Synthesis and Study of 1-Aryl-1*H*-4,5-dihydroimidazoles

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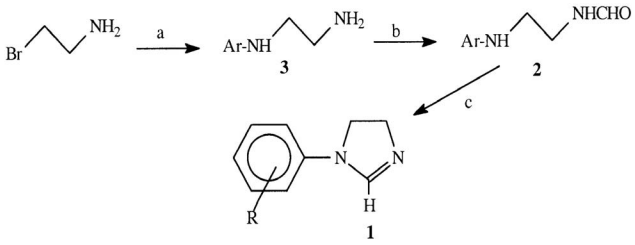
Abstract: An easy synthesis of 1-aryl-1*H*-4,5-dihydroimidazoles **1** by cyclocondensation of *N*-aryl-*N*′-formylethylenediamines **2** is described. Such precursors were synthesized by selective formylation of *N*-arylethylenediamines **3** with *p*-nitrophenyl formate. Cyclizations were performed using trimethylsilyl polyphosphate. Chemical properties of compounds **1**, typical of amidine system, were studied. Reaction of **1** with methyl iodide leads to the corresponding 1-aryl-3-methyl-1*H*-4,5-dihydroimidazolium salts **5**. Reduction of dihydroimidazoles **1** with sodium cyanoborohydride provides a convenient access to *N*-aryl-*N*′-methylethylenediamines **4**.

Key words: heterocycles, nitrogen, cyclization, reductions, alkylations

1*H*-4,5-Dihydroimidazoles **1** (2-imidazolines) are cyclic amidines of pharmacological interest due to the properties shown by some members, such as antihypertensive (halobenzyl-2-imidazolines),[1] antihelminthic (2-alkenylimidazolines),[2] anti-inflamatory and analgesic (2,5-diarylimidazolines).[3] Other 1*H*-4,5-dihydroimidazoles derivatives were studied as hypoglycemic agents.[4] Biological effects were attributed to activation of three groups of imidazoline receptors (I_1, I_2, I_3).[5] From a chemical point of view, the synthesis and study of such compounds became of interest because they are synthetic intermediates in the preparation of pentagonal 1,3-diazaheterocycles[6–8] and acyclic compounds carrying the ethylenediamine structural unit.[8–11] Imidazoline moiety was also employed as a source of carbon units in transfer reactions.[11,12]

2-Substituted and 1,2-disubstituted 4,5-dihydroimidazoles were largely studied. Instead there are only scanty reports on C2 unsubstituted analogs, most of them *N*-alkyl derivatives. However, only one *N*-aryl derivative was reported in the literature.[13] These compounds were obtained classically by condensation of 1,2-diaminoethanes and formic acid derivatives such as ethyl formate,[14] the corresponding iminoether[15] or ethyl orthoformate.[6a] As a source of C2, hydrogen cyanide[13] and triazine[16] were also employed. Alternative synthetic methods such as imidazolidine dehydrogenation,[17] cyclization of *N*,*N*′-diformylethylenediamines[18] and reaction of ethylenediamines with formimines and sulfur[19] were also reported.

In this work an easy synthesis of 1-aryl-1*H*-4,5-dihydroimidazoles **1** (Scheme 1) which involves ring closure of *N*-aryl-*N*′-formylethylenediamines **2** by polyphosphoric acid esters (PPE, PPSE) is described. This method is an extension of that previously employed by us to obtain 1,2-diaryl derivatives by cyclization of *N*-aryl-*N*′-aroylethylenediamines.[10] The synthetic route from bromoethylamine is depicted in Scheme 1.



Compounds 1-3	Ar
a	C_6H_5
b	4-$CH_3C_6H_4$
c	2-$CH_3C_6H_4$
d	2,4,6-$(CH_3)_3C_6H_2$
e	4-$CH_3OC_6H_4$
f	4-ClC_6H_4
g	4-$NO_2C_6H_4$

Scheme 1 (a) Arylamines; (b) *p*-nitrophenyl formate; (c) PPE, PPSE.

Chemical properties of compounds **1**, typical of the amidine system, were studied: reduction with a nucleophilic agent (sodium cyanoborohydride) and quaternization with methyl iodide.

N-Arylethylenediamines **3a**–**f** were obtained by aminolysis of 2-bromoethylamine (hydrobromide) with aromatic amines. This method presents advantages compared to other aminoethylation reactions described in the literature.[20] However, the procedure can not be employed for arylamines containing electron acceptor substituents such as *ortho* and *para* nitro groups. Compound **3g** was obtained from *p*-nitrochlorobenzene and ethylenediamine according with literature procedure.[21]

Formylation of *N*-arylethylenediamines was performed with formic acid. However, reactions lead to a mixture of *N*-aryl-*N*′-formylethylenediamines **2** (50–70%) (Table 1) and *N*-aryl-*N*,*N*′-diformylethylenediamines (25–45%). Yields depend on the aromatic substitution: diformylation increased with the electron donor effect of the aryl substituent. In order to increase formylation selectivity, *p*-nitro-

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Table 1 Data for Products **2a**–**g**

Product[a]	MS *m/z* (M^+)	Yield[b] (%)	^{1}H NMR ($CDCl_3$/TMS) δ, *J* (Hz)
2a	164	83	8.20 (s, 1 H, CHO), 7.20 (m, 2 H_{arom}), 6.70 (t, 1 H_{arom} *J* = 7.40), 6.60 (d, 2 H_{arom}, *J* = 7.60), 5.95 (br s, 1 H, NHCO), 3.87 (br s, 1 H N*H*Ar), 3.45 (q, 2 H, *J* = 6.20, CH_2NHCHO), 3.15 (t, 2 H, *J*= 6.20, CH_2NHAr)
2b	178	77	8.19 (s, 1 H, CHO), 7.01 (dd, 2 H_{arom}, *J* = 6.41, 2.03), 6.56 (dd, 2 H_{arom}, *J* = 6.41, 2.03), 6.15 (br s, 1 H, N*H*CHO), 3.85 (br s, 1 H, N*H*Ar), 3.51 (q, 2 H, *J* = 6.15, CH_2NHCHO), 3.20 (t, 2 H, *J* = 6.15, CH_2NHAr), 2.20 (s, 3 H, CH_3)
2c	178	75	8.15 (s, 1 H, CHO), 7.20 (m, 2 H_{arom}), 6.71 (m, 2 H_{arom}), 6.02 (br s, 1 H, N*H*-CHO), 3.80 (br s, 1 H, N*H*Ar), 3.47 (q, 2 H, *J* = 5.81, CH_2NHCHO), 3.17 (t, 2 H, *J* = 5.81, CH_2NHAr), 2.18 (s, 3 H, CH_3)
2d	206	75	8.19 (s, 1 H, CHO), 6.97 (s, 2 H_{arom}), 6.12 (br s, 1 H, N*H*CHO), 3.90 (br s, 1 H, N*H*Ar), 3.50 (q, 2 H, *J* = 5.15, CH_2NHCHO), 3.19 (t, 2 H, *J*= 5.15, CH_2NHAr), 2.20 (s, 3 H, CH_3), 2.16 (s, 6 H, CH_3)
2e	194	89	8.20 (s, 1 H, CHO), 6.76 (dd, 2 H_{arom}, *J* = 8.80, 2.20), 6.55 (dd, 2 H_{arom}, *J* = 8.80, 2.20), 6.10 (br s, 1 H, N*H*CHO), 3.79 (s, 3 H, CH_3O), 3.55 (q, 2 H, *J* = 5.77, CH_2NHCHO), 3.35 (br s, 1 H, N*H*Ar), 3.18 (t, 2 H, *J* = 5.77, CH_2NHAr)
2f	198, 200	85	8.12 (s, 1 H, CHO), 7.25 (d, 2 H_{arom}, *J* = 8.78), 6.59 (d, 2 H_{arom}, *J* = 8.78), 5.99 (br s, 1 H, N*H*CHO), 3.57 (q, 2 H, *J* = 5.80, CH_2NHCHO), 3.35 (br s, 1 H, NHAr), 3.24 (t, 2 H, *J* = 5.80, CH_2NHAr)
2g[c]	209	91	8.20 (br s, 1 H, NH), 8.09 (s, 1 H, CHO), 8.01 (dd, 2 H_{arom}, *J* = 10.10, 2.50), 7.40 (br s, 1 H, NH), 6.70 (dd, 2 H_{arom}, *J* = 10.10, 2.50), 3.21 (m, 4 H, CH_2CH_2)

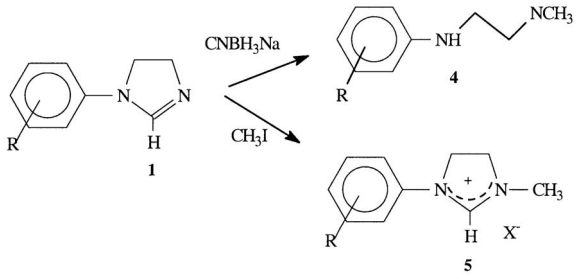
[a] Satisfactory microanalyses obtained: C ± 0.08, H ± 0.10, N ± 0.09.
[b] Pure products.
[c] Mp 157 °C. ^{1}H NMR was recorded in DMSO-d_6.

phenyl formate was employed; in this case yields higher than 75% for all monoformyl derivatives **2** were obtained.

Cyclization of compounds **2** was initially carried out with PPE (polyphosphate ester) which had been an appropriate agent to obtain 1,2-diarylimidazolines.[8,10] However, yields did not exceed 40%. Better results (72–82% yields) were obtained with trimethylsilyl polyphosphate (PPSE). This aprotic cyclizing reagent has been previously employed in the synthesis of several types of heterocycles, and specially for the synthesis of cyclic amidines.[22,23] Compounds **1** (Table 2) proved to be highly unstable (they easily undergo hydrolysis at room temperature, giving the formyl derivatives **2**), which hampers their isolation, purification and spectroscopic characterization.

In order to evaluate the 1*H*-4,5-dihydroimidazoles **1** as potential precursors of cyclic and acyclic compounds carrying the ethylenediamine structural moiety (NCH_2CH_2N), reactions resulting from C2 electrophilic character (reduction) and to N3 nucleophilic properties (quaternization) were studied (Scheme 2).

Treatment of **1a**–**g** with sodium cyanoborohydride in ethanol at room temperature lead regiospecifically to the asymmetric *N*,*N*′-disubstituted ethylenediamines **4**. The reaction can be interpreted as the result of initial hydride ion attack at the electrophilic C2, with formation of the corresponding 2,3-unsubstituted imidazolidine (Scheme 3).



Scheme 2

The final isolated product may arise either from direct reduction of the aminoimine in equilibrium with the aminal[24,25] or through an intermediary iminium ion arising from imidazolidine ring opening in the reaction conditions (Scheme 3). In this case, regioselectivity results from the selective cleavage of the C2–NAr bond, with the elimination of the less basic amine and formation of the more stable iminium ion A. A similar mechanism has been previously proposed by us in order to justify the products obtained in the reduction of 1,3-disubstituted imidazolidines.[8]

1*H*-4,5-Dihydroimidazoles **1** behave as good nucleophiles and may be easily N3-alkylated by reaction with methyl iodide in dichloromethane at reflux giving the corresponding 1*H*-4,5-dihydroimidazolium salts **5** (Scheme 2). They were isolated as stable solids, purified

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Table 2 Data for Products **1a–g**

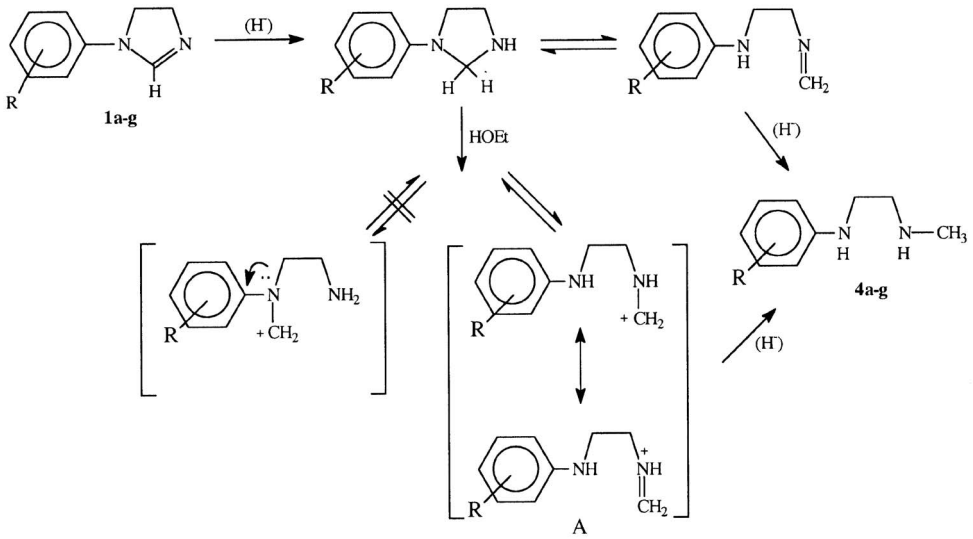
Product[a]	MS *m/z* (M^+)	Yield[b] (%)	^{1}H NMR ($CDCl_3$/TMS) δ, *J* (Hz)
1a	146	72	7.48 (s, 1 H, NCHN), 7.30–6.70 (m, 5 H_{arom}), 3.61 (t, 2 H, *J* = 9.15, CH_2), 3.52 (t, 2 H, *J* = 9.15, CH_2)
1b	160	82	7.80 (s, 1 H, NCHN), 7.23 (dd, 2 H_{arom}, *J* = 6.81, 2.70), 6.70 (dd, 2 H_{arom}, *J* = 6.81, 2.70), 3.61 (t, 2 H, *J* = 8.91, CH_2), 3.49 (t, 2 H, *J* = 8.91, CH_2), 2.07 (s, 3 H, CH_3)
1c	160	73	7.81 (s, 1 H, NCHN), 7.47–7.10 (m, 4 H_{arom}), 4.10 (t, 2 H, *J* = 9.25, CH_2), 3.61 (t, 2 H, *J* = 9.25, CH_2), 2.10 (s, 3 H, CH_3)
1d	188	75	7.73 (s, 1 H, NCHN), 7.21 (s, 2 H_{arom}), 4.15 (t, 2 H, *J* = 10.07, CH_2), 3.54 (t, 2 H, *J* = 10.07, CH_2), 2.21 (s, 3 H, CH_3), 2.15 (s, 6 H, CH_3)
1e	176	68	7.45 (s, 1 H, NCHN), 7.15 (dd, 2 H_{arom}, *J* = 8.50, 2.50), 6.90 (dd, 2 H_{arom}, *J* = 8.50, 2.50), 3.79 (s, 3 H, OCH_3), 3.67 (t, 2 H, *J* = 8.90, CH_2), 3.51 (t, 2 H, *J* = 8.90, CH_2)
1f	180, 182	69	7.83 (s, 1 H, NCHN), 7.32 (d, 2 H_{arom}, *J* = 8.57), 6.89 (d, 2 H_{arom}, *J* = 8.57), 3.56 (t, 2 H, *J* = 8.40, CH_2), 3.49 (t, 2 H, *J* = 8.40, CH_2)
1g[c]	191	75	8.20 (d, 2 H_{arom}, *J* = 9.19), 8.10 (s, 1 H, NCHN), 7.19 (d, 2 H_{arom}, *J* = 9.19), 3.95 (t, 2 H, *J* = 8.83, CH_2), 3.71 (t, 2 H, *J* = 8.83, CH_2)

[a] Satisfactory microanalyses obtained: C ± 0.11, H ± 0.09, N ± 0.13.
[b] Pure products.
[c] Hygroscopic solid.

by recrystallization and spectroscopically characterized (Table 3). Compounds **5** represent a potential source of imidazolidines and *N*,*N*,*N*′-trisubstituted ethylenediamines.[8,9]

Melting points were determined with a Büchi capillary apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker MSL 300 MHz spectrometer using $CDCl_3$ as the solvent unless otherwise indicated. Standard concentration of the samples was 20 mg/mL. Chemical shifts are reported in ppm (δ) relative to TMS as an internal standard. D_2O was employed to confirm exchangeable protons. Maas spectra (EI) were recorded with a GC-MS Shimadzu QP-1000 spectrometer operating at 20 eV. HRMS determinations were performed on a VG ZAB-SEQ (VG Analytical, Manchester, UK) hybrid tandem mass spectrometer of BeqQ geometry, equipped with an electron impact ion source. TLC analyses were carried out on aluminum sheets silica gel 60 F_{254}. Column chromatography was performed on silica gel 60 (0.063–0.200 mesh) with typically 30–50 g of stationary phase per gram substance.

N-(4-Nitrophenyl)ethylenediamine (**3g**) was described in the literature.[21]



Scheme 3

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Table 3 Data for Products **5a–g**

Product[a]	Mp (°C)	Yield[b] (%)	^{1}H NMR ($CDCl_3$/TMS) δ, *J* (Hz)
5a	182	92	9.87 (s, 1 H, NCHN), 7.25 (m, 2 H_{arom}), 7.15–7.20 (m, 3 H_{arom}), 4.43 (t, 2 H, CH_2NAr, *J* = 11.00), 4.17 (t, 2 H, CH_2NCH$_3$, *J* = 11.00), 3.47 (s, 3 H, CH_3)
5b	178	87	9.90 (s, 1 H, NCHN), 7.40–7.30 (m, 2 H_{arom}), 7.20–7.10 (m, 2 H_{arom}), 4.45 (t, 2 H, *J* = 11.40, CH_2NAr), 4.20 (t, 2 H, *J* = 11.40, CH_2NCH$_3$), 3.50 (s, 3 H, NCH_3), 2.30 (s, 3 H, CH_3Ar)
5c	168	89	8.90 (s, 1 H, NCHN), 7.50 (d, 2 H_{arom}, *J* = 7.69), 7.30–7.10 (m, 4 H_{arom}), 4.40–4.20 (m, 4 H, CH_2CH_2), 3.40 (s, 3 H, NCH_3), 2.40 (s, 3 H, CH_3Ar)
5d	175	86	9.01 (s, 1 H, NCHN), 6.90 (s, 2 H_{arom}), 4.40 (t, 2 H, *J* = 11.01, CH_2NAr), 4.15 (t, 2 H, *J* = 11.01, CH_2NCH$_3$), 3.51 (s, 3 H, NCH_3), 2.30 (s, 6 H, CH_3), 2.20 (s, 3 H, CH_3)
5e	178	75	9.85 (s, 1 H, NCHN), 7.45 (dd, 2 H_{arom}, *J* = 6.80, 2.31), 6.90 (dd, 2 H_{arom}, *J* = 6.80, 2.31), 4.41 (t, 2 H, *J* = 11.3, CH_2NAr), 4.15 (t, 2 H, *J* = 11.3, CH_2NCH$_3$), 3.80 (s, 3 H, OCH_3), 3.51 (s, 3 H, NCH_3)
5f	179	91	10.12 (s, 1 H, NCHN), 7.43 (d, 2 H_{arom}, *J* = 9.22), 7.35 (d, 2 H_{arom}, *J* = 9.22), 4.43 (t, 2 H, *J* = 11.2, CH_2NAr), 4.17 (t, 2 H, *J* = 11.2, CH_2NCH$_3$), 3.51 (s, 3 H, NCH_3)
5g	183	92	9.91 (s, 1 H, NCHN), 7.90 (d, 2 H_{arom}, *J* = 9.23), 7.50 (d, 2 H_{arom}, *J* = 9.23), 4.30–4.45 (m, 4 H, CH_2CH_2), 3.50 (s, 3 H, NCH_3)

[a] Satisfactory microanalyses obtained: C ± 0.10, H ± 0.10, N ± 0.12.
[b] Pure products.

***N*-Arylethylenediamines 3 a–f; General Procedure**

A mixture of 2-bromoethylamine hydrobromide (2.05 g, 10 mmol) and the corresponding arylamine (30 mmol) in toluene (40 mL) was refluxed for 40 min. The precipitate was filtered and treated with 20% aq NaOH (30 mL) and the mixture was extracted with CH_2Cl_2 (3 × 30 mL). The organic layer was shaken with acetic/acetate buffer (pH 5.5, 20 mL) after which the aqueous layer was separated, made alkaline with 20% aq NaOH (20 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The organic phases were combined, washed with H_2O, dried and filtered. The solvent was removed in vacuo and the crude products were purified by column chromatography (benzene–MeOH, 7:3 to 1:9).

***N*-Phenylethylenediamine (3a)[20b]**

Yield: 75%.

^{1}H NMR: δ = 7.15 (m, 2 H_{arom}), 6.50 (m, 3 H_{arom}), 4.15 (br s, 1 H, NH), 3.45 (t, 2 H, *J* = 5.31 Hz, CH_2NAr), 2.95 (t, 2 H, *J* = 5.35 Hz, CH_2NH$_2$), 1.87 (br s, 2 H, NH_2).

HRMS: *m*/*z* calcd for $C_8H_{12}N_2$: 136.1001; found: 136.1005.

***N*-(4-Methylphenyl)ethylenediamine (3b)[20b]**

Yield: 79%.

^{1}H NMR: δ = 7.00 (d, 2 H_{arom}, *J* = 8.30 Hz), 6.56 (d, 2 H_{arom}, *J* = 8.30 Hz), 4.30 (br s, 1 H, NH), 3.17 (t, 2 H, *J* = 5.48 Hz, CH_2NAr), 2.94 (t, 2 H, *J* = 5.48 Hz, CH_2NH$_2$), 2.23 (s, 3 H, CH_3), 1.60 (br s, 2 H, NH_2).

HRMS: *m*/*z* calcd for $C_9H_{14}N_2$: 150.1158; found: 150.1151.

***N*-(2-Methylphenyl)ethylenediamine (3c)[20b]**

Yield: 75%.

^{1}H NMR: δ = 7.10 (m, 2 H_{arom}), 6.65 (m, 2 H_{arom}), 4.70 (br s, 1 H, NH), 3.25 (t, 2 H, *J* = 5.64 Hz, CH_2NAr), 2.99 (t, 2 H, *J* = 5.64 Hz, CH_2NH$_2$), 2.15 (s, 3 H, CH_3), 2.01 (br s, 2 H, NH_2).

HRMS: *m*/*z* calcd for $C_9H_{14}N_2$: 150.1158; found: 150.1163.

***N*-(2,4,6-Trimethylphenyl)ethylenediamine (3d)**

Yield: 86%; oil.

^{1}H NMR: δ = 6.95 (s, 2 H_{arom}), 4.56 (br s, 1 H, NH), 3.42 (t, 2 H, *J* = 5.47 Hz, CH_2NAr), 2.93 (t, 2 H, *J* = 5.47 Hz, CH_2NH$_2$), 2.21 (s, 3 H, CH_3), 2.17 (s, 6 H, CH_3), 1.95 (br s, 2 H, NH_2).

MS: *m*/*z* = 178 ($M^{+\cdot}$).

Anal. Calcd for $C_{11}H_{18}N_2$: C, 74.11; H, 10.18; N, 15.71. Found: C, 74.13; H, 10.12; N, 15.68.

***N*-(4-Methoxyphenyl)ethylenediamine (3e)[20b]**

Yield: 78%.

^{1}H NMR: δ = 6.80 (dd, 2 H_{arom}, J_1 = 6.69, J_2 = 2.20 Hz), 6.60 (dd, 2 H_{arom}, J_1 = 6.69, J_2 = 2.20 Hz), 4.70 (br s, 1 H, NH), 3.80 (s, 3 H, OCH_3), 3.15 (t, 2 H, *J* = 5.49 Hz, CH_2NAr), 2.90 (t, 2 H, *J* = 5.49 Hz, CH_2NH$_2$), 2.02 (br s, 2H, NH_2).

HRMS: *m*/*z* calcd for $C_9H_{14}N_2O$: 166.1107; found: 166.1113.

***N*-(4-Chlorophenyl)ethylenediamine (3f)**

Yield: 81%; oil.

^{1}H NMR: δ = 7.10 (d, 2 H_{arom}, *J* = 8.98 Hz), 6.54 (d, 2 H_{arom}, *J* = 8.98 Hz), 4.30 (br s, 1 H, NH), 3.13 (t, 2 H, *J* = 5.48 Hz, CH_2NAr), 2.93 (t, 2 H, *J* = 5.48 Hz, CH_2NH$_2$), 1.65 (br s, 2 H, NH_2).

MS: *m*/*z* = 170 and 172 ($M^{+\cdot}$).

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Anal. Calcd for $C_8H_{11}ClN_2$: C, 56.31; H, 6.50; N, 16.42. Found: C, 56.40; H, 6.42; N, 16.55.

_N_-Aryl-_N′_-formylethylenediamines 2a–g; General Procedure

p-Nitrophenyl formate (1.67 g, 10 mmol) was added in small portions to a solution of the corresponding *N*-arylethylenediamine **3** (10 mmol) in anhyd THF (15 mL) with stirring on an ice bath. The reaction was monitored by TLC (EtOAc). After complete disappearance of the starting material, the solvent was removed in vacuo. The crude products were washed with aq sat. $NaHCO_3$ solution and purified by columm chromatography (EtOAc) affording compounds **2** as oils. Yields and spectroscopic data of compounds are given in Table 1.

Reaction of compounds **3** (10 mmol) with formic acid (40 mmol) under reflux afforded a mixture of the corresponding compounds **2** (50–70%) and *N*-aryl-*N*,*N′*-diformylethylenediamines (25–45%).

_N_-Aryl-1*H*-4,5-dihydroimidazoles 1a–g; General Procedures

Using PPSE: The corresponding *N*-aryl-*N′*-formylethylenediamine **2** (0.5 g) was dissolved in a CH_2Cl_2 solution of PPSE (prepared according the method of Imamoto,[26] 10 mL) and refluxed for 1 h. The solution was cooled and extracted with H_2O (3 × 20 mL). The aqueous phases were pooled and made alkaline with Na_2CO_3 to pH 9. The aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with H_2O, dried (Na_2SO_4), filtered and evaporated in vacuo affording compounds **1** as oils (Table 2).

Using PPE: Reactions of compounds **2** with PPE[27] in the same manner as described for PPSE afforded compounds **1** (25–40% yield).

Reduction of 1-Aryl-1*H*-4,5-dihydroimidazoles; General Procedure

$NaBH_3CN$ (3.142 g, 0.05 mol) was added during 5 min to a solution of the appropriate 1*H*-4,5-dihydroimidazole **1** (0.01 mol) in EtOH (20 mL) keeping the mixture at r.t. When total transformation had occurred (ca. 30 min), the suspension was extracted with $CHCl_3$ (3 × 15 mL). The organic layers were pooled, washed with H_2O, dried and concentrated in vacuo affording compounds **4a**–**g** which were purified by columm chromatography. Compounds **4a**,**b**,**e**,[28] **4f**[29] and **4g**[30] were described in the literature.

***N*-Methyl-*N′*-(2-methylphenyl)ethylenediamine (4c)**

Yield: 78%; oil.

^{1}H NMR: δ = 7.20 (m, 2 H_{arom}), 6.60 (m, 2 H_{arom}), 3.47 (t, 2 H, *J* = 5.64 Hz, CH_2NAr), 3.30 (br s, 1 H, *H*NAr), 2.79 (t, 2 H, *J* = 5.64 Hz, CH_2NCH$_3$), 2.43 (br s, 1 H, *H*NCH$_3$), 2.35 (s, 3 H, NCH$_3$), 2.18 (s, 3 H, CH_3C$_6$H$_4$).

MS: *m*/*z* = 164 ($M^{+\cdot}$).

Anal. Calcd for $C_{10}H_{16}N_2$: C, 73.13; H, 9.82, N, 17.06. Found: C, 73.20; H, 9.74; N, 17.12.

***N*-Methyl-*N′*-(2,4,6-trimethylphenyl)ethylenediamine (4d)**

Yield: 81%; oil.

^{1}H NMR: δ = 6.90 (m, 2 H_{arom}), 3.48 (t, 2 H, *J* = 5.20 Hz, CH_2NAr), 3.32 (br s, 1 H, *H*NAr), 2.75 (t, 2 H, *J* = 5.20 Hz, CH_2NCH$_3$), 2.72 (s, 3 H, NCH$_3$), 2.45 (br s, 1 H, N*H*CH$_3$), 2.21 (s, 3 H, CH_3C$_6$H$_4$).

MS: *m*/*z* = 192 ($M^{+\cdot}$).

Anal. Calcd for $C_{12}H_{20}N_2$: C, 74.95; H, 10.48, N, 14.57. Found: C, 74.77; H, 10.55; N, 14.44.

1-Aryl-3-methyl-1*H*-4,5-dihydroimidazolium Salts 5a–g; General Procedure

A solution of the appropriate compound **1** (3 mmol) in CH_2Cl_2 (10 mL) and MeI (10 mmol) was heated under reflux until the disappearance of starting material was observed by TLC (benzene–MeOH, 9:1). The solution was concentrated in vacuo and the solid products were recrystallized from anhyd propan-2-ol (Table 3). MS (IE) of compounds **5** showed thermal decomposition before fragmentation.

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