1-ARYLAMINO-1*H*-IMIDAZOLES BY "OXIDATIVE REDUCTION" – CONVERSION OF 1-ARYLAMINO-2,3-DIHYDRO-1*H*-IMIDAZOLE-2-THIONES

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Abstract - Desulfurization of the thione function of *N*-arylthiosemicarbazides incorporated in a heterocyclic ring was achieved with 30 % hydrogen peroxide in acetic acid. This reagent proved superior for the title transformation of thiones (**1**) into 2-unsubstituted 1*H*-imidazoles (**5**). In addition, structurally related substrates were also subjected to this procedure.

INTRODUCTION

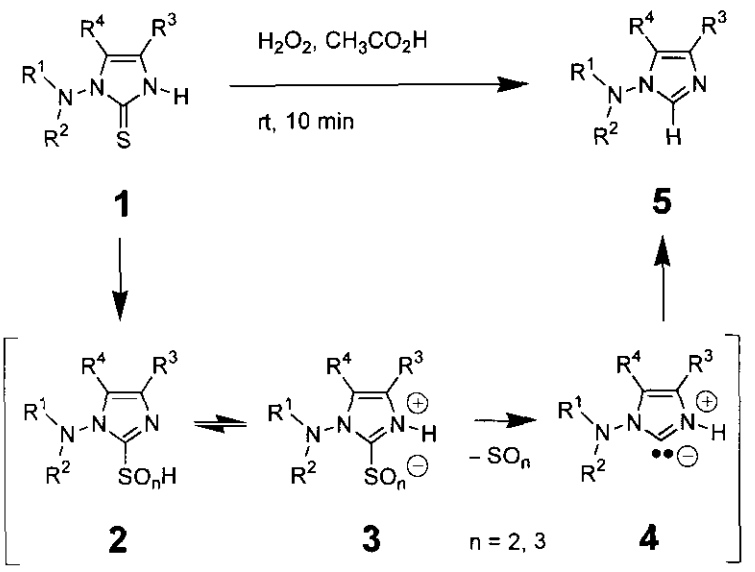
The structural unit of imidazole plays an essential role in many biologically active and important systems both of natural and synthetic origin.[1] Continued interest in imidazole chemistry is reflected among others by numerous procedures available for the construction of this ring system,[1] many of them furnishing 2-functionalized imidazole derivatives including imidazoline-2-thiones.[2-4] For some applications, e.g. for the generation of imidazole-derived nucleophilic carbenes[5,6] there is a demand for 2-unsubstituted imidazoles as starting materials.

Desulfurization of (mainly cyclic) thioamides and thioureas has been achieved by various methods using Raney nickel,[7] nitric acid,[8] singlet oxygen,[9] ozone,[10] ferric chloride,[11] and hydrogen peroxide.[12, 13] The latter appears to be a convenient though not generally applicable reagent; the actual product may differ depending on the substrate and the reaction conditions.[12]

Recently, we reported a facile preparation of 1-arylamino-2,3-dihydro-1*H*-imidazole-2-thiones (**1**).[4] The task of converting thiones (**1**) into 2-unsubstituted 1-arylamino-1*H*-imidazoles (**5**) was spurred by the intention to employ compounds (**5**) as precursors for the generation of nucleophilic carbenes.[14]

RESULTS AND DISCUSSION

A recent account on the desulfurization of cyclic thiourea derivatives[12] prompts this report on the conversion of the cyclic thiosemicarbazide moiety of 1-arylamino-2,3-dihydro-1*H*-imidazole-2-thiones (**1**) into 2-unsubstituted 1-arylaminoimidazole derivatives (**5**). For this transformation hydrogen peroxide proved to be the reagent of choice mainly due to the convenience of its application.



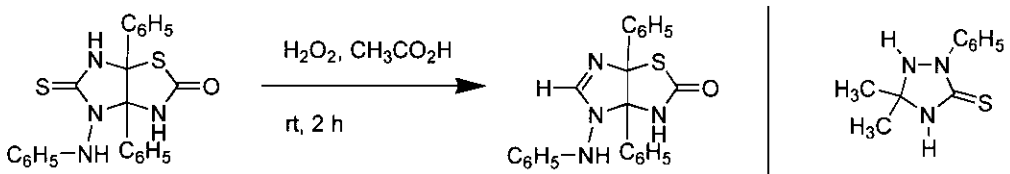
	R^1	R^2	R^3	R^4
a	H	C_6H_5	CH_3	CH_3
b	H	C_6H_5	$(CH_2)_4$	
c	H	C_6H_5	CH_3	C_6H_5
d	H	C_6H_5	C_6H_5	CH_3
e	H	C_6H_5	C_6H_5	C_6H_5
f	H	4-$O_2NC_6H_4$	CH_3	CH_3
g	H	4-$O_2NC_6H_4$	$(CH_2)_4$	
h	H	4-$O_2NC_6H_4$	CH_3	C_6H_5
i	H	4-$O_2NC_6H_4$	C_6H_5	CH_3
j	H	4-ClC_6H_4	CH_3	C_6H_5
k	H	4-$CH_3C_6H_4$	CH_3	C_6H_5
l	H	4-$CH_3OC_6H_4$	CH_3	C_6H_5
m	CH_3	C_6H_5	CH_3	C_6H_5

Scheme 1

Treatment of compounds (**1**)[4] with 30% hydrogen peroxide in acetic acid at room temperature (Scheme 1) selectively affected the thione function of the 1-arylthiosemicarbazide moiety of **1** leaving the arylamino side chain (the *N*-methyl-*N*-phenylamino side chain in **1m**) unchanged. The sulfur atom of the 2-thione function of **1** was oxidatively cleaved off and replaced by hydrogen. Within a short reaction time 2-unsubstituted 1-arylaminoimidazole derivatives (**5**) were produced as single and mostly pure products in good yields. When the reaction was carried out under analogous conditions but with hydrogen peroxide in hydrochloric acid, no product formation was observed inferring that peracetic acid is the actual reagent.[15] The overall reaction [–NH–C(=S)–N< (**1**) → –N=CH–N< (**5**)] is considered an "oxidative reduction". For conversions of this type two mechanisms have been discussed in the literature (Scheme 1): Gradual oxidation of the thione function of **1** to the sulfinic acid intermediate (**2**, n = 2) followed by expulsion of sulfur dioxide and its subsequent oxidation to sulfur trioxide by the reagent.[16] A conceivable alternative is the formation of the sulfonic acid intermediate (**2**, n = 3) followed by extrusion of sulfur trioxide.[13] In fact, conversion of **1** into **5** was accompanied by the evolution of sulfur trioxide (irrespective of the way

of its actual formation) which was trapped by precipitation as barium sulfate. Upon loss of SO_n from **2** or possibly from the zwitterionic isomer (**3**) the resultant carbene-type intermediate (**4**) is transformed into the final product (**5**) by proton transfer.

The IR spectra of compounds (**5**) are insignificant, the UV spectra of **5a-e** resemble that of the structurally related diphenylamine.[17] The structure of **5** was confirmed mainly by NMR data; the ^1H shift range found for 2-H in **5** (δ_H 7.5 – 7.9) is in agreement with data reported for imidazoles (2-H, δ_H 7.3 – 7.8).[18] Based on HMQC techniques, the ^{13}C signal at higher field (δ_C 117 – 127) is assigned to 5-C, 4-C being less shielded (δ_C 128 – 137).

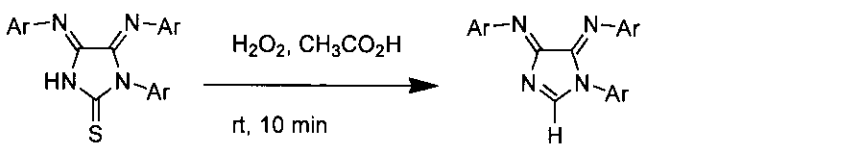


6 **7** **8**

Scheme 2

Under similar reaction conditions the bicyclic substrate[19] 3,3a,4,5,6,6a-hexahydro-3a,6a-diphenyl-4-phenylamino-5-thioxo-2*H*-imidazo[4,5-*d*][1,3]thiazol-2-one (**6**) (a cyclic 1-phenythiosemicarbazide) underwent reduction of the thione function and afforded the 2,3,3a,4-tetrahydro-6a*H*-imidazo[4,5-*d*]-[1,3]thiazole derivative (**7**) (Scheme 2). Other functions (endocyclic sulfur and nitrogen functions) remained unaffected.

In an attempt to explore the scope of this method, 5,5-dimethyl-2-phenyl[1,2,4]triazolidine-3-thione (**8**) (Scheme 2), a cyclic 2-phenylthiosemicarbazide derivative and representing compounds known to undergo facile oxidation,[20] was subjected to the reaction with hydrogen peroxide in acetic acid; however, no major product could be isolated from the complex reaction mixture.



9 **10** Ar = 4-$CH_3OC_6H_4$

Scheme 3

On the other hand, 1-(4-methoxyphenyl)-4,5-bis[*N*-(4-methoxyphenyl)imino]imidazolidine-2-thione (**9**)[21] (a probe with a cyclic thiourea moiety) smoothly underwent desulfurization with hydrogen peroxide in acetic acid and afforded the 4,5-dihydro-1*H*-imidazole derivative (**10**) almost quantitatively (Scheme 3).

EXPERIMENTAL

Starting materials were prepared as described in the literature: **1a-d**,[4] **1e**,[19] **1f-m**,[4] **6**,[19] **8**,[20] and **9**.[21] Spectroscopic data were recorded on the following instruments: MATTSON Galaxy Series GL-3020 (IR), Hewlett-Packard HP-8452 (UV-Vis), Bruker AM 300 (^{1}H-NMR, 300 MHz; ^{13}C-NMR, 75 MHz; using solvent signals for calibration with reference to tetramethylsilane), Varian Unity (^{1}H-NMR, 500 MHz, HMQC), Finnigan MAT 95 (EI-MS 70 eV; FAB-MS Cs gun, 20 KeV, 0.2 μA). Melting points were determined with a Reichert Kofler hot stage microscope. Thin layer chromatography (TLC) was carried out on silica gel (Polygram Sil G/UV$_{254}$, Macherey-Nagel), column chromatography was performed on silica (230-400 mesh, Merck) using a glass column (20 cm length, 2 cm I.D.).

4,5-Disubstituted 1-Arylamino-2,3-dihydro-1*H*-imidazoles (5). General Procedure: A suspension of 1-arylamino-2,3-dihydro-1*H*-imidazole-2-thione (**1**)[4] (2.0 mmol) in glacial acetic acid (10 mL) was stirred in an ice bath. Upon dropwise addition of 30 % hydrogen peroxide (1 mL, 9.76 mmol) the reaction mixture turned yellow, then green, and finally became an almost clear brown solution. After stirring for another 10 min the mixture was filtrated, the filtrate was made alkaline with 10 % aqueous sodium hydroxide thereby converting the first precipitated acetate salt (**5**·HO*Ac*) into the free base (**5**). Occasionally, **5** first separated as oil and turned crystalline upon scratching with a glass rod. The resultant solid was sucked off and washed with water. Purification was achieved either by recrystallization from methanol with little charcoal or by column chromatography on silica with ether as eluent. The resultant crystalline product (**5**) was dried over phosphorus pentoxide. For the preparation of an analytical sample, the crude product (**5**) was dissolved in 10 % hydrochloric acid, the solution was extracted with dichloromethane, and the base (**5**) was recovered from the aqueous layer upon addition of 10 % sodium hydroxide. The purity of all products was monitored with TLC. ^{1}H- and ^{13}C-NMR data are collected in Tables 1 and 2.

4,5-Dimethyl-1-phenylamino-1*H*-imidazole (5a): Colorless crystals (75 %); mp 175-177°C (methanol); R_f 0.29 (acetonitrile); IR (KBr): ν 3182, 3109, 3028, 2920, 1599, 1494, 1448, 1377, 1234, 1209, 908, 758 cm^{-1}; UV ($CHCl_3$, λ_{max} (log ε)): 246.0 (3.73), 280.0 (3.12); (EI-MS (*m/z* (%)): 187 (27, $M^{\bullet+}$), 160 (33, M – HCN), 145 (23, M – CH_3CNH), 104 (43, $C_6H_4N_2$), 92 (100, C_6H_5NH), 77 (34, C_6H_5). Anal. Calcd for $C_{11}H_{13}N_3$: C, 70.56; H, 7.00; N, 22.44. Found: C, 70.25, H. 7.25; N, 22.44.

4,5,6,7-Tetrahydro-1-phenylamino-1*H*-benzimidazole (5b): Colorless crystals (80 %); mp 160-163°C (methanol); R_f 0.24 (acetonitrile); IR (KBr): ν 3178, 3115, 3028, 2957, 2918, 1602, 1494, 1444, 1215, 771, 752, 694 cm^{-1}; UV ($CHCl_3$, λ_{max} (log ε)): 246.0 (3.72), 282.0 (3.10); EI-MS (*m/z* (%)): 213 (100, $M^{\bullet+}$), 149 (22), 121 (20, M – C_6H_5NH), 104 (43, $C_6H_4N_2$), 92 (87, C_6H_5NH), 77 (58, C_6H_5), 65 (67). Anal. Calcd for $C_{13}H_{15}N_3$: C, 73.20; H, 7.09; N, 19.70. Found: C, 73.30; H, 6.92; N, 19.78.

4-Methyl-5-phenyl-1-phenylamino-1*H*-imidazole (5c): Colorless crystals (83 %); mp 165-167°C (methanol); R_f 0.34 (acetonitrile); IR (KBr): ν = 3174, 3119, 3026, 2962, 1601, 1494, 1244, 1201, 758, 694 cm^{-1}; UV ($CHCl_3$, λ_{max} (log ε)): 248.0 (3.99), 260 (3.97); EI-MS (*m/z* (%)): 249 (100, $M^{\bullet+}$), 207 (45, M – CH_3CNH), 157 (46, M – C_6H_5NH), 104 (53, $C_6H_4N_2$), 89 (53, C_6H_5C), 77 (39, C_6H_5). Anal. Calcd for $C_{16}H_{15}N_3$: C, 77.08; H, 6.06; N, 16.85. Found: C, 77.37; H, 6.23; N, 16.65.

5-Methyl-4-phenyl-1-phenylamino-1*H*-imidazole (5d): Colorless crystals (87 %); mp 172-174°C (methanol); R_f 0.54 (acetonitrile); IR (KBr): ν = 3178, 3115, 3028, 2957, 2918, 1602, 1494, 1444, 1215, 771, 752, 694 cm^{-1}; UV ($CHCl_3$, λ_{max} (log ε)): 254.0 (4.06); EI-MS (*m/z* (%)): 249 (100, $M^{\bullet+}$), 207 (27, M – CH_3CNH), 157 (29, M – C_6H_5NH), 145 (14, M – C_6H_5CNH), 104 (31, C_6H_5CNH or $C_6H_4N_2$), 92 (35, C_6H_5NH), 77 (12, C_6H_5). Anal. Calcd for $C_{16}H_{15}N_3$: C, 77.08; H, 6.06; N, 16.85. Found: C, 76.96; H, 5.82, N, 17.14.

4,5-Diphenyl-1-phenylamino-1*H*-imidazole (5e):[18] Colorless crystals (97 %); mp 158-161°C (methanol; lit.[18] 153-155°C); R_f 0.80 (acetonitrile); IR (KBr): ν 3173, 3059, 3024, 2993, 1601, 1568, 1496, 1443, 1228, 947, 748, 692, 648 cm^{-1}; UV ($CHCl_3$, λ_{max} (log ε)): 246.0 (3.95), 276.0 (3.87); EI-MS (*m/z* (%)): 311 (21, $M^{\bullet+}$), 207 (28, M – $C_6H_4N_2$), 165 (21), 116 (31, C_6H_5CNCH), 105 (25, $C_6H_5N_2$), 89 (100, C_6H_5C), 77 (28, C_6H_5).

4,5-Dimethyl-1-(4-nitrophenylamino)-1*H*-imidazole (5f): Orange crystals (70 %); mp 243-246°C (methanol); R_f 0.05 (ether); IR (KBr): ν 3173, 3124, 2924, 2866, 1601, 1500, 1346, 1114, 839, 750 cm^{-1}; UV ($CHCl_3$, λ_{max} (log ε)): 240.0 (3.84), 324.5 (4.10); EI-MS (*m/z* (%)): 232 (100, $M^{\bullet+}$), 186 (18, M – NO_2), 149 (20, $O_2NC_6H_3N_2$), 95 (21, M – $O_2NC_6H_4NH$). Anal. Calcd for $C_{11}H_{12}N_4O_2$: C, 56.89; H, 5.21; N, 24.12. Found: C, 56.74; H, 5.13; N, 23.94.

4,5,6,7-Tetrahydro-1-(4-nitrophenylamino)-1*H*-benzimidazole (5g): Beige crystals (68 %); mp 274-278°C (methanol); R_f 0.06 (ether); IR (KBr): ν = 3192, 3128, 2945, 2899, 2845, 1599, 1502, 1323, 1203, 1111, 922, 837 cm^{-1}; UV ($CHCl_3$, λ_{max} (log ε)): 238.5 (3.80), 325.5 (3.93); EI-MS (*m/z* (%)): 258 (35, $M^{\bullet+}$), 121 (17, M – $O_2NC_6H_4NH$), 113 (100), 77 (34, C_6H_5), 46 (29, NO_2). Anal. Calcd for $C_{13}H_{14}N_4O_2$: C, 60.45; H, 5.46; N, 21.69; Found: C, 60.12; H, 5.15; N, 21.74.

4-Methyl-1-(4-nitrophenylamino)-5-phenyl-1*H*-imidazole (5h): Orange crystals (74 %); mp 279-284°C (methanol); R_f 0.17 (ether); IR (KBr): ν = 3188, 3126, 2918, 2860, 2805, 1595, 1491, 1329, 1109, 842, 700 cm^{-1}; UV ($CHCl_3$, λ_{max} (log ε)): 243.5 (3.92), 331.0 (3.95); EI-MS (*m/z* (%)): 294 (19, $M^{\bullet+}$), 280 (83), 269 (100), 267 (61, M – HCN), 132 (37), 117 (21, C_6H_5CNHCH), 104 (30, C_6H_5CNH), 77 (35, C_6H_5). Anal. Calcd for $C_{16}H_{14}N_4O_2$: C, 65.30; H, 4.79; N, 19.04. Found: C, 65.80; H, 4.49; N, 18.85.

Table 1: ^{1}H-NMR Data of 1-Arylamino-1*H*-imidazoles (**5**) (Solvent DMSO-d_6).

	2-H	R^1 [a]	R^2	R^3	R^4
5a	7.51	9.14	6,32 (d, J = 8.2 Hz), 6.71 (t J = 7.3 Hz), 7.10 (dd, J = 7.3, 8.2 Hz)	1.89 (s)	2.06 (s)
5b	7.50	9.08	6.39 (d, J = 7.8 Hz), 6.80 (t, J = 7.3 Hz), 7.18 (dd, J = 7.3, 7.8 Hz)	1.66 (br m, 5,6-CH_2), 2.23 (br m, 4-CH_2), 2.48 (br m, 7-CH_2)	
5c	7.70	9.31	6,32 (d, J = 8.2 Hz), 6.71 (t, J = 7.3 Hz), 7.10 (dd, J = 7.3, 8.2 Hz)	2.21 (s)	7.21-7.38 (m,)
5d	7.82	9.36	6.47 (d, J = 8.3 Hz), 6.84 (t, J = 7.3 Hz), 7.18-7.26 (m, 3,5-H of R^2, 4-H of R^3)	7.38 (dd, J = 7.3, 7.8 Hz), 7.70 (d, J = 7.8 Hz)	2.22 (s)
5e[13]	7.92	9.46	6.35 (d, J = 8.3 Hz), 6.65 (t, J = 7.8 Hz), 7.08-7.46 (m, 3,5-H of R^2, C_6H_5 of R^3, R^4)		
5f	7.61	10.22	6.45, 6.48, 8.09, 8.12 (AA'BB', J = 8.8 Hz)[b]	1.90 (s)	2.07 (s)
5g	7.60	10.20	6.48, 6.51, 8.09, 8.12 (AA'BB', J = 9.2 Hz)[b]	1.69 (br m, 5,6-CH_2), 2.24 (br m, 4-CH_2), 2.47 (br m, 7-CH_2)	
5h	7.86	10.46	6.43, 6.46, 8.01, 8.04 (AA'BB', J = 8.8 Hz)[b]	2.23 (s)	7.32-7.36 (m)
5i	7.80	10.38	6.48, 6.51, 8.06, 8.09 (AA'BB', J = 8.8 Hz)[b]	7.23 (t, J = 7.6 Hz), 7.40 (dd, J = 7.0, 7.6 Hz), 7.69 (d, J = 7.0 Hz)	2.21 (s)
5j	7.71	10.03	6.33, 6.36, 7.10, 7.13 (AA'BB', J = 8.3 Hz)[b]	2.20 (s)	7.24-7.38 (m)
5k	7.66	9.34	2.11 (s); 6.24, 6.27, 6.89, 6.92 (AA'BB', J = 8.3 Hz)[b]	2.20 (s)	7.23-7.38 (m)
5l	7.66	9.28	3.60 (s); 6.31, 6.33, 6.69, 6.72 (AA'BB', J = 8.8 Hz)[b]	2.20 (s)	7.24-7.36 (m)
5m	7.88	3.32[c]	6,44 (d, J = 8.2 Hz), 6.83 (t, J = 7.3 Hz) 7.20 (dd, J = 7.3, 8.2 Hz)	2.21 (s)	7.30-7.38 (m)

[a] br s of NH. [b] A = 2,6-H C_6H_4, B = 3,5-H C_6H_4; the determination of J (AA'BB') is based on the assumption of an AB quartet.[22] [c] R^1 = CH_3.

Table 2: ^{13}C-NMR Data of 1-Arylamino-1*H*-imidazoles (**5**) (Solvent DMSO-d_6).

	2-C 4-C 5-C [a]	R^2	R^3	R^4
5a	135.4, 131.3, 122.6	111.9, 120.1, 129.3, 148.1[b]	13.1	7.3
5b	137.2, 134.7, 128.9	111.5, 119.7, 129.1, 148.1[b]	14.1	127.2, 128.2, 128.8, 133.1[c]
5c	136.7, 134.4, 124.5	112.0, 120.3, 129.4, 147.8[b]	125.1, 126.0, 128.4, 135.1[b]	8.9
5d	135.5, 134.4, 125.6	112.1, 120.1, 129.2, 148.1[b]	19.4 (7-C), 22.2 (4-C), 23.0 (5-C), 24.1 (6-C)	
5e[g]	138.1, 135.6, 128.3	111.7, 119.8, 130.2, 148.0[b]	126.2, 128.4, 129.1, 134.5[b]	126.4, 128.3, 130.2, 132.2[c]
5f	135.1, 131.6,122.3	110.9, 126.2, 139.6, 153.6[d]	13.1	7.1
5g	134.2, 134.8, 125.4	111.0, 126.2, 139.2, 154.1[d]	19.2 (7-C), 22.2 (4-C), 22.9 (5-C), 24.1 (6-C)	
5h	137.0, 128.8, 125.6	110.6, 126.1, 139.3, 153.3[d]	14.0	127.6, 128.3, 128.4, 133.7[c]
5i	136.0, 134.7, 123.9	110.9, 126.3, 138.5, 154.8[d]	125.8, 126.0, 128.3, 135.1[b]	8.8
5j	137.1, 128.8, 122.8	113.1, 127.4, 128.2, 147.2[e]	14.1	127.3, 128.7, 128.9, 133.2[c]
5k	137.1, 129.0, 127.5	20.0 111.7, 128.3, 129.4, 145.9[f]	14.1	127.1, 128.1, 128.7, 132.9[c]
5l	137.2, 129.1,127.6	55.2 113.1, 114.5, 142.1, 153.1[f]	14.2	127.1, 128.2, 128.8, 133.0[c]
5m[h]	135.4, 128.9,127.1	127.6, 128.4, 129.0, 132.5[b]	14.0	112.4, 120.0, 129.2, 149.7[b]

[a] The assignment of 4-C and 5-C signals is based on HMQC spectra. [b-f] Order of aryl signals:[23] [b] 2,6-C, 4-C, 3,5-C, 1-C; [c] 4-C, 2,6-C, 3,5-C, 1C; [d] 2,6-C, 3,5-C, 4-C, 1-C; [e] 2,6-C, 4-C, 3,5-C, 1C; [f] 2,6-C, 4C, 3,5-C, 1C. [h] $R^1 = CH_3$, $\delta_C = 41.8$.

5-Methyl-1-(4-nitrophenylamino)-4-phenyl-1*H*-imidazole (5i): Orange-red crystals (72 %); mp 193-197°C (methanol); R_f 0.08 (ether); IR (KBr): ν = 3188, 3119, 3080, 2993, 2920, 1597, 1498, 1329, 1263, 1109, 841, 700 cm^{-1}; UV ($CHCl_3$, λ_{max} (log ε)): 248.0 (3.96), 261.0 (3.95), 327.5 (3.93); EI-MS (*m/z* (%)): 294 (100 $M^{\bullet+}$), 157 (72, M – $O_2NC_6H_4NH$), 116 (14, $C_6H_5CCCH_3$), 104 (10), 89 (20, C_5N_2H), 77 (9, C_6H_5). Anal. Calcd for $C_{16}H_{14}N_4O_2$: C, 65.30; H, 4.79; N, 19.04. Found: C, 64.90; H, 5.0; N, 18.95.

1-(4-Chlorophenylamino)-4-methyl-5-phenyl-1*H*-imidazole (5j): Colorless crystals (89 %); mp 186-190°C (methanol); R_f 0.17 (ether); IR (KBr): ν = 3400, 3115, 3032, 2927, 1655, 1614, 1568, 1512, 1410, 812, 696 cm^{-1}; UV ($CHCl_3$, λ_{max} (log ε)): 243.0 (3.95), 265.0 (3.72); EI-MS (*m/z* (%)): 285 (26, M + 2), 283 (100, $M^{\bullet+}$), 241 (78, M – CH_3CNH), 157 (55, M – ClC_6H_4NH), 138 (20, $ClC_6H_3N_2$), 126 (60, ClC_6H_4NH), 89 (39, C_6H_5C), 77 (11, C_6H_5). Anal. Calcd for $C_{16}H_{14}N_3Cl$: C, 67.72; H, 4.97; N; 14.81; Cl, 12.49. Found: C, 67.68; H, 4.88; N; 14.79; Cl, 12.39.

4-Methyl-1-(4-methylphenylamino)-5-phenyl-1*H*-imidazole (5k): Colorless crystals (94 %); mp 191-193°C (methanol); R_f 0.20 (ether); IR (KBr): ν = 3400, 3229, 3034, 2980, 2949, 1658, 1568, 1510, 1410, 1244, 1030, 827, 698 cm^{-1}; UV ($CHCl_3$, λ_{max} (log ε)): 242.5 (4.00), 262.5 (3.91); EI-MS (*m/z* (%)): 263 (99, $M^{\bullet+}$), 221 (64, M – CH_3CNH), 158 (31, M – $CH_3C_6H_4N$), 118 (15, $CH_3C_6H_3N_2$), 106 (100, $CH_3C_6H_4NH$), 77 (23, C_6H_5). Anal. Calcd for $C_{17}H_{17}N_3$: C, 77.54; H, 6.51; N, 15.96. Gef: C, 77.14; H, 6.57; N, 15.82.

1-(4-Methoxyphenylamino)-4-methyl-5-phenyl-1*H*-imidazole (5l): Colorless crystals (86 %); mp 202-206°C (methanol); R_f 0.13 (ether); IR (KBr): ν = 3398, 3115, 3050, 2980, 1655, 1568, 1491, 1410, 1244, 1030, 765, 696 cm^{-1}; UV ($CHCl_3$, λ_{max} (log ε)): 242.5 (3.88), 265.0 (3.83); EI-MS (*m/z* (%)): 279 (34 $M^{\bullet+}$), 157 (12, M – $CH_3OC_6H_4NH$), 122 (100, $CH_3OC_6H_4NH$), 95 (18), 83 (21), 77 (8, C_6H_5). Anal. Calcd for $C_{17}H_{17}N_3O$: C, 73.10; H, 6.13; N, 15.04. Found: C, 73.10; H, 6.40; N, 14.66.

2,3-Dihydro-4-methyl-1-(*N*-methyl-*N*-phenylamino)-5-phenyl-1*H*-imidazole-2-thione (1m): A stirred mixture of α-bromopropiophenone (6.39 g, 30 mmol) and finely ground potassium thiocyanate (4.40 g, 45 mmol) in acetic acid (15 mL) was kept at 20°C for 1 h. Upon dropwise addition of *N*-methyl-*N*-phenylhydrazine (4.10 g, 30 mmol) the color of the reaction mixture changed to red, and after 1 h the crystalline product began to separate. After 2 h ether (10 mL) was added, the precipitate was filtered off, thoroughly washed with water and dried over phosphorus pentoxide affording 6.02 g (68 %) colorless crystals (**1m**); mp 223-225°C (methanol); R_f 0.40 (ether / ethyl acetate 9:1); IR (KBr): ν 3061, 2918, 2712, 1597, 1501, 1366, 1244, 750, 694, cm^{-1}; UV ($CHCl_3$, λ_{max} (log ε)): 291.5 (4.35), 241.5 (4.26); ^{1}H-NMR (DMSO-d_6): δ 2.12 (s, 4-CH_3), 3.35 (s, NCH_3), 6.43 (d, *J* = 8.2 Hz, 2,6-H 1-NC_6H_5), 6.74 (t, *J* = 7.6 Hz, 4-H 1-NC_6H_5), 7.15 (dd, *J*= 8.2, 7.6 Hz, 3,5-H 1-NC_6H_5), 7.28-7.35 (m, 5-C_6H_5), 12.45 (br s, NH); ^{13}C-NMR: δ 9.9 (4-CH_3), 38.6 (NCH_3), 111.8, 118.6, 128.8, 147.6 (2,6-C, 4-C, 3,5-C, 1-C 1-NC_6H_5), 120.0 (4-C), 126.1 (5-C), 127.3, 128.0, 128.3, 128.8 (1-C, 4-C, 2,6-C 5-C_6H_5), 160.6 (2-C); EI-MS (*m/z* (%)): 295 (75, $M^{\bullet+}$), 190 (100, M – $C_6H_5NCH_2$), 131 (36, $C_6H_5CCCH_3NH$), 107 (18, $C_6H_5NHCH_3$), 77 (12, C_6H_5). Anal. Calcd for $C_{17}H_{17}N_3S$: C, 69.12; H, 5.80; N, 14.22; S, 10.85. Found: C, 68.92; H, 5.50; N, 14.52; S, 10.60.

4-Methyl-1-(*N*-methyl-*N*-phenylamino)-5-phenyl-1*H*-imidazole (5m): Colorless crystals (67 %); mp 110°C (methanol); R_f 0.32 (acetonitrile); IR (KBr): ν = 3115, 3041, 2918, 2874, 1597, 1496, 1300, 1095, 1032, 766 cm^{-1}; UV ($CHCl_3$, λ_{max} (log ε)): 250.0 (4.15); EI-MS (*m/z* (%)): 263 (100, $M^{\bullet+}$), 221 (23, M – CH_3CNH), 158 (58, M - $C_6H_5NCH_2$), 118 (28, $CH_3C_6H_3N_2$), 106 (68, $C_6H_5NCH_3$), 77 (36, C_6H_5). Anal. Calcd for $C_{17}H_{17}N_3$: C, 77.54; H, 6.51; N, 15.96. Found: C, 77.80; H, 6.36; N, 15.80.

2,3,3a,4-Tetrahydro-3a,6a-diphenyl-4-phenylamino-7a*H*-imidazo[4,5-*d*][1,3]thiazol-2-one (7): The general procedure was applied to **6**,[19] except the reaction time was 2 h, affording colorless crystals (98 %); mp 248°C (turning red at 199°C, decomposition starts at 221°C) (acetic acid); R_f 0.90 (acetonitrile); IR (KBr): ν = 3327, 3067, 2988, 2799, 1693, 1602, 1495, 1439, 1252, 759, 698, 642 cm^{-1};

UV ($CHCl_3$, λ_{max} (log ε)): 240.5 (3.76), 266.5 (sh, 3.28), 286.5 (sh, 3.08); ^{1}H-NMR (DMSO-d_6): δ 6.76 (t, J = 7.3 Hz, 4-H 4-NC_6H_5), 6.89 (d, J = 8.2 Hz, 2,6-H 4-NC_6H_5), 7.07-7.22 (m, 2-H, 3a-, 6a-C_6H_5, 3,5-H 4-NC_6H_5), 8.16 (s, 4-NH), 9.71 (s, 3-H); ^{13}C-NMR[23] (DMSO-d_6): δ 92.8, 93.3, 159.7, 171.4 (3a-C, 6a-C, 5-C, 2-C), 112.3, 119.4, 129.02, 148.6 (2,6-C, 4-C, 3,5-C, 1-C 4-NC_6H_5), 127.2, 127.7, 128.3, 133.9 (4-C, 2,6-C, 3,5-C, 1-C 3a-C_6H_5), 127.4, 127.6, 128.6, 128.7 (2,6-C, 3,5-C, 4-C, 1-C of 6a-C_6H_5); MS-FAB$^+$ (*m/z* (%)): 387 (100, M + 1). Anal. Calcd for $C_{22}H_{18}N_4OS$: C, 68.37; H, 4.69; N, 14.50; S, 8.30. Found: C, 68.19; H, 4.68; N, 14.90; S, 8.25.

1-(4-Methoxyphenyl)-4,5-bis[(*N*-4-methoxyphenyl)imino]-4,5-dihydro-1*H*-imidazole (10): Following the general procedure, **9**[21] was transformed into an orange-yellow crystalline product (98 %); mp 150-154°C (methanol); R_f 0.94 (acetonitrile); IR (KBr): ν = 3048, 3002, 2955, 2836 1631, 1500, 1247, 827 cm^{-1}; UV ($CHCl_3$, λ_{max} (log ε)): 241.0 (4.11), 291.5 (4.14); ^{1}H-NMR (DMSO-d_6): δ 3.68 (s, 4-, 5-CH_3OArN), 3.70 (s, 1-CH_3OAr), 6.82, 6.85, 7.35, 7.38 (AA'BB', J = 7.5 Hz,[24] 1-C_6H_4), 6.82, 6.85, 7.75, 7.78 (AA'BB' AA'BB', J = 7.5 Hz,[24] 4-, 5-NC_6H_4), 10.33 (s, 2-CH); ^{13}C-NMR[26] (DMSO-d_6): δ = 55.1 (3 CH_3OAr), 121.8, 131.0, 150.6 (2-C, 4-C, 5-C), 113.7 (3,5-C 4-, 5-NAr, 2,3,5,6-C 1-Ar), 121.5 (2,6-C 4-, 5-NAr), 154.5 (1-C 1-Ar), 155.7 (1-C 4-, 5-NAr), 158.2 (4-C 4-, 5-NAr), 160.8 (4-C 1-Ar). Anal. Calcd for $C_{24}H_{22}N_4O_3$: C, 69.55; H, 5.35; N, 13.52. Found: C, 69.75; H, 5.20; N, 13.25.

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