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Unusual methylene transfer in reactions of Simmons–Smith reagent with 1,3-diazabuta-1,3-dienes: synthesis of functionalised imidazole derivatives

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Abstract—The reactions of Simmons–Smith reagent with 1-aryl-2-phenyl-4-methylthio-4-secondary amino 1,3-diazabuta-1,3-dienes **1** underwent an unusual 1,4-methylene transfer resulting in the formation of 1-aryl-2-phenyl-4-secondary amino imidazoles **4**. Whereas, its reactions with 1-aryl-2-phenyl-4-secondary amino-1,3-diazabuta-1,3-dienes **8** underwent an initial 1,2-methylene transfer leading to an aziridine intermediate which rearranges to 1-aryl-4-phenyl-imidazoles **11**.

1. Introduction

The discovery and development of new chemical reactions is a major focus of research activity in organic chemistry. The chemical synthesis of molecules provided by nature has traditionally been the arena in which the utilities of new reactions are critically evaluated.[1] A vast array of new methods and creative strategies has arisen from this activity. The development of new strategies and reactions are stimulated by efforts to rationally design synthesis of natural and non-natural compounds with interesting molecular architectures.[1] Reactions, which form multiple bonds, rings, and/or stereocenters are particularly important tools for the efficient assembly of complex molecular structures.[2]

Since the discovery of the Simmons–Smith reagent[3] it has been widely used in the cyclopropanation of a variety of alkenes. In the case of olefins bearing heteroatomic substituents, the hetero atom reportedly co-ordinates with the reagent thereby enhancing its proximity to the π-bond, and influencing the stereochemical outcome of the reaction.[4] Accordingly, rate acceleration and stereo-directing effects of allylic alcohols and ethers were interpreted on the basis of complexation induced proximity effects.[5,6] The preferential 1,2-methylene transfer mode has also been observed in reactions of the Simmon–Smith reagents with 1,3-dienes.[7] The fascinating stereospecific methylene transfer process involved in these reactions has also attracted the attention of theoretical chemists.[8] However the reactions of this reagent with imines and azadienes appears to have evaded the attention of chemists and is an almost neglected area. The reagent reportedly fails to react with aldimines bearing aryl/alkyl substituents and to our knowledge the only known addition of the reagent to an imine involves methylene transfer from the reagent to *C*-ethoxycarbonyl-*N*-*t*-butyl imine, yielding aziridine.[9] In continuation of our efforts to develop synthetic strategies around 1,3-diazabuta-1,3-dienes, in a recent communication, we have reported[10] an unusual 1,4-methylene transfer in their reactions with the Simmons–Smith reagent. We report herein a detailed account of such methylene transfer reactions of the reagent with 1,3-diazabuta-1,3-dienes.

2. Results and discussion

The treatment of 1-aryl-2-phenyl-4-secondary amino-4-methylthio-1,3-diazabuta-1,3-diene **2** with the Simmons–Smith reagent, generated from diiodomethane and zinc–copper couple, in an ethereal solution gave good yields of 1-aryl-2-phenyl-4-secondary amino imidazoles **4**. The products were characterised on the basis of analytical data and spectral evidences. The detailed spectral features of these imidazoles are discussed in Section 4, however; only the salient features are presented here. For example, the imidazole **4a** analysed for $C_{17}H_{17}N_3$ and its mass spectrum exhibited a molecular ion peak at *m/z* 263. Its ^{1}H NMR spectrum exhibited singlets at δ 2.49 (6H) for the dimethyl amino group and at δ 6.69 (1H) for the C5-H in addition to the aromatic protons. The assigned structure was further supported by the ^{13}C NMR chemical shifts. The resonance at δ 44.32 attest to the presence of dimethylamino group. The C-5 resonance at δ 114.67 also supports the assigned structure. Multi-functionalised imidazoles so obtained are of special interest because of the wide range of biological

Keywords: Simmons–Smith reagent; imidazole derivatives; 1,4-addition; proximity effect; 1,3-diazabutadienes.

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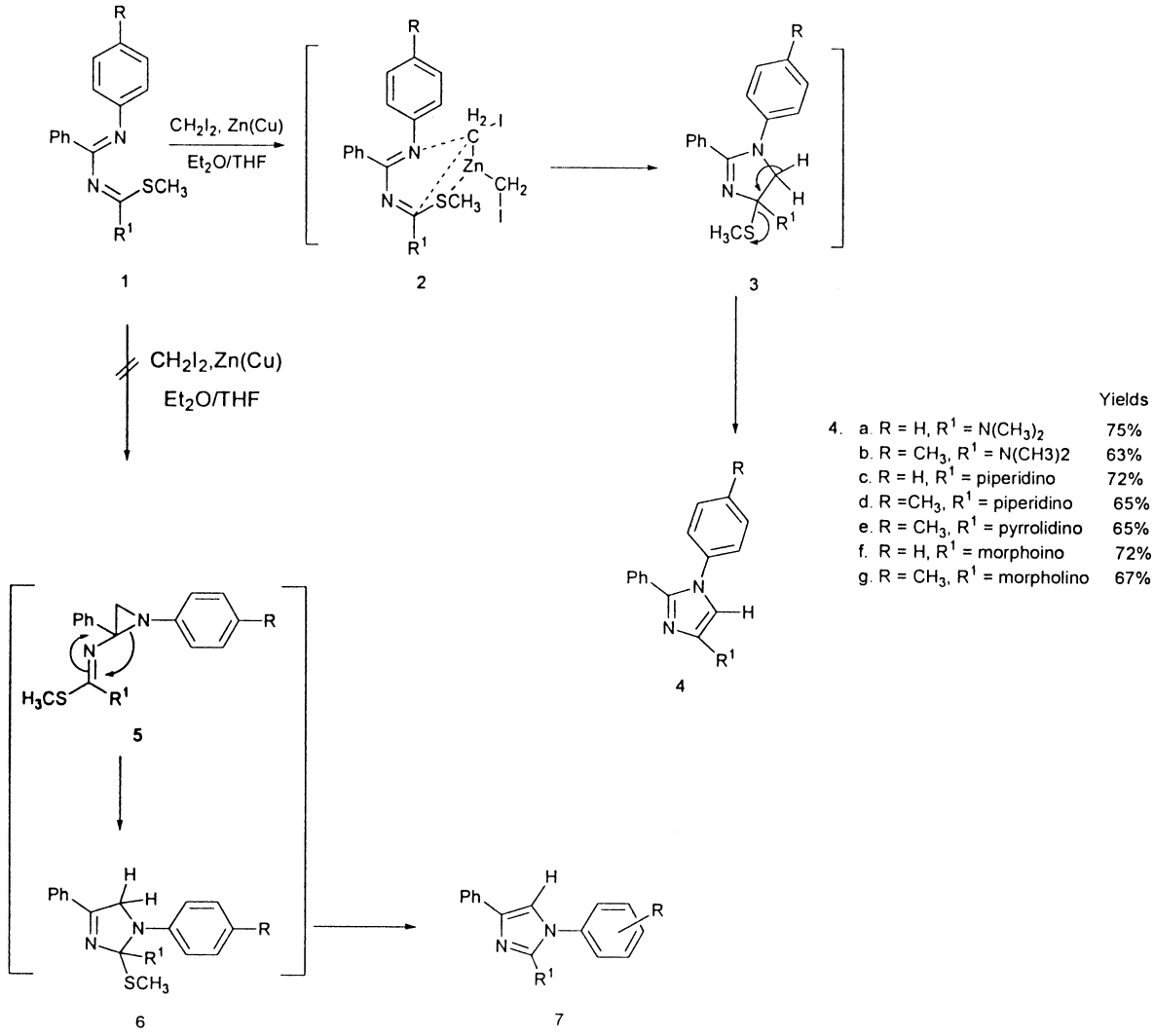
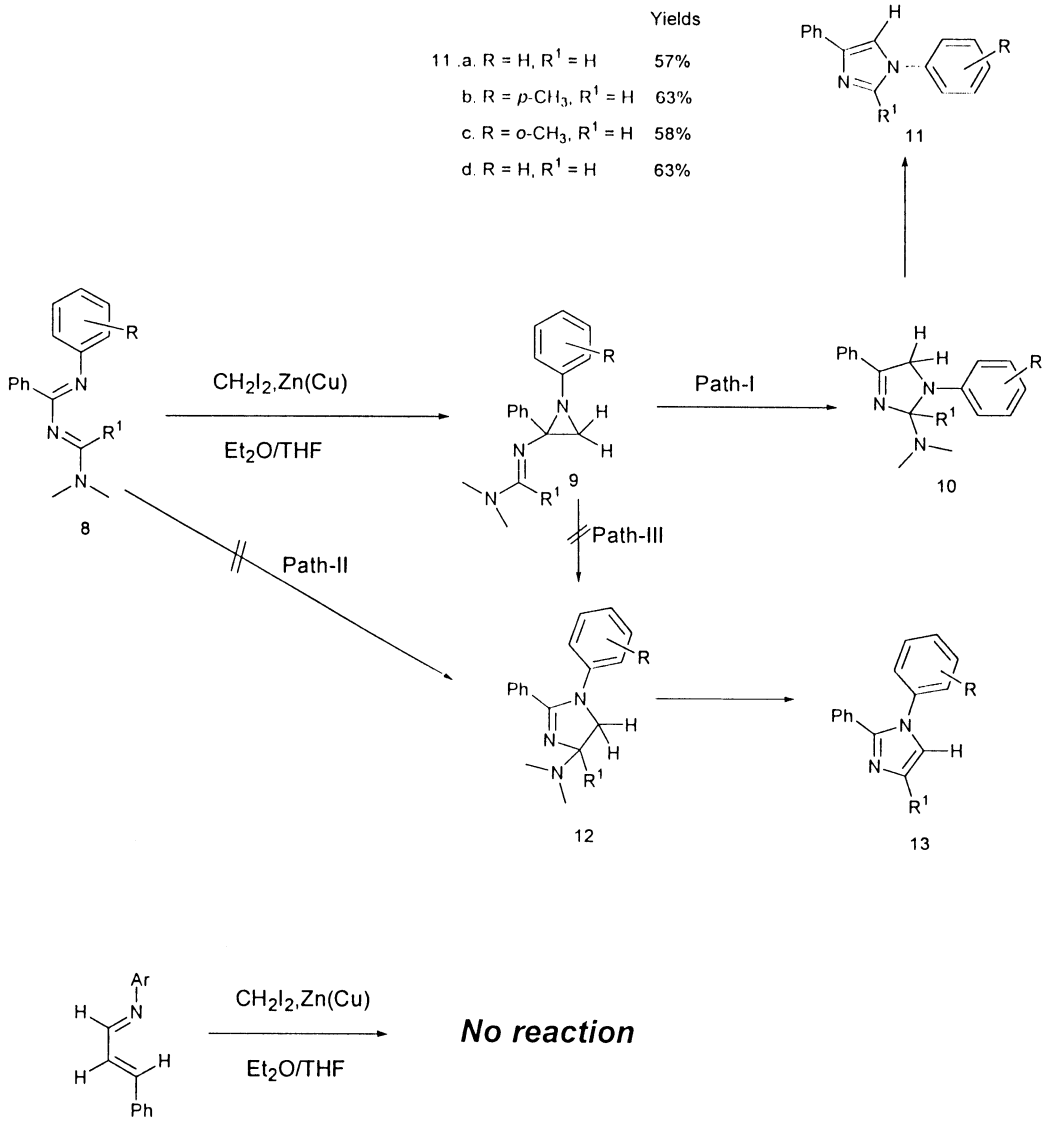


Scheme 1.

properties ascribed to such systems and consequently the search for alternative, convenient routes to their synthesis continues to be of great interest.

The plausible mechanism for the formation of imidazoles **4** is depicted in Scheme 1. In this scheme it is assumed that the Simmons–Smith reagent co-ordinates with the sulfur of the methylthio group, with simultaneous interaction of methylene with N-1 and C-4 of 1,3-diazabuta-1,3-dienes, leads to an intermediate **2**. The intermediate **2** on methylene transfer forms to another intermediate **3** which on elimination of methylmercaptan finally yields imidazole **4**. It is also likely that an initial [1+2] addition of the Simmons–Smith reagent across the carbon–nitrogen (1,2) double bond of the 1,3-diazabuta-1,3-diene may lead initially to an aziridine intermediate **5**, which rearranges to another intermediate **6** and then undergoes an elimination of methylmercaptan to yield imidazole **7**. On the basis of available analytical, ^{1}H and ^{13}C NMR spectral data it is difficult to discriminate this isomeric imidazole structure in favour of structure **5**. However, the structure **4** for the formed imidazoles is favoured over the alternative structure **7**, on the basis of mass spectral fragmentation data. For example, the compound **4a**, showed in its mass spectrum a molecular ion peak at *m/z* 263 (M^{+}, 100%), and an intense peak at *m/z* 180 (59%) corresponding to the fragment Ph-C=N-Ph^{*+} which most likely can arise only from imidazole **4a** and not from imidazole **7a**. These results assume further significance in light of the reported reactions of the Simmons–Smith reagent with α-oxoketene dithioacetals leading to thiophene derivatives via intramolecular aldol type reaction of initially formed sulfur ylides.[11] The obviation of such a possibility in present studies, despite the fact that sulfur ylide formation is reported to be much faster than carbene insertion,[12] lends further credence to the proposed double coordination of the reagent with the N1 and sulfur of the methylthio of 1,3-diazabuta-1,3-diene **1**. These observations further highlight the significance of the role the heteroatomic substitutents play in directing the methylene transfer from the Simmons–Smith reagent.

In order to have a better understanding of this mechanistically fascinating and synthetically valuable route to substituted imidazoles, we have also examined the reactions of 1-aryl-2-phenyl-4-secondary amino-1,3-diazabuta-1,3-dienes **8** with the Simmons–Smith reagent. Thus, the treatment of the Simmons–Smith reagent with 1,3-diazabuta-1,3-dienes **8** resulted in the isolation of products which



Scheme 2.

were characterised as imidazoles **11** on the basis of analytical data and spectral evidences. The detailed spectral features of these imidazoles are reported in Section 4, while the salient features are presented here. For example, the imidazole **11b** analysed for $C_{16}H_{14}N_2$ and its mass spectrum exhibited a molecular ion peak at *m/z*: 234 (M^+). Its ^1H NMR spectrum exhibited singlet at δ 2.33 (3H) for the aromatic substituted methyl group and two singlets at δ 7.03 (1H) and δ 7.05 (1H) in addition to aromatic protons. The assigned structure was further corroborated by the ^{13}C NMR and ^{13}C DEPT (135) chemical shifts. The resonance at δ 20.81 attest to the presence of aromatic substituted methyl group and the C-5 resonance at δ 120.41 and C-2 resonance at δ 129.72 further supports the assigned structure.

The plausible mechanism for the formation of imidazoles **11** is depicted in Scheme 2. In this scheme it is assumed that the Simmons–Smith reagent undergoes an initial 1,2-methylene transfer to yield aziridine intermediate **9** which undergoes dimethyl amino group assisted aziridine ring opening and its expansion to form an imidazole intermediate **10** which finally isomerises to imidazole **11**. It is also likely that these reactions may result in imidazoles **13** via elimination of dimethyl amine from initially formed imidazoline **12** as an intermediate. The formation of **12** may involve either a 1,4-methylene transfer from the Simmons–Smith reagent to 1,3-diazabuta-1,3-diene **8** (Path II) or a rearrangement involving the scission of the carbon–carbon single bond of aziridine (Path III). However, the structure **11** for the formed imidazoles was unequivocally decided on the basis of ^1H NMR spectra, which exhibited singlets for the vinylic protons instead of the doublets expected for structure **13**. The variation in the reaction pathways followed in reactions of 1,3-diazabuta-1,3-dienes **1** and **8** with the Simmons–Smith reagent may be attributed to the difference in substituents at C-4 of these 1,3-diazabuta-1,3-dienes. The presence of a strongly coordinating methylthio group in 1,3-diazabuta-1,3-diene **1** may result in a hetero-atom induced proximity effect favourable for 1,4-addition.

Surprisingly, the Simmons–Smith reagent failed to react with 1-azadiene under similar experimental conditions and may possibly be ascribed to the absence of any polar donating/co-ordinating group at C-4 and lower nucleophilicity of

the terminal nitrogen of such azadienes. This gives further credence to the requirement of suitably placed sulfur or nitrogen containing functional groups in azadienes for the realisation of 1,4 or 1,2 addition of the Simmons–Smith reagent.

3. Conclusion

The reactions of 1-aryl-2-phenyl-4-secondary amino-4-thiomethyl-1,3-diazabuta-1,3-dienes **1** with the reagent underwent an unusual 1,4-methylene transfer to yield 1-aryl-2-phenyl-4-secondary amino imidazoles **4**. Whereas, the reactions of 1-aryl-2-phenyl-4-dimethyl amino-1,3-diazabuta-1,3-dienes **8** with the reagent underwent regioselective 1,2 additions followed by rearrangement to yield 1-aryl-4-phenyl-imidazoles **11**. These investigations have shown that the hetero atom present at C-4 of 1,3-diazabuta-1,3-dienes facilitates the methylene transfer through complexation with the reagent.

4. Experimental

4.1. General

Melting points were determined by open capillary method using Veego Precision Digital Melting Point apparatus (MP-D) and are uncorrected. IR spectra were recorded on a Shimadzu D-8001 spectrophotometer. ^{1}H NMR spectra were recorded in deuterochloroform with Brucker AC-E 200 (200 MHz) spectrometer using TMS as internal standard. Chemical shift values are expressed as δ (ppm) downfield from TMS and J values are in Hz. Splitting patterns are indicated as s: singlet, d: doublet, t: triplet, m: multiplet, q: quartet and br: broad peak. ^{13}C NMR spectra were also recorded on a Brucker AC-200E (50.4 MHz) spectrometrer in deuterochloroform using TMS as internal standard. Mass spectra were recorded on Shimadzu GCMS-QP-2000 mass spectrometer. Elemental analyses were performed on Heraus CHN-O-Rapid Elemental Analyser. Column chromatography was performed on a silica gel (60–120) or Harrison Research Chromatotron using 2 mm plates (Silica gel 60 PF_{254}). THF/Diethyl ether were dried over sodiumbenzophenone ketyl and distilled under nitrogen. All manipulations were conducted over a purified nitrogen atmosphere (BASF-Catalyst-R3-11) by use of standard Schlenck techniques.

4.2. Starting materials

1-Aryl-2-phenyl-4-thiomethyl-4-secondary amino-1,3-diazabuta-1,3-dienes **1**,[13] 1-Aryl-2-phenyl-4-*N*,*N*-dimethyl-amino-1,3-diazabuta-1,3-dienes **8**,[13] were prepared by reported methods.

4.3. Reactions of Simmons–Smith reagent with 1,3-diazabuta-1,3-dienes 1

To a well stirred solution of zinc–copper couple (10 mmol) in dry ether (20 ml) under a nitrogen atmosphere a small crystal of iodine and diiodomethane (25 mmol) were added and the reaction mixture refluxed with striring for 10 min. A solution of 1,3-diazabuta-1,3-diene **1** (10 mmol) in dry THF (25 ml) was added slowly and the reaction mixture refluxed with stirring for a further period of 3–4 h. After completion of the reaction (TLC), solvent was removed under reduced pressure and the residue treated with water (100 ml) and chloroform (75 ml). The reaction mixture was filtered and the residue washed with chloroform (30 ml) and the combined organic extract was washed with water (2×50 ml), dried over anhydrous sodium sulfate and evaporated to give crude product which was purified by column chromatography over silica gel using a mixture of ethyl acetate and hexane (10:1) as eluent.

4.3.1. 1,2-Diphenyl-4-*N*,*N*-dimethylamino imidazole 4a. Yield: 75%; mp 134–136°C; Anal. Calcd for $C_{17}H_{17}N_3$: C, 77.52; H, 6.51; N, 15.96. Found: C, 77.48; H, 6.53; N, 15.99%; IR (KBr) ν_{max}: 1597, 1556, 1514, 1466, 1406, 1363 cm^{-1}; δ_H (200 MHz, $CDCl_3$): 2.49 {6H, s, $(NCH_3)_2$}, 6.69 (1H, s, C5-H), 7.15–7.27 (7H, m, ArHs), 7.36–7.42 (3H, m, ArHs); δ_C (50.4 MHz, $CDCl_3$): 44.32 {$N(CH_3)_2$), 114.67, 127.83, 127.99, 128.13, 128.55, 129.29, 137.03, 143.14, 145.53; *m*/*z*: 264 (M^++1, 20%), 263 (M^+, 100%), 248 (17%), 180 (58%), 118 (37%), 116 (12%), 89 (18%), 77 (63%).

4.3.2. 1-(*p*-Tolyl)-2-phenyl-4-*N*,*N*-dimethylamino imidazole 4b. Yield: 63%; mp 148–149°C; Anal. Calcd for $C_{18}H_{19}N_3$: C, 77.95; H, 6.90; N, 15.15. Found: C, 77.97; H, 6.98; N, 15.05%; IR (KBr) ν_{max}: 1597, 1556, 1514, 1466, 1406, 1363 cm^{-1}; δ_H (200 MHz, $CDCl_3$): 2.39 (3H, s, $-CH_3$), 2.68 {6H, s, $N(CH_3)_2$}, 6.71 (1H, s, C5-H), 7.08 (2H, d, J=8.1 Hz, ArH), 7.16 (2H, d, J=8.1 Hz, ArH), 7.21–7.28 (5H, m, ArH); δ_C (50.4 MHz, $CDCl_3$): 21.19 ($-CH_3$), 44.45, {$N(CH_3)_2$, 114.72, 127.33, 127.50, 127.76, 128.33, 129.49, 130.86, 133.92, 137.69, 142.62 and 145.53; *m*/*z*: 278 (M^++1, 21%), 277 (M^+, 72%).

4.3.3. 1,2-Diphenyl-4-piperidino imidazole 4c. Yield: 72%; mp 154–156°C; Anal. Calcd for $C_{20}H_{21}N_3$: C, 79.17; H, 6.98; N, 13.85. Found: C, 79.23; H, 6.95; N, 13.82%; IR (KBr) ν_{max}: 1597, 1559, 1520 1406 cm^{-1}; δ_H (200 MHz, $CDCl_3$): 1.44 (6H, br, $-CH_2-CH_2-CH_2-$), 2.72 (4H, br, $-CH_2-N-CH_2-$), 6.66 (1H, s, C5-H), 7.14–7.42 (10H, m, ArHs); δ_C (50.4 MHz, $CDCl_3$): 21.06 ($-CH_2-$), 25.64 ($-CH_2-$), 53.03 ($-CH_2-N-CH_2$), 114.67, 127.83, 127.99, 128.13, 128.55, 129.29, 137.03, 143.14, and 145.53; *m*/*z*: 303 (M^+).

4.3.4. 1-(*p*-Tolyl)-2-phenyl-4-piperidino imidazole 4d. Yield: 65%; mp 164–165°C; Anal. Calcd for $C_{21}H_{23}N_3$: C, 79.46; H, 7.30; N, 13.24. Found: C, 79.45; H, 7.34; N, 13.21%; IR (KBr) ν_{max}: 1597, 1556, 1514, 1466, 1406, 1364 cm^{-1}; δ_H (200 MHz, $CDCl_3$): 1.43 (6H, br, $-CH_2-CH_2-CH_2-$), 2.39 (3H, s, $-CH_3$), 2.71 (4H, br, $-CH_2-N-CH_2-$), 6.72 (1H, s, C5-H), 7.09 (2H, d, J=8.3 Hz, ArH), 7.18 (2H, d, J=8.3 Hz, ArH), 7.21–7.29 (5H, m, ArH); δ_C (50.4 MHz, $CDCl_3$): 21.09 (–CH2–), 23.76 ($-CH_2-$), 25.64 ($-CH_3$), 53.03 ($-CH_2-N-CH_2-$), 114.67 (C5), 127.83, 127.99, 128.13, 128.55, 129.29, 137.03, 143.14, 145.53; *m*/*z*: 318 (M^++1, 27%), 317 (M^+, 100%), 207 (9%).

4.3.5. 1-(*p*-Tolyl)-2-phenyl-4-pyrrolidino imidazole 4e. Yield: 65%; mp 147–148°C; Anal. Calcd for $C_{20}H_{21}N_3$: C,

79.17; H, 6.98; N, 13.85. Found: C, 79.20; H, 6.92; N, 13.90%; IR (KBr) ν_{max}: 1597, 1556, 1514, 1466, 1406, 1363 cm^{-1}; δ_H (200 MHz, $CDCl_3$), 1.77 (4H, br, $-CH_2-CH_2-$), 2.36 (3H, s, $-CH_3$), 3.08 (4H, br, $-CH_2-N-CH_2-$), 6.72 (1H, s, C5-H), 7.09 (2H, d, J=8.3 Hz, ArH), 7.18 (2H, d, J=8.3 Hz, ArH), 7.21–7.29 (5H, m, ArH); δ_C (50.4 MHz, $CDCl_3$): 21.09 ($-CH_2-CH_2-$), 25.64 ($2\times-CH_2-$), 48.7 ($-CH_2-N-CH_2-$), 114.67 (C-5), 127.83, 127.99, 128.13, 128.55, 129.29, 137.03, 143.14, 145.53; *m/z*: 304 (M^++1, 27%), 303 (M^+, 73%).

4.3.6. 1,2-Diphenyl-4-morpholino imidazole 4f. Yield: 72%: mp 103–105°C; Anal. Calcd for $C_{19}H_{19}N_3O$: C, 74.73; H, 6.27; N, 13.76. Found: C, 74.77; H, 6.30; N, 13.79%; IR (KBr) ν_{max}: 1597, 1556, 1514, 1466, 1406, 1363 cm^{-1}; δ_H (200 MHz, $CDCl_3$): 3.70 (4H, m, $-CH_2-N-CH_2-$), 3.93 (4H, m, $-CH_2-O-CH_2-$), 6.84 (d, J=7.5 Hz), 7.03–7.48 {9H, m, consisting in at 7.12 (1H, s, C5-H) ArH}; *m/z*: 305 (M^+).

4.3.7. 1-(*p*-Tolyl)-2-phenyl-4-morpholino imidazole 4g. Yield: 67%; mp 132–133°C. Anal. Calcd For $C_{20}H_{21}N_3O$: C, 75.21; H, 6.63; N, 13.16. Found: C, 75.24; H, 6.68; N, 13.20%; IR (KBr) ν_{max}: 1597, 1561, 1516, 1466, 1406, 1331 cm^{-1}; δ_H (200 MHz, $CDCl_3$): 2.25 (3H, s, $-CH_3$), 3.66 (4H, br, $-CH_2-N-CH_2-$), 3.91 (4H, br, $-CH_2-O-CH_2-$), 6.72 (2H, d, J=8.2 Hz, ArH), 6.93 (2H, d, J=8.2 Hz, ArH), 7.21–7.45 {10H, m, consisting in at 7.28 (1H, s, C5-H), ArH}; δ_C (50.4 MHz, $CDCl_3$): 20.66 ($-CH_3$), 42.3 ($-CH_2-N-CH_2-$), 45.4 ($-CH_2-O-CH_2-$), 123.5, 127.8, 129.2, 130.0, 134.2, 136.3, 163.4, 164.0; *m/z*: 319 (M^+, 7.5%), 237 (100%), 236 (83%).

4.3.8. 1,4-Diphenyl-imidazole 11a. Yield: 57%; mp 132–133°C; Anal. Calcd for. $C_{15}H_{12}N_2$: C, 81.79; H, 5.49; N, 12.72. Found: C, 81.82; H, 5.52; N, 12.67%; IR (KBr) ν_{max}: 1566, 1497, 1467, 1396, 1363 cm^{-1}; δ_H (200 MHz, $CDCl_3$): 6.99–7.37 {11H, m, consisting in at 7.02 (1H, 9 s, C3-H) and 7.03 (1H, s, C5-H) ArH)}; *m/z*: 221 (M^++1, 12%), 220 (M^+,72%).

4.3.9. 1-(*p*-Tolyl)-4-phenyl-imidazole 11b. Yield: 63%; mp 106–107°C; Anal. Calcd for $C_{16}H_{14}N_2$: C, 82.05; H, 5.98; N, 11.97. Found: 82.06; H, 6.05; N, 11.89%; IR (KBr) ν_{max}: 1565, 1496, 1464, 1410, 1307%; δ_H (200 MHz, $CDCl_3$): 2.33 (3H, s, $-CH_3$), 6.97–7.31{10H, m, consisting in at 7.04 (1H, s, C3-H) and 7.07 (1H, s, C5-H) ArH}; δ_C: 20.8 (q, $-CH_3$), 122.6 (d), 125.3 (d), 127.8 (d), 128.0 (d), 128.3 (d), 128.4 (d), 129.8 (d), 129.9 (s), 135.7 (s), 137.7 (s), 146.1 (s); *m/z*: 235 (M^++1, 17%), 234 (M^+, 100%), 233 (94%).

4.3.10. 1,4-Diphenyl-2-methyl imidazole 11c. Yield: 58%; mp 67–68°C; Anal. Calcd for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02; N, 11.96. Found: 82.05; H, 6.06; N, 11.89%; IR (KBr) ν_{max}: 1568, 1496, 1464, 1410, 1307 cm^{-1}; δ_H (200 MHz, $CDCl_3$): 1.93 (3H, s, $-CH_3$), 6.98 (1H, s, C2-H), 7.19 {10H, m, consisting in at 7.22 (1H, s, C5-H) ArH}; δ_C: 17.3 (q, $-CH_3$), 122.3 (d), 126.8 (d), 127.2 (d), 127.3 (d), 127.9 (d), 128.8 (d), 128.9 (d), 130.4 (s), 131.0 (d), 134.8 (s), 137.9 (s) and 146.5 (s); *m/z*: 235 (M^++1, 17%), 234 (M^+, 100%), 233 (31%), 219 (36%), 206 (41%).

4.3.11. 1-(*o*-Tolyl)-4-phenyl-imidazole 11d. Yield: 63%; mp 87–89°C; Anal. Calcd for $C_{16}H_{14}N_2$: C, 82.05; H, 5.98; N, 11.97. Found: 82.09; H, 6.02; N, 11.89%; IR (KBr) ν_{max}: 1566, 1497, 1466, 1398, 1363 cm^{-1}; δ_H (200 MHz, $CDCl_3$): 2.01 (3H, s, $-CH_3$), 6.92 (1H, s, C5-H), 7.10–7.39 (10 H, m, ArH); δ_C: 10.3 (q, $-CH_3$), 126.5 (d), 127.9 (d), 128.1 (d), 128.6 (d), 129.5 (d), 130.2 (s), 130.9 (s), 137.6 (s), 146.8 (s); *m/z*: 235 (M^++1, 15%), 234 (M^+, 92%), 233 (100%).

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