the strong absorption at 1620–1669 cm⁻¹, corresponding to stretching C-N of the amidinium system [15–17] [24]. In the mass spectrum under electron impact, the base peak corresponds to the M⁺ ion ($m/z = 308$), which is remarkably stable [26].

Some chemical properties of compounds 5a,b,e obtained were studied. Reaction with mineral acids was found to regenerate salts 1. On the other hand, the cyano group may be readily substituted by several types of nucleophiles providing cyclic compounds which may undergo subsequent transformation. Hydrolysis may be carried out simply by treatment with water and leads, as in compounds 1, to the acyclic *N*-acylethylenediamines 6 probably through the carbinolamine (A, Nu = OH) [28].

With reducing agents acting *via* hydride transfer (lithium aluminum hydride in tetrahydrofuran and sodium borohydride under different conditions), imidazolidines 7 (A, Nu = H) are obtained in good yields, though in the case of 7b with sodium borohydride in ethanol partial over-reduction may be observed. Likewise, 5b and 5e reacts efficiently with methylmagnesium iodide producing as main products 3b and 4 in the first case and 2e in the second, with better yields than in the case of the corresponding salts [29]. This is probably due to the greater solubility of the compounds 5 in ethers which allows working in homogeneous media. Thus, the preparation of compounds 5 and their subsequent reaction with nucleophiles is a valuable synthetic alternative when direct attack of the nucleophile on the salt is hindered by the low solubility of the latter in the reaction solvent.

When compound 1a was treated with aromatic or secondary aliphatic amines in various reaction conditions, it remained unchanged. On the other hand, the reaction with an excess of primary aliphatic or arylalkyl amines (isopropylamine and benzylamine), led in each case to single products which were isolated as yellow crystalline solids. Assuming that the aminolysis of the salt could proceed in a way similar to hydrolysis [15–17], three possible structures were considered for these compounds: the cyclic triamino derivative I (A, Nu = NHR), corresponding to the simple adduct analogous to the carbinolamine of hydrolysis, or the two possible acyclic benzimidoyl derivatives II and III resulting from the rupture of one of the C-N bonds. The orthoamide structure I was ruled out on the basis of chemical and spectroscopic evidence [31]. The appearance of a band at 1635 cm⁻¹ in the ir spectrum and a signal at 165 ppm in the ^{13}C nmr spectrum discloses the presence of a C=N group and validates the open structure of a benzimidoyl derivative II or III consistent with data corresponding to ^1H nmr spectra in which methylene hydrogens present as triplets characteristic of a AA'BB' pattern, typical of open chain compounds. The presence in this

Scheme II



spectrum of a broad singlet at $\delta = 7.8$ that disappears by deuteration (*p*-nitroaniline hydrogen), and the similarity in chemical shifts of methylene and methyl groups to those of related acyclic compounds such as the benzamide **6a** [15], allow the proposed structure **III**, compound **9a** ($R = i\text{-C}_3\text{H}_7, \text{CH}_2\text{-C}_6\text{H}_5$) to be assigned to the products obtained by aminolysis. Structure **III** was likewise supported by the characteristic electron-impact induced fragmentation pattern in the mass spectra (Scheme II).

With regards to the origin of the products, the following considerations seem pertinent. Given the reactivity of 1*H*-4,5-dihydroimidazolium salts [15], the first precursor must be the cyclic orthoamide **I** ($A, \text{Nu} = \text{NHR}$), resulting from the attack of the amine nitrogen on the electrophilic C-2 of the salt. This could be transformed directly into the final product **III**, or else, to originate compound **II** in conditions of kinetic control, which would isomerize rapidly to **III**, through a transamidation reaction (Scheme III). In order to detect any intermediate, the reaction was performed in the cold maintaining the amine in defect. However, no intermediate could be detected by monitoring the reaction by tlc.

Taking into account that in related isomerizations involving acyl migrations in *N*-acyl-*N*-aryl-*N'*-methylethylene-

diamines the rate of rearrangement increases upon reducing the basicity of the aryl nitrogen [37], an attempt was made to detect a similar rapid rearrangement by examining the aminolysis reaction of a salt with a strongly electron-donor group in the aryl group. The reaction of compound **1d** with an excess of benzylamine at room temperature afforded an oil whose spectroscopic features correspond to structure **III**, compound **9d** ($R = \text{CH}_2\text{-C}_6\text{H}_5$). On the other hand, when the amine was added slowly at 0° and the reaction monitored by tlc, two products of lower *R_f* that the final product were initially detected, presumably the triamino

Scheme III

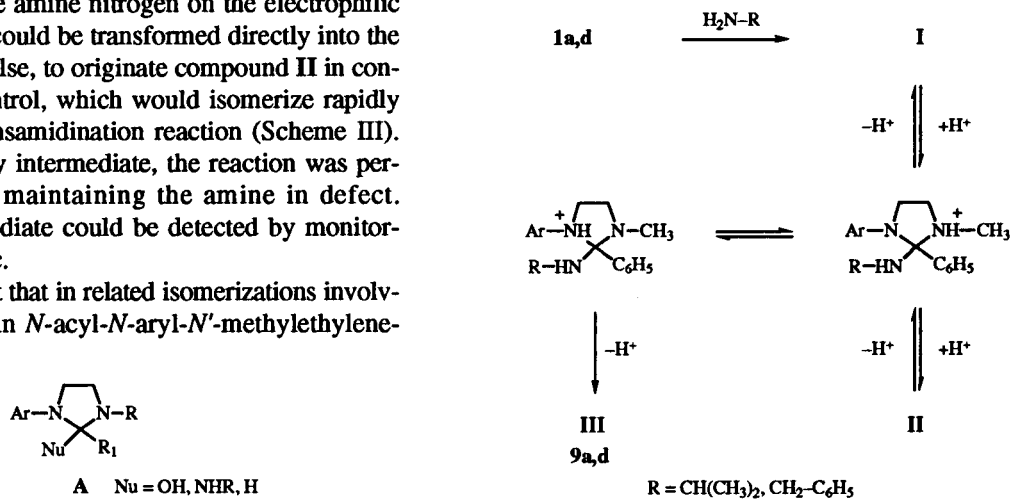
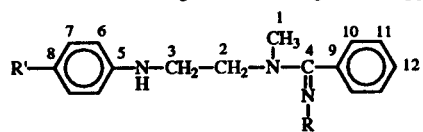


Table III
¹³C Chemical Shifts Assignment of Compounds 9 (ppm) [a]

							
Compound 9a	C-1	C-2	C-3	C-4	C-5	C-6	
	39.6	48.5	52.3	165.1	152.4	111.2	
R' = NO ₂ , R = CH ₂ - 	C-7	C-8	C-9	C-12	C-13	C-14	C-10, C-11, C-15-C-17
	130.1	138.0	132.7	131.2	41.8	136.3	125.0, 125.5, 126.5, 126.6, and 127.8
9a	C-1	C-2	C-3	C-4	C-5	C-6	C-7
	39.5	50.2	52.3	164.1	152.2	110.3	129.1
R' = NO ₂ , R = HC-(CH ₃) ₂	C-8	C-9	C-10	C-11	C-12	C-13	C-14
	137.1	132.29	126.17	125.4	130.14	50.7	23.1
9d	C-1	C-2	C-3	C-4	C-5	C-6	C-7
	39.7	48.2	52.1	164.2	141.3	113.3	115.2
R' = OCH ₃ , R = CH ₂ - 	C-8	C-9	C-12	C-13	C-14	C-18	C-10, C-11, C-15-C-17
	152.3	132.4	130.9	42.5	135.8	55.4	125.1, 126.4, 126.5 127.3, and 128.9

[a] Assignments were made on the basis of literature data for attached proton test and fully coupled ¹³C nmr spectra.

derivative I and the benzimidoyl derivative II. Attempts to isolate them by tlc failed, 9d being obtained in all cases. The ¹H nmr spectrum of the reaction mixture after 10 minutes showed a detectable signal at δ ca. 1.5, that disappeared by deuteration, presumably the hydrogen atom of the secondary aliphatic amine suggesting the presence of structure II. Bearing in mind these results and related data [9], we propose that the equilibria indicated in Scheme III would lead to the final product. Since the expulsion of nitrogen invariably requires addition of a proton, so that the leaving group is the free amine rather than the unstable amine anion [9,11,38], after initial formation of adduct I the preferred mode of decomposition would be governed by protonation of the more basic nitrogen atom (prototropic control). Thus, the benzimidoyl derivative II (product of kinetic control) which could not be isolated, would be formed. The transamidination reaction would then occur as a result of an unfavorable proton transfer process in the orthoamide I with subsequent expulsion of the less basic amine to give rise to the more stable and thermodynamically favored amidine III, compound 9.

On the basis of the findings in this work, as well as in previous reports, it may be concluded that the reactions of

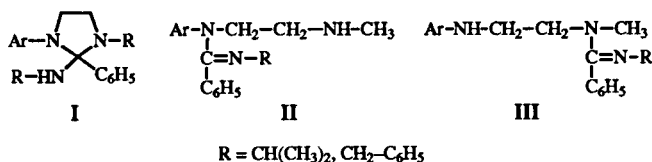
dihydroimidazolium salts 1 take place as a result of the initial attack of the nucleophilic center on the electrophilic C-2 originating a tetrahedral species which may be stable, or else undergo transformation into acyclic compounds.

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 ¹H nmr spectra were obtained on a Bruker MSL 300 Hz 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. The uv spectra were recorded on a Jasco 7850 UV-VIS spectrophotometer. Analytical tlc was carried out on aluminium sheets Silica Gel 60 F₂₅₄ using benzene-methanol (9:1) as the solvent. Column chromatography was carried out Silica Gel 60 (79-325 mesh). Preparative thin layers separations (plc) were performed on Silica Gel PF₂₅₄ on 20 x 20 x 0.25 cm layers. Samples used as reference compounds were synthesized and purified according to literature procedures.

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

Compounds 1a [15], 1b [17], 1c [16], and 1d [16] were obtained by treatment of the corresponding 1*H*-4,5-dihydroimidazole with



methyl iodide. Compound **1e** [13] was prepared by cyclization of *N*-formyl-*N,N'*-diphenylethylenediamine with 6*N* hydrochloric acid.

Reaction of Compounds **1b-e** with Methylmagnesium Iodide.

A solution of methylmagnesium iodide (from 9 mmoles of magnesium, 9 mmoles of methyl iodide and 35 ml of tetrahydrofuran) was prepared in the usual way, and 3 mmoles of compounds **1b-e** were added all at once as a powder. The mixture was stirred at room temperature and the reaction monitored by tlc. Together with compounds **1** (*R_f* ca. 0.2) two additional spots (*R_f* ca. 0.5 and 0.7) were detected. When salts **1** were no longer detectable (ca. 3 hours), the reaction was quenched by adding concentrated solution of ammonium chloride (20 ml). After stirring for 1 hour, the reaction mixture was extracted with ether. The organic layer was washed with water, dried and concentrated. The crude product obtained from compounds **1b-d** showed three spots by tlc (*R_f* ca. 0.2, 0.5 and 0.8) but no traces of compound of *R_f* ca. 0.7. Separation of the products was achieved by column chromatography eluting with chloroform-methanol (9:1). Appropriate fractions were pooled and evaporated to dryness affording acetophenone (**4**) (30-40%), *N*-aryl-*N'*-methylethylenediamines (**3b-d**) (30-40%) and 1,2-diaryl-1*H*-4,5-dihydroimidazoles (5-8%) which were identified by comparison with authentic samples [39].

In the case of the reaction involving compound **1e**, the crude product showed a single spot (*R_f* 0.75). Solvent removal afforded the imidazolidine **2e**, mp and mixed mp with an authentic sample [41] 97° (ethanol).

Reaction of 1*H*-4,5-Dihydroimidazolium Salts **1a,b,e** with Potassium Cyanide.

A.

Potassium cyanide in absolute ethanol (saturated solution, 3 ml), was added to compound **1a** (0.001 mole) in absolute ethanol (3 ml). After 5 minutes the yellow precipitate was collected affording 2-cyano-1-methyl-3-(*p*-nitrophenyl)-2-phenylimidazolidine (**5a**) (75%), mp 130°; ir: ν 2900 (C-H), 2750 (C-H), 1600 (C=C), 1370 (C-NO₂), 1310 (C-N), 935 (imidazolidine), 920 (imidazolidine) and 720 (C₆H₅) cm⁻¹; ¹H nmr: δ 8.10 (d, 2H, NO₂-C₆H₄, 2 *ortho* H), 7.35 (s, 5H, C₆H₅), 6.80 (d, 2H, NO₂-C₆H₄, 2 *meta* H), 4.30-3.20 (m, 4H, CH₂-CH₂), 2.30 (s, 3H, CH₃); ms: *m/z* 308 (M⁺).

Anal. Calcd. for C₁₇H₁₆N₄O₂: C, 66.23; H, 5.19; N, 18.18. Found: C, 66.13; H, 5.24; N, 18.25.

Attempts to crystallize **5a** from 96° ethanol afforded **6a** [15].

Reaction of compounds **1b** and **1e** under the same conditions as above afforded *N*-benzoyl-*N*-methyl-*N'*-phenylethylenediamine (**6b**) [17] and *N*-formyl-*N,N'*-diphenylethylenediamine (**6e**) [13] respectively which were identified by comparison with authentic samples.

B.

To a stirred solution of compounds **1a,b,e** (0.001 mole) in anhydrous methylene chloride (15 ml), potassium cyanide supported on alumina (3 g) [19,20] was added in two portions at 10 minute intervals. Stirring was continued at room temperature for 30 minutes and the reaction followed by tlc. When transformation **1** $\rightarrow$ **5** was achieved the reagent was filtered, washed with anhydrous methylene chloride and the filtrate concentrated *in vacuo* keeping the reaction flask in a water bath at 18-20°, affording **5a,b,e**. The physical data and elemental analyses for new compounds are as follows:

2-Cyano-1-methyl-2,3-diphenylimidazolidine (**5b**).

This compound was obtained as an oil and was purified by column chromatography eluting with chloroform-methanol (9:1); ir: ν 2930 (C-H), 2840 (C-H), 1610 (C=C), 1680 (C=C), 1330 (C-N), 940 (imidazolidine), 920 (imidazolidine) and 750 (C₆H₅) cm⁻¹; ¹H nmr: δ 7.35 (s, 5H, C₆H₅), 7.40-6.30 (m, 5H, aromatics), 4.10-3.40 (m, 4H, CH₂-CH₂), 2.35 (s, 3H, CH₃); ms: *m/z* 263 (M⁺).

Anal. Calcd. for C₁₇H₁₇N₃: C, 77.57; H, 6.46; N, 15.97. Found: C, 77.31; H, 6.55; N, 15.73.

2-Cyano-1,3-diphenylimidazolidine (**5e**).

This compound was obtained as an oil and was purified by column chromatography eluting with chloroform-methanol (9:1); ir: ν 2750 (C-H), 1620 (C=C), 1600 (C=C), 1335 (C-N), 940 (imidazolidine), 915 (imidazolidine) and 720 (C₆H₅) cm⁻¹; ¹H nmr: δ 7.50-6.50 (m, 10H, aromatics), 6.40 (s, 1H, CH(CN)), 3.54 (s, 4H, CH₂-CH₂); ms: *m/z* 249 (M⁺).

Anal. Calcd. for C₁₆H₁₅N₃: C, 77.11; H, 6.02; N, 16.87. Found: C, 77.41; H, 6.22; N, 16.72.

C.

Powdered compounds **1b,e** (0.001 mole) were added to a well stirred mixture of ether (10 ml) and saturated aqueous potassium cyanide (10 ml). After 5 minutes the organic layer was separated. The aqueous portion was extracted twice with ether (5 ml). The ethereal solutions were collected and concentrated at room temperature affording compounds **5b,e**.

Chemical Properties of Compounds **5**.

Typical reactions are described.

A.

Dissolution of compound **5a** in 10% hydrochloric acid and precipitation with aqueous picric acid yielded a picrate identical with that obtained from **1a** [15], mp and mixed mp 193°.

B.

Treatment of compounds **5a,b,e** with water afforded *N*-benzoylethylenediamines **6a** [15], **6b** [17] and **6e** [13] respectively. When the hydrolysis of **5b** was monitored by tlc, two transient compounds of low *R_f* were detected.

C.

To a solution of **5b,e** (0.001 mole) in dry THF (15 ml) lithium aluminum hydride (0.001 mole) was added. The mixture was refluxed for 30 minutes and then filtered. The organic solution was concentrated *in vacuo* affording imidazolidines **7b** [18], mp 64° (ethanol) and **7e** [13], mp 125° (methanol-water).

D.

Sodium borohydride (0.05 mole) was added during 5 minutes to a solution of compounds **5a,b,e** (0.01 mole) in absolute ethanol (20 ml) keeping the mixture at room temperature for one hour. The solvent was removed *in vacuo* and water (20 ml) was added to the residue. The suspension was extracted with chloroform. The organic solutions obtained from compounds **5a** and **5e** were concentrated affording the corresponding imidazolidines **7a** [15] mp 82° (methanol) and **7e**. The organic solution obtained from compound **5b** was examined by tlc, showing the presence of two spots identified by comparison with standard samples: the one of greatest *R_f* (ca. 0.8) as the imidazolidine **7b**

and the one of least *R_f* (ca. 0.6) as the *N*-benzyl-*N*'-methyl-*N*'-phenylethylenediamine **8b** [18].

E.

Reaction of compounds **5b,e** with methylmagnesium iodide was performed following the procedure indicated for compounds **1b,e**. Complete transformation of the cyano compounds was accomplished after 1.30 hours. Compound **5b** afforded *N*-methyl-*N*'-phenylethylenediamine (**3b**) [39] (60%) and acetophenone (**4**) (60%). Compound **5e** afforded **2e** [41] (85%), mp 97° (ethanol).

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

General Procedure.

The corresponding amine (0.004 mole) was added to a solution of compound **1** (0.001 mole) in anhydrous methanol (5 ml) and the resulting solution stored at room temperature. The reaction mixture was monitored by tlc. When disappearance of **1** (*R_f* ca. 0.2) was observed (10 minutes), water (20 ml) was added. If the product crystallized, it was collected, washed and recrystallized. If not, the emulsion was extracted three times with chloroform and the organic solution washed, dried and concentrated.

The physical data and elemental analyses of new compounds are as follows.

N-(*N*-Benzylbenzimidoyl)-*N*-methyl-*N*'-(*p*-nitrophenyl)ethylenediamine (**9a**, R = CH₂-C₆H₅).

This compound was obtained by treatment of **1a** with benzylamine (71%), mp 90° (ethanol); ir: ν 3010 (C-H), 2910 (C-H), 1635 (C=N), 1540 (C-NO₂), 1345 (C-NO₂), 1315 (C-N), 720 and 685 (C₆H₅) cm⁻¹; ¹H nmr: δ 7.90 (d, 2H, NO₂-C₆H₄, 2 *ortho* H), 7.35 (m, 10H, C₆H₅), 6.00 (d, 2H, NO₂-C₆H₄, 2 *meta* H), 4.15 (s, 2H, =N-CH₂-C₆H₅), 3.80 (t, 2H, CH₂-NH-C₆H₅), 3.35 (t, 2H, CH₂-N-CH₃), 2.75 (s, 3H, CH₃); ms: (20 eV) *m/z* (%) 388 (100, M⁺), 251 (13), 224 (24), 223 (54), 182 (20), 58 (24); ¹³C nmr spectrum data are given in Table III.

Anal. Calcd. for C₂₃H₂₄N₄O₂: C, 71.13; H, 6.18; N, 14.43. Found: C, 70.93; H, 6.32; N, 14.33.

Compound **9a** (R = CH₂-C₆H₅) remained unchanged after treatment with 10% hydrochloric acid solution. When it was refluxed with methanol-water (8:2), partial transformation to **6a** was observed.

N-(*N*-Isopropylbenzimidoyl)-*N*-methyl-*N*'-(*p*-nitrophenyl)ethylenediamine (**9a**, R = CH(CH₃)₂).

This compound was obtained by treatment of **1a** with isopropylamine (68%), mp 122° (ethanol); ir: ν 3015 (C-H), 3900 (C-H), 1635 (C=N), 1535 (C-NO₂), 1350 (C-NO₂), 1310 (C-N), 720 (C₆H₅) and 680 (C₆H₅) cm⁻¹; ¹H nmr: δ 8.00 (d, 2H, O₂N-C₆H₄, 2 *ortho* H), 7.30 (m, 5H, C₆H₅), 6.55 (d, 2H, O₂N-C₆H₄, 2 *meta* H), 3.75 (t, 2H, NH-CH₂), 3.50 (t, 2H, CH₂-N-CH₃), 3.15 (m, 1H, CH(CH₃)₂), 2.75 (s, 3H, N-CH₃), 1.15 (d, 6H, CH(CH₃)₂); ms: (20 eV) *m/z* (%) 340 (100, M⁺), 189 (15), 176 (23), 175 (54), 146 (17), 58 (24); ¹³C nmr spectrum data are given in Table III.

Anal. Calcd. for C₁₉H₂₄N₄O₂: C, 67.05; H, 7.06; N, 16.47. Found: C, 66.92; H, 7.25; N, 16.15.

N-(*N*-Benzylbenzimidoyl)-*N*'-(*p*-methoxyphenyl)-*N*-methyl-ethylenediamine (**9d**, R = CH₂-C₆H₅).

This compound was obtained by treatment of **1d** with benzylamine (30%). It was isolated as an oil from a complex mixture

by column chromatography eluting with chloroform-methanol (9:1); ir: ν 3010 (C-H), 2950 (C-H), 1630 (C=N), 1310 (C-N), 720 and 680 (C₆H₅) cm⁻¹; ¹H nmr: δ 7.15 (d, 2H, CH₃OC₆H₄, 2 *ortho* H), 7.30 (m, 10 H, C₆H₅), 6.80 (d, 2H, CH₃OC₆H₄, 2 *meta* H), 4.10 (s, 2H, C=N-CH₂-C₆H₅), 3.90 (s, 3H, OCH₃), 3.35 (t, 2H, CH₂-NH-), 3.20 (t, 2H, CH₂-N-CH₃), 2.80 (s, 3H, N-CH₃); ms: *m/z* 373 (M⁺); ¹³C nmr spectrum data are given in Table III.

Anal. Calcd. for C₂₄H₂₇N₃O: C, 77.21; H, 7.24; N, 11.26. Found: C, 77.42; H, 7.39; N, 11.33.

When compound **1a** was treated with aniline or diethylamine under the conditions indicated above, it remained unchanged after 5 days.

Attempts to detect some intermediary in the transformation 1 → 9 were performed as follows.

A solution of benzylamine (0.001 mole) in anhydrous chloroform (2 ml) was added dropwise to a solution of **1a,c** (0.001 mole) in the same solvent (5 ml) keeping the reaction mixture at -10°. The reactions were monitored by tlc.

The organic solution obtained from **1a** showed the presence of compounds **1a** and **9a** (R = CH₂-C₆H₅) alone. No further spot attributable to any intermediary could be detected.

In turn, in the case of the reaction involving compound **1d**, when this compound and the amine had already disappeared (several minutes after completing addition), together with compound **9c** (R = CH₂-C₆H₅) (*R_f* ca. 0.45) two new spots (*R_f* ca. 0.2 and 0.3) were detected under the uv light. On concentrating the reaction mixture, the ¹H nmr spectrum of the crude product displayed a singlet (δ = 1.30), attributable to the amino hydrogen of structure II. Attempts to isolate the new compounds by plc were unsuccessful and only **9d** was obtained.

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