Synthesis of functionalised cyclic nitrones *via* regioselective and unusual [3 + 2] cycloadditions of α-nitrosostyrenes with 1,3-diazabuta-1,3-dienes and imines

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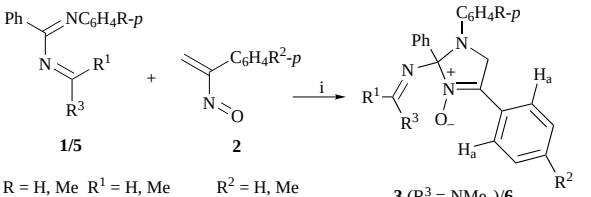
The α-nitrosostyrenes 2, generated *in situ* from α-halogeno oximes, undergo regioselective [3 + 2] cycloaddition with 1,3-diazabuta-1,3-dienes 1 and 5 leading to the cyclic nitrones 3 and 6, respectively. Similarly, the cyclic nitrones 12 are also formed in reactions of 2 with the trisubstituted amidines 11. Thermolysis of the nitrones 3 and 12d–f gives imidazole derivatives 13. The nitrones 6, on the other hand, on thermolysis under similar conditions, give the amidine derivatives 17. Interestingly, the treatment of both 3 and 6 with $NaBH_4$ in methanol and the reactions of 2 with *N*-arylbenzamidines also yield the imidazole derivatives 13.

The nitroso group is known to participate effectively as a 2π component in Diels–Alder cycloadditions.[1] On the other hand nitrosoalkenes, usually generated *in situ* by the reactions of α-halogeno ketoximes with bases,[2] have been successfully trapped as 4π components in Diels–Alder cycloadditions with a variety of polarised and unpolarised alkenes,[2] allenes[3] and all-carbon dienes.[4] In almost all these cases, the major isolable product is an oxazine derivative. Recently, an unusual [3 + 2] cycloaddition has been observed in the reactions of α-nitrosostyrenes with a carbon–carbon double bond attached to the pyrimidinone ring.[5]

There are numerous reports concerning the cycloadditions of α-nitrosostyrenes with carbon–carbon double bonds. In contrast, the reports concerning the cycloadditions with carbon–nitrogen double bonds are very rare.[6] Mackay *et al*., while investigating the reactions of 2,5-dimethylfuran with α-nitrosoalkenes, isolated, in addition to an oxazine derivative, a second product, a cyclic nitrone, arising from [3 + 2] cycloaddition of the second nitrosoalkene molecule with the oxazine derivative. However, the authors failed to observe the reactions of α-nitrosoalkenes with various cyclic and acyclic models bearing a carbon–nitrogen double bond and hence such a cycloaddition mode could not be generalised. Thus, they concluded that the preliminary requirement for such reactions are (i) oxazine oxygen and (ii) an alkene function allylic to this oxygen in a rigid bicyclic system.

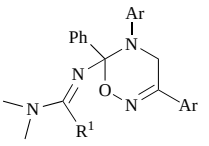
The observed formation of cyclic nitrones resulting from the [3 + 2] cycloaddition of nitrosoalkene is thought to be of great synthetic utility since the methods of preparing such nitrones, which can provide a flexible entry into a range of heterocyclic targets, are limited to a relatively few routes.[7–10] Since so little was known about the cycloadditions of carbon–nitrogen double bonds with nitrosoalkenes and because of the reported structural limitations upon the carbon–nitrogen double bond systems for carrying out such cycloadditions, we earlier investigated the reactions of 1,3-diazabuta-1,3-dienes and amidines with α-nitrosostyrenes.[11] Here we report further work in this area in which we have attempted to generalise the observed cycloaddition pathway.

The 1,3-diazabuta-1,3-dienes **1** reacted with the nitrosostyrenes **2**, generated *in situ* from α-halogeno oximes and sodium carbonate, in methylene chloride, to give good yields



1 R = H, Me R^1 = H, Me R^2 = H, Me
R^3 = NMe_2
5 R = H, Me R^1 = SMe, SEt
R^3 = Secondary amine

3a R = R^1 = R^2 = H
b R = Me, R^1 = R^2 = H
c R = Cl, R^1 = R^2 = H
d R = Br, R^1 = R^2 = H
e R = R^1 = H, R^2 = Me
f R = R^2 = Me, R^1 = H
g R = Cl, R^1 = H, R^2 = Me
h R = Br, R^1 = H, R^2 = Me
i R = R^1 = Me, R^2 = H
j R = R^1 = R^2 = Me



4

6
a R = R^2= H, R^1 = SMe, R^3 = Mor
b R = R^2 = H, R^1 = SMe, R^3 = Pip
c R = R^2 = H, R^1 = SMe, R^3 = Pyr
d R = R^2 = H, R^1 = SMe, R^3 = NMe_2
e R = Me, R^1 = SMe, R^2= H, R^3 = Mor
f R = Me, R^1 = SMe, R^2 = H, R^3 = Pip
g R = Me, R^1 = SMe, R^2 = H, R^3 = Pyr
h R = Me, R^1 = SMe, R^2 = H, R^3 = NMe_2
i R = R^2 = H, R^1 = SEt, R^3 = Mor
j R = R^2 = H, R^1 = SEt. R^3 = Pyr
k R = H, R^1 = SMe, R^2 = Me, R^3 = Mor
l R = R^2 = Me, R^1 = SMe, R^3 = Mor
m R = R^2 = Me, R^1 = SMe, R^3 = Pip
n R = R^2 = Me, R^1 = SMe, R^3 = Pyr
o R = R^2 = Me, R^1 = SMe, R^3 = NMe_2
p R = Cl, R^1 = SMe, R^2 = H, R^3 = Pip
q R = Cl, R^1 = SMe, R^2 = Me, R^3 = NMe_2
r R = Cl, R^1 = SEt, R^2 = H, R^3 = Pyr
s R = Cl, R^1 = SEt, R^2 = H, R^3 = NMe_2

Scheme 1 *Reagents and conditions:* i, Na_2CO_3, CH_2Cl_2, 34–48 h (Mor = morpholino, Pyr = pyrrolidinyl, Pip = piperidino)

(78–93%) of the cyclic nitrones **3** (Scheme 1). The products were characterised as 1,4-diaryl-2-(dimethylaminomethyleneamino/dimethylaminoethylideneamino)-2-phenyl-1,2-dihydro-5*H*-imidazole 3-oxides **3** on the basis of analytical and spectral data. The detailed spectral features are discussed in the Experimental section, only the salient features being mentioned here. Their IR spectra showed strong absorptions around 1590 and 1521 cm^{-1} and *ca.* 1220 cm^{-1} ascribed to C=N and N–O of a nitrone, respectively. The nitrone structure **3**, as opposed to the oxadiazine structure **4**, for the products was supported by the ^1H NMR signals for the methylene and *ortho* phenyl protons of the nitrone ring. The former gave an AB quartet (unresolved at 90 MHz but resolved at 200 MHz) at δ *ca.* 4.95

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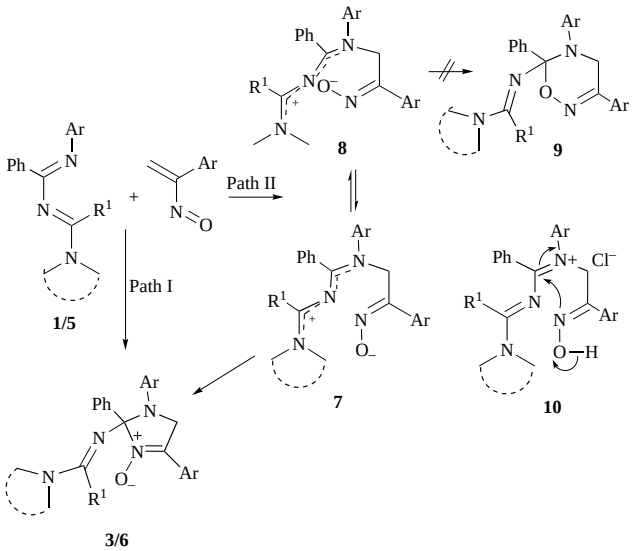
(*J* 14.4 Hz) downfield from the position, δ *ca.* 3.50, typical of oxadiazine.[6a] Similarly, the *ortho* protons of the phenyl group attached to the nitrone ring resonated at δ *ca.* 8.40 downfield from the corresponding signals, δ *ca.* 7.70 of typical oxazines.[2b] The signals around δ 140 and 160 in their ^{13}C NMR spectra were assigned to nitrone carbon and amidino carbon, respectively. Their mass spectra exhibited intense M − 16 peaks diagnostic of nitrones,[6a] in addition to strong M − amidino and imidazole ion peaks. The oxadiazine structure **4** thus was clearly ruled out on the basis of the above spectral information.

Further to our studies on such regioselective [3 + 2] cycloadditions, we examined the reactions of α-nitrososostyrenes with various 1-aryl-4-secondary amino-4-alkylthio-2-phenyl-1,3-diazabuta-1,3-dienes **5** having two polarising functions at the 4-position. Thus, the reactions of α-nitrosoalkenes with 1,3-diazabuta-1,3-dienes **5**, performed under similar conditions, were found to follow a similar regioselective [3 + 2] cycloaddition pathway to yield the nitrones **6** in almost quantitative yields (Scheme 1). The reaction products were characterised as 1,4-diaryl-2-phenyl-2-[(methylthio) secondary aminomethyleneamino]-1,2-dihydro-5*H*-imidazole 3-oxides **6** on the basis of analytical and spectral observations. The ^{1}H NMR spectra (90 MHz, $CDCl_3$) of these nitrones exhibited a two-proton doublet/multiplet centred around δ 8.40, assigned to two *ortho* phenyl protons H_a characteristic of cyclic nitrones. The methylene protons appeared, in these cases, as a singlet around δ 5.00.

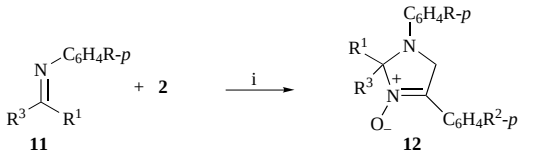
A possible mechanism leading to the formation of nitrones **3** and **6** is illustrated in Scheme 2. The addition of nitrosoalkenes



Scheme 2

to a C=C bond has been reported to be a single-step reaction,[12] which is less likely in the case of addition to a more polar C=N bond of diazabuta-1,3-dienes. Hence, the possibility of path I in these cases is ruled out. α-Nitrososostyrene is known to react with morpholine[13] preferentially in the *transoid* form and may also do so with weakly nucleophilic N-1, which is more nucleophilic as compared to N-3 of 1,3-diazabuta-1,3-dienes. Hence, these reactions may follow path II leading to resonance stabilised zwitterionic intermediate **7** which then leads to the preferential formation of the nitrones **3** and **6**. Even though intermediate **7** may be preferred, still a crossover mechanism between the intermediates **7** and **8** is possible, which could result in a six-membered oxadiazine ring structure **9**. The crossing over of the zwitterionic intermediate **7** to **8** perhaps is discouraged due to steric constraints as evidenced by the total absence of oxadiazines **9**. Thus, the nitrones are probably the result of the formal [3 + 2] dipolar addition of free α-nitrostyrene in a 1,3-mode to a 1,2-carbon–nitrogen double bond of the polarised 1,3-diazabuta-1,3-dienes. The formation of the nitrones may also be explained by the initial formation of a resonance-stabilised cationic intermediate **10** *via* nucleophilic displacement of halide by N-1 of 1,3-diazabuta-1,3-dienes **1** and **5** from α-chloroacetophenone oxime. The intermediates **10** after possible deprotonation may then cyclise to yield the nitrones **3** and **6**. Analogies to such a two-step cyclisation of α-chloro oximes are known[14] including ones to *N*-oxides.[15] However, in all such cases, a recognisably strong nucleophile is involved and it is unlikely that weaker nucleophiles like N-1 of imino nitrogen in the present case could behave in a similar fashion. This is also in agreement with the earlier conclusions drawn about the intermediacy of nitrososostyrenes under similar reaction conditions.[6a]

In view of the above observations, it was felt that all polarised carbon–nitrogen double bonds might perhaps behave in a similar fashion with addition to α-nitrosoalkenes in a similar [3 + 2] manner. Hence, in order to generalise the synthetic versatility of this reaction we have examined the reactions of the α-nitrososostyrenes **2** with *N*,*N*,*N*′-trisubstituted amidines **11**. As expected, these reactions were also found to follow the unusual and exclusive [3 + 2] cycloaddition mode resulting in good yields of the nitrones **12** (Scheme 3) which were character-



R = H, Me
R^1 = H, Ph
R^3 = NMe_2, Pyr, Pip

11,12a R = R^1 = R^2 = H, R^3 = NMe_2
b R = Me, R^1 = R^2 = H, R^3 = NMe_2
c R = R^1= H, R^2 = Me, R^3 = NMe_2
d R = H, R^1 = Ph, R^2 = Me, R^3 = Pyr
e R = R^2 = H, R^1 = Ph, R^3 = Pip
f R = H, R^1 = Ph, R^2 = Me, R^3 = Pip

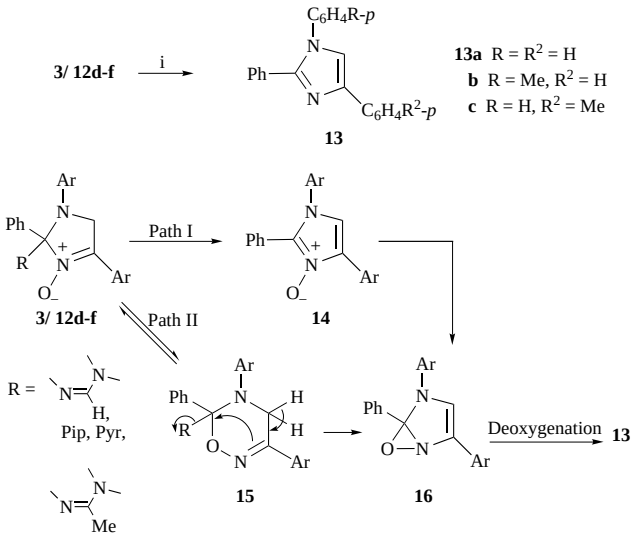
Scheme 3 *Reagents and conditions:* i, Na_2CO_3, CH_2Cl_2, 40–52 h

ised on the basis of analytical and spectral data. Interestingly, the ^{1}H NMR (300 MHz) spectrum of **12b** indicated that two methylene protons couple with each other as well as with the methine proton and appeared as a doublet of doublets. The corresponding coupling constants are also exhibited by the methine proton signal which couple with both methylene protons and appear as a doublet of doublets. Further support for this was derived from the ^{1}H NMR spectrum of **12d** in which the two methylene protons appeared as doublets instead of a doublet of doublets. In contrast to the formation of nitrones in the above reactions, Nakanishi *et al.*[16] reported the formation of imidazole derivatives probably *via* oxadiazines, in the reactions of α-halogeno oximes with *N*-phenyl-*N*-methylbenzamidines in the presence of iron carbonyls.

The structures **3**, **6** and **12** for cyclic nitrones were further confirmed by thermal degradation studies. Thermolysis of the nitrones **3** in dry benzene in a sealed tube at 140–150 °C for 6–7 h resulted in the isolation of products which were characterised as 1,4-diaryl-2-phenylimidazoles on the basis of analytical data and spectral evidences. Compound **13a**, for example, had an analysis consistent with its formation as $C_{21}H_{16}N_2$ and exhibited a molecular ion peak at *m*/*z* 296. Its ^{1}H NMR spectrum showed both the absence of a formamidino unit and the presence of two downfield (*ca.* δ 7.92) *ortho* phenyl protons together with a multiplet consisting of other aromatic protons and an olefinic proton. The products **13** were initially assigned the corresponding *N*-oxide structures **14**[11] because of expected similar spectral features and the tendency of nitrones to show the absence of a molecular ion peak and the presence of intense M^+ − 16 peaks in their mass spectra. However, elemental analysis, which indicated the absence of oxygen in these compounds, and other spectroscopic features are more consistent with the revised structure **13**.

To gain insight into the mechanism of formation of product

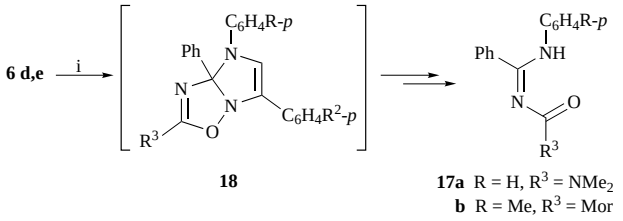
13, the thermolysis of imidazole *N*-oxides **12d**–**f** was carried out under similar conditions. Interestingly, this also resulted in the formation of the imidazoles **13**. The formation of **13** by the thermolysis of **3** and **12d**–**f** may possibly arise *via* any of the two paths illustrated in Scheme 4. Path I assumes the initial



Scheme 4 *Reagents and conditions:* i, Sealed tube, 140–150 °C, C_6H_6, 6–7 h

elimination of a dimethylaminomethyleneamino/dimethylaminoethylideneamino/secondary amino moiety to give the *N*-oxide **14**, which is then transformed into a bicyclic intermediate **16** and finally deoxygenated to yield **13**. Path II proposes that the nitrones **3** and **12d**–**f**, at elevated temperatures, are interconvertible with the corresponding oxadiazines **15**. Elimination of a formamidino/acetamidino/secondary amino moiety from this oxadiazine intermediate **15** leads to the bicyclic intermediate **16** which then undergoes the customary deoxygenation to give **13**. Pathway II seems to be more plausible because such nitrone to oxazine[17] and oxazine to imidazole[16] interconversions are already known in the literature.

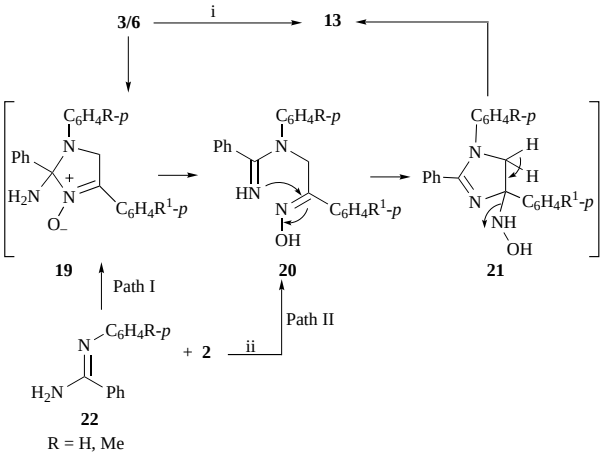
However, the thermolysis of the nitrones **6**, under similar conditions, yielded the amidine derivatives **17** (Scheme 5).



Scheme 5 *Reagents and conditions:* i, Sealed tube, 140–150 °C, C_6H_6, 6–7 h

Structure **17** was readily established on the basis of analytical and spectral evidence. Compound **17a**, for example, showed a molecular ion peak at *m*/*z* 267 and IR absorptions at 3422br and 1635 cm^{-1} assigned to NH and CO groups respectively. Its ^1H NMR spectrum exhibited the absence of alkylthio and the presence of dimethylamino protons, in addition to an exchangeable proton (δ 12.40). The mechanism involved in the transformation of nitrones **6** to **17** is not well understood. However, it is assumed that there might be an initial attack of *N*-oxide oxygen on the imino carbon leading to an intermediate **18** which on subsequent degradation might yield the products **17**.

Interestingly, the treatment of both the nitrones **3** and **6** with sodium borohydride in methanol at room temperature for 20–22 h resulted again in the isolation of the imidazoles **13**. The plausible mechanistic pathways involved in this transformation are shown in Scheme 6. In this mechanism it is assumed that the



Scheme 6 *Reagents and conditions:* i, $NaBH_4$, MeOH, RT, 20–22 h; ii, Na_2CO_3, CH_2Cl_2, 2–3 h

sodium borohydride reduction of the amidino carbon–nitrogen double bond of the nitrones **3** and **6** leads initially to the 2-amino *N*-oxide intermediate **19**, which, probably being unstable, is transformed into the intermediate **20**. The intermedate **20** then cyclises, as shown, to yield another intermediate **21** which ultimately undergoes elimination of H_2NOH to yield the imidazoles **13**. The mechanistic paths I and II proposed earlier (Scheme 4) for the transformation of imidazole *N*-oxides into the imidazoles **13** may be ruled out in this case because the conversion of *N*-oxide intermediate **14** into bicyclic intermediate **16** (Path I) and interconversion of nitrones to oxazines (Path II) are less likely at room temperature.

In order to confirm the mechanism proposed above, we have investigated the reactions of simple *N*-arylbenzamidines **22** with α-nitrosostyrenes **2**. It was thought that the absence of any *N*-oxide **19** should confirm its unstable nature and the formation of the imidazoles **13** could confirm the mechanism proposed in Scheme 6. The reaction of **22** with **2** resulted in the isolation of the expected imidazoles **13**. The formation of **13** in this case could either be explained *via* the intermediates **19**, **20** and **21** (Path I) or *via* initial displacement of halide from the α-chloro oxime leading to the intermediate **20** which by the depicted path II then yields **13** *via* **21** (Scheme 6).

In conclusion, the reactions of various polarised 1,3-diazabuta-1,3-dienes and amidines with α-nitrosostyrenes undergo regioselective and unusual [3 + 2] cycloadditions and offer an interesting route to a variety of substituted cyclic nitrones. The thermolysis of most of these cyclic nitrones resulted in the formation of imidazole derivatives *via* oxazine intermediates.

Experimental

Melting points were determined with a Toshniwal melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 983 Infrared Spectrophotometer. ^1H NMR spectra were recorded in deuteriochloroform, with a Varian 390 (90 MHz) and Bruker AC-F 300 (300 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, q = quartet, m = multiplet and br = broad. ^{13}C NMR spectra were also recorded on a Bruker AC-F 300 spectrometer in deuteriochloroform using TMS as internal standard. Mass spectra were obtained by electron impact at 70 eV. Column chromatography was performed on silica gel 60–120 mesh.

Starting materials

All the 1,3-diazabuta-1,3-dienes **1**, **5**,[18] *N*-arylformamidines

11a–c,[19] *N*-arylbenzamidines **22**,[20] and the chloro oximes **2**[21] of acetophenone and *p*-methylacetophenone were prepared by reported procedures.

General procedure for the preparation of *N*-aryl-2-secondary amino benzamidines 11d–f

A solution of imidoyl chloride (10 mmol) and secondary amine (22 mmol) in THF (30 ml) was stirred at room temperature (RT) for 3 h. The reaction mixture was then filtered and the residue washed with THF (10 ml). The combined filtrates were concentrated *in vacuo* and the residue thus obtained was diluted with CH_2Cl_2 (30 ml), washed with water (3 × 100 ml), dried (Na_2SO_4) and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel.

Reactions of 1,3-diazabuta-1,3-dienes 1 and 5 with α-nitroso-styrenes 2

General procedure for nitrones 3 and 6. A solution of the 1,3-diazabuta-1,3-diene **1/5** (4.0 mmol) and the α-chloro oxime (4.2 mmol) in dry CH_2Cl_2 (40 ml) was stirred at RT in the presence of anhydrous sodium carbonate (6 mmol) for 34–48 h. The deposited salt and excess of sodium carbonate were filtered off and washed with small portions (2 × 10 ml) of CH_2Cl_2. The combined filtrates were washed with water, dried (Na_2SO_4) and concentrated under reduced pressure. Trituration of the residue with ether gave the crude product which was recrystallised from benzene–hexane (2:1).

2-(Dimethylaminomethyleneamino)-1,2,4-triphenyl-1,2-dihydro-5*H*-imidazole 3-oxide 3a. Yield 80%; mp 131–132 °C (Found: C, 75.52; H, 6.31; N, 14.60. $C_{24}H_{24}N_4O$ requires C, 74.96; H, 6.30; N, 14.58); ν_{max}/cm^{-1} (KBr) 1591, 1525 and 1225; δ_H(90 MHz) 2.81–2.93 [br d, 6H, N(CH$_3$)$_2$], 4.93–4.97 (unresolved ABq, 2H, CH$_2$), 6.72–6.80 (m, 2H, ArH), 7.01–7.43 (m, 9H, ArH), 7.48 (s, 1H, N=CH), 7.60–7.74 (m, 2H, ArH) and 8.30–8.43 (d, *J* 8.0, 2H, ArH); δ_C(75.5 MHz) 49.2, 51.0 [N(CH$_3$)$_2$], 66.8 (C-5), 100.9 (C-2), 113.1 (C-8/8′), 118.2 (C-10), 140.5, 141.2, 141.5 (C-7/8/9), 133.2 (C-6), 126.8, 127.9, 128.2, 128.7, 128.8, 130.5 and 160.7 (C-12); *m*/*z* 384 (M$^+$).

2-(Dimethylaminomethyleneamino)-2,4-diphenyl-1-(*p*-tolyl)-1,2-dihydro-5*H*-imidazole 3-oxide 3b. Yield 86%; mp 151 °C (Found: C, 75.50; H, 6.57; N, 14.00. $C_{25}H_{26}N_4O$ requires C, 75.35; H, 6.58; N, 14.07); ν_{max}/cm^{-1} (KBr) 1597, 1520 and 1221; δ_H(90 MHz) 2.42 (s, 3H, CH$_3$), 2.86–2.97 [br d, 6H, N(CH$_3$)$_2$], 4.85–4.93 (unresolved ABq, 2H, CH$_2$), 6.66–6.80 (m, 2H, ArH), 7.03–7.36 (m, 8H, ArH), 7.51 (s, 1H, N=CH), 7.56–7.88 (m, 2H, ArH) and 8.23–8.33 (d, *J* 8.0, 2H, ArH); δ_C(75.5 MHz) 20.2 (CH$_3$), 34.4 and 40.3 [N(CH$_3$)$_2$], 50.5 (C-5), 104.2 (C-2), 113.8 (C-7), 127.0, 127.4 (C-8/10), 131.7 (C-9), 139.9, 140.1 (C-4/6), 126.7, 128.0, 128.2, 128.5, 128.7, 129.2, 130.4 and 154.8 (C-12); *m*/*z* 398 (M$^+$).

1-(*p*-Chlorophenyl)-2-(dimethylaminomethyleneamino)-2,4-diphenyl-1,2-dihydro-5*H*-imidazole 3-oxide 3c. Yield 76%; mp 188–189 °C (Found: C, 69.10; H, 5.53; N, 13.42. $C_{24}H_{23}N_4OCl$ requires C, 68.87; H, 5.54; N, 13.38); ν_{max}/cm^{-1} (KBr) 1589, 1521 and 1223; δ_H(90 MHz) 2.85–2.92 [br d, 6H, N(CH$_3$)$_2$], 4.92–4.95 (unresolved ABq, 2H, CH$_2$), 6.66–6.76 (m, 2H, ArH), 7.03–7.36 (m, 8H, ArH), 7.54 (s, 1H, N=CH), 7.57–7.70 (m, 2H, ArH) and 8.33–8.43 (d, *J* 8.0, 2H, ArH); *m*/*z* 418 (M$^+$).

1-(*p*-Bromophenyl)-2-(dimethylaminomethyleneamino)-2,4-diphenyl-1,2-dihydro-5*H*-imidazole 3-oxide 3d. Yield 78%; mp 193–194 °C (Found: C, 62.01; H, 4.91; N, 12.14. $C_{24}H_{23}N_4OBr$ requires C, 62.32; H, 5.02; N, 12.12); ν_{max}/cm^{-1} (KBr) 1586, 1521 and 1225; δ_H(90 MHz) 2.85–3.00 [br d, 6H, N(CH$_3$)$_2$], 4.92–4.95 (unresolved ABq, 2H, CH$_2$), 6.63–6.73 (m, 2H, ArH), 7.20–7.56 (m, 9H, ArH and N=CH), 7.58–7.70 (m, 2H, ArH) and 8.30–8.43 (d, *J* 8.0, 2H, ArH); *m*/*z* 463 (M$^+$).

2-(Dimethylaminomethyleneamino)-1,2-diphenyl-4-(*p*-tolyl)-1,2-dihydro-5*H*-imidazole 3-oxide 3e. Yield 85%; mp 149–150 °C (Found: C, 75.10; H, 6.56; N, 14.10. $C_{25}H_{26}N_4O$ requires C, 75.35; H, 6.58; N, 14.06); ν_{max}/cm^{-1} (KBr) 1593, 1519 and 1223; δ_H(90 MHz) 2.38 (s, 3H, CH$_3$), 2.80–3.00 [br d, 6H, N(CH$_3$)$_2$], 4.93–5.00 (unresolved ABq, 2H, CH$_2$), 6.63–6.76 (m, 2H, ArH), 7.03–7.40 (m, 8H, ArH), 7.50 (s, 1H, N=CH), 7.63–7.80 (m, 2H, ArH) and 8.26–8.35 (d, *J* 8.0, 2H, ArH); *m*/*z* 398 (M$^+$).

1,4-Bis(*p*-tolyl)-2-(dimethylaminomethyleneamino)-2-phenyl-1,2-dihydro-5*H*-imidazole-3-oxide 3f. Yield 90%; mp 135 °C (Found: C, 76.12; H, 6.78; N, 13.47. $C_{26}H_{28}N_4O$ requires C, 75.70; H, 6.84, N, 13.58); ν_{max}/cm^{-1} (KBr) 1589, 1523 and 1226; δ_H(90 MHz) 2.16 (s, 3H, CH$_3$), 2.36 (s, 3H, CH$_3$), 2.80–2.98 [br d, 6H, N(CH$_3$)$_2$], 4.90–4.94 (unresolved ABq, 2H, CH$_2$), 6.63–7.00 (m, 2H, ArH), 7.20–7.33 (m, 8H, ArH), 7.50 (s, 1H, N=CH), 7.62–7.76 (m, 2H, ArH) and 8.20–8.33 (d, *J* 8.0, 2H, ArH); *m*/*z* 412 (M$^+$).

1-(*p*-Chlorophenyl)-2-(dimethylaminomethyleneamino)-2-phenyl-4-(*p*-tolyl)-1,2-dihydro-5*H*-imidazole 3-oxide 3g. Yield 76%; mp 193 °C (Found: C, 69.67; H, 5.78; N, 12.84. $C_{25}H_{25}N_4OCl$ requires C, 69.42; H, 5.83; N, 12.96); ν_{max}/cm^{-1} (KBr) 1583, 1520 and 1219; δ_H(90 MHz) 2.38 (s, 3H, CH$_3$), 2.83–2.93 [br d, 6H, N(CH$_3$)$_2$], 4.90–4.93 (unresolved ABq, 2H, CH$_2$), 6.63–6.74 (m, 2H, ArH), 7.14–7.36 (m, 7H, ArH), 7.50 (s, 1H, N=CH), 7.60–7.73 (m, 2H, ArH) and 8.23–8.35 (d, *J* 8.0, 2H, ArH); *m*/*z* 432 (M$^+$).

1-(*p*-Bromophenyl)-2-(dimethylaminomethyleneamino)-2-phenyl-4-(*p*-tolyl)-1,2-dihydro-5*H*-imidazole 3-oxide 3h. Yield 90%; mp 198 °C (Found: C, 63.29; H, 5.27; N, 11.71. $C_{25}H_{25}N_4OBr$ requires C, 63.01; H, 5.29; N, 11.76); ν_{max}/cm^{-1} (KBr) 1585, 1521 and 1223; δ_H(200 MHz) 2.42 (s, 3H, CH$_3$), 2.87 (s, 3H, NCH$_3$), 3.40 (s, 3H, CH$_3$), 4.94 (ABq, *J* 14.4, 2H, CH$_2$), 6.72 (AA′BB′, *J* 9.1, 2H, ArH), 7.20–7.40 (m, 7H, ArH), 7.54 (s, 1H, N=CH), 7.65–7.73 (m, 2H, ArH) and 8.30 and 8.34 (d, *J* 8.3, 2H, ArH); δ_C(75.5 MHz) 21.5 (CH$_3$), 34.3 (NCH$_3$), 40.3 (NCH$_3$), 50.4 (C-5), 103.8 (C-2), 110.2 (C-10), 115.6 (C-8, 8′), 139.5, 141.1, 141.5 (C-2, 4, 7), 124.4, 126.8, 128.1, 128.8, 129.2, 131.3, 131.9 (ArH) and 154.7 (C-12); *m*/*z* 476 (M$^+$).

2,4-Diphenyl-1-(*p*-tolyl)-2-(1-dimethylaminoethylideneamino)-1,2-dihydro-5*H*-imidazole 3-oxide 3i. Yield 86%; mp 140–141 °C (Found: C, 75.81; H, 6.81; N, 13.51. $C_{26}H_{28}N_4O$ requires C, 75.70; H, 6.84; N, 13.58); ν_{max}/cm^{-1} (KBr) 1580, 1521 and 1217; δ_H(90 MHz) 1.82 (s, 3H, CH$_3$), 2.23 (s, 3H, CH$_3$), 3.17 [s, 6H, N(CH$_3$)$_2$], 5.08 (s, 2H, CH$_2$), 6.72 (d, *J* 8.2, 2H, ArH), 7.00 (d, *J* 8.2, 2H, ArH), 7.25–7.56 (m, 6H, ArH), 7.72–7.87 (m, 2H, ArH) and 8.40–8.56 (m, 2H, ArH); *m*/*z* 412 (M$^+$) and 396 (M$^+$ − 16).

1,4-Bis(*p*-tolyl)-2-phenyl-2-(1-dimethylaminoethylideneamino)-1,2-dihydro-5*H*-imidazole 3-oxide 3j. Yield 89%; mp 141–143 °C (Found: C, 75.94; H, 7.12; N, 13.19. $C_{27}H_{30}N_4O$ requires C, 76.03; H, 7.09; N, 13.13); ν_{max}/cm^{-1} (KBr) 1596, 1521 and 1221; δ_H(90 MHz) 1.75 (s, 3H, CH$_3$), 2.17 (s, 3H, CH$_3$), 2.36 (s, 3H, CH$_3$), 3.05 [s, 6H, N(CH$_3$)$_2$], 4.88 (s, 2H, CH$_2$), 6.62 (d, *J* 8.4, 2H, ArH), 6.90 (d, *J* 8.4, 2H, ArH), 7.11–7.28 (m, 5H, ArH), 7.56–7.71 (m, 2H, ArH) and 8.20 (d, *J* 8.0, 2H, ArH); δ_C(75.5 MHz) 13.5 (CH$_3$), 20.1 (CH$_3$), 21.5 (CH$_3$), 38.4 [N(CH$_3$)$_2$], 50.6 (CH$_2$), 101.8 (C-2), 113.2, 124.7, 126.5, 126.6, 127.7, 127.8, 128.2, 129.1, 129.2, 131.3, 140.0, 140.7 (C-4), 142.7, 161.8 (C-dimethylaminoethylideneamino); *m*/*z* 426 (M$^+$), 410 (M$^+$ − 16).

2-[Methylthio(morpholino)methyleneamino]-1,2,4-triphenyl-1,2-dihydro-5*H*-imidazole 3-oxide 6a. Yield 72%; mp 161.5–162.5 °C (Found: C, 68.59; H, 5.96; N, 11.87. $C_{27}H_{28}N_4O_2S$ requires C, 68.62; H, 5.97; N, 11.85); ν_{max}/cm^{-1} (KBr) 1599, 1547 and 1229; δ_H(90 MHz) 2.06 (s, 3H, CH$_3$), 3.73 (br s, 8H, morpholino), 5.03 (s, 2H, CH$_2$), 6.78 (d, *J* 8.5, 2H, ArH), 7.18 (d, *J* 8.5, 2H, ArH), 7.33–7.56 (m, 7H, ArH), 7.73–7.90 (m, 2H, ArH) and 8.40–8.56 (m, 2H, ArH); *m*/*z* 472 (M$^+$).

2-[Methylthio(piperidino)methyleneamino]-1,2,4-triphenyl-1,2-dihydro-5*H*-imidazole 3-oxide 6b. Yield 88%; mp 145–146.5 °C (Found: C, 71.40; H, 6.43; N, 11.97. $C_{28}H_{30}N_4OS$

requires C, 71.46; H, 6.42; N, 11.90); ν_{max}/cm^{-1} (KBr) 1599, 1553 and 1222; δ_H(90 MHz) 1.56–1.75 (br s, 6H, $CH_2CH_2CH_2$), 2.06 (s, 3H, SCH_3), 3.60–3.76 (br s, 4H, CH_2NCH_2), 5.06 (s, 2H, CH_2), 6.78 (d, 2H, ArH), 7.20 (d, 2H, ArH), 7.40–7.60 (m, 7H, ArH), 7.83–7.95 (m, 2H, ArH) and 8.35–8.60 (m, 2H, ArH); *m*/*z* 470 (M^+).

2,4-Diphenyl-1-(*p*-tolyl)-2-[methylthio(pyrrolidino)methyleneamino]-1,2-dihydro-5*H*-imidazole 3-oxide 6g. Yield 91%; mp 145–146.5 °C (Found: C, 71.55; H, 6.48; N, 11.82. $C_{28}H_{30}N_4OS$ requires C, 71.46; H, 6.42; N, 11.90); ν_{max}/cm^{-1} (KBr) 1597, 1549 and 1229; δ_H(90 MHz) 1.96–2.00 (m, 4H, 2 × CH_2), 2.06 (s, 3H, SCH_3), 2.20 (s, 3H, CH_3), 3.70–3.76 (m, 4H, CH_2NCH_2), 5.03 (s, 2H, CH_2), 6.71 (d, *J* 8.8, 2H, ArH), 7.01 (d, *J* 8.8, 2H, ArH), 7.30–7.50 (m, 6H, ArH), 7.80–7.90 (m, 2H, ArH) and 8.43–8.53 (m, 2H, ArH); *m*/*z* 470 (M^+).

2-[Dimethylamino(methylthio)methyleneamino]-2,4-diphenyl-1-(*p*-tolyl)-1,2-dihydro-5*H*-imidazole 3-oxide 6h. Yield 78%; mp 140–141.5 °C (Found: C, 70.20; H, 6.33; N, 12.67. $C_{26}H_{28}N_4OS$ requires C, 70.24; H, 6.35; N, 12.60); ν_{max}/cm^{-1} (KBr) 1594, 1548 and 1222; δ_H(90 MHz) 2.00 (s, 3H, SCH_3), 2.20 (s, 3H, CH_3), 3.20 [s, 6H, $N(CH_3)_2$], 5.00 (s, 2H, CH_2), 6.65 (d, *J* 8.5, 2H, ArH), 6.98 (d, *J* 8.5, 2H, ArH), 7.30–7.53 (m, 6H, ArH), 7.80–7.93 (m, 2H, ArH) and 8.40–8.53 (m, 2H, ArH); *m*/*z* 444 (M^+).

2-[Ethylthio(morpholino)methyleneamino]-1,2,4-triphenyl-1,2-dihydro-5*H*-imidazole 3-oxide 6i. Yield 69%; mp 154–155 °C (Found: C, 69.18; H, 6.15; N, 11.60. $C_{28}H_{30}N_4O_2S$ requires C, 69.11; H, 6.21; N, 11.51); ν_{max}/cm^{-1} (KBr) 1597, 1551 and 1226; δ_H(90 MHz) 0.88 (t, *J* 8.0, 3H, CH_3), 2.53 (q, *J* 8.0, 2H, SCH_2), 3.70 (br s, 8H, morpholino), 5.00 (s, 2H, CH_2), 6.68 (d, *J* 8.6, 2H, ArH), 7.15 (d, *J* 8.6, 2H, ArH), 7.26–7.50 (m, 7H, ArH), 7.73–7.50 (m, 2H, ArH) and 8.36–8.46 (m, 2H, ArH); *m*/*z* 486 (M^+).

1,2-Diphenyl-4-(*p*-tolyl)-2-[methylthio(morpholino)methyleneamino]-1,2-dihydro-5*H*-imidazole 3-oxide 6k. Yield 75%; mp 149–150 °C (Found: C, 69.23; H, 6.16; N, 11.43. $C_{28}H_{30}N_4O_2S$ requires C, 69.11; H, 6.21; N, 11.51); ν_{max}/cm^{-1} (KBr) 1598, 1548 and 1228; δ_H(90 MHz) 2.10 (s, 3H, SCH_3), 2.43 (s, 3H, CH_3), 3.75 (br s, 8H, morpholino), 5.00 (s, 2H, CH_2), 6.71 (d, *J* 8.8, 2H, ArH), 7.10–7.46 (m, 6H, ArH), 7.73–7.86 (m, 2H, ArH) and 8.30–8.40 (d, *J* 8.4, 2H, ArH); *m*/*z* 486 (M^+).

1,4-Bis(*p*-tolyl)-2-[methylthio(piperidino)methyleneamino]-1,2-dihydro-5*H*-imidazole 3-oxide 6m. Yield 81%; mp 147–149 °C (Found: C, 72.36; H, 6.84; N, 11.20. $C_{30}H_{34}N_4OS$ requires C, 72.25; H, 6.87; N, 11.23); ν_{max}/cm^{-1} (KBr) 1593, 1548 and 1229; δ_H(90 MHz) 1.64 (br s, 6H, $CH_2CH_2CH_2$), 2.06 (s, 3H, SCH_3), 2.20 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 3.63 (br s, 4H, CH_2NCH_2), 4.95 (s, 2H, CH_2), 6.72 (d, *J* 8.6, 2H, ArH), 7.00 (d, *J* 8.6, 2H, ArH), 7.23–7.43 (m, 5H, ArH), 7.76–7.96 (m, 2H, ArH) and 8.30–8.40 (d, *J* 8.5, 2H, ArH); *m*/*z* 498 (M^+).

1-(*p*-Chlorophenyl)-2-[dimethylamino(methylthio)methyleneamino]-1,2-dihydro-5*H*-imidazole 3-oxide 6q. Yield 83%; mp 169–170 °C (Found: C, 65.31; H, 5.61; N, 11.65. $C_{26}H_{27}N_4OSCl$ requires C, 65.25; H, 5.68; N, 11.70); ν_{max}/cm^{-1} (KBr) 1598, 1552 and 1226; δ_H(300 MHz) 2.00 (s, 3H, SCH_3), 2.38 (s, 3H, CH_3), 3.18 [s, 6H, $N(CH_3)_2$], 4.94 (s, 2H, CH_2), 6.62 (d, *J* 9.0, 2H, ArH), 7.06 (d, *J* 9.0, 2H, ArH), 7.24–7.32 (m, 5H, ArH), 7.74–7.78 (m, 2H, ArH) and 8.26 (d, *J* 8.3, 2H, ArH); δ_C(75.5 MHz) 16.2 (SCH_3), 21.7 (CH_3), 40.0 [$N(CH_3)_2$], 51.4 (CH_2), 101.0 (C-2), 114.0, 122.6, 124.8, 126.8, 127.9, 128.2, 128.7, 128.9, 129.3, 133.0, 140.4, 141.0, 141.6 and 159.0 (C-4); *m*/*z* 478 (M^+).

1-(*p*-Chlorophenyl)-2,4-diphenyl-2-[ethylthio(pyrrolidino)-methyleneamino]-1,2-dihydro-5*H*-imidazole 3-oxide 6r. Yield 89%; mp 163.5–164 °C (Found: C, 66.53; H, 5.77; N, 11.15. $C_{28}H_{29}N_4OSCl$ requires C, 66.64; H, 5.79; N, 11.11); ν_{max}/cm^{-1} (KBr) 1597, 1551 and 1225; δ_H(90 MHz) 0.85 (t, *J* 8.0, 3H, CH_3), 1.83–2.00 (m, 4H, CH_2CH_2), 2.65 (q, *J* 8.0, 2H, SCH_2), 3.63–3.90 (m, 4H, CH_2NCH_2), 5.00 (s, 2H, CH_2), 7.70 (d, *J* 8.8, 2H, ArH), 7.11 (d, *J* 8.8, 2H, ArH), 7.30–7.50 (m, 6H, ArH), 7.75–7.85 (m, 2H, ArH) and 8.36–8.50 (m, 2H, ArH); *m*/*z* 504 (M^+).

Table 1

Entry	Product	Yield (%)	Mp (°C)
1	**6c**	79	143–144.5
2	**6d**	75	149–150
3	**6e**	82	147.5–148.5
4	**6f**	82	149–150
5	**6j**	83	154–155
6	**6l**	88	154–155
7	**6n**	93	158–159
8	**6o**	78	158.5–159
9	**6p**	88	161.5–162.5
10	**6s**	84	143.5–145

The structures of other derivatives of **6** were supported by their microanalysis and spectroscopic data and are listed in Table 1 together with their yields and melting points.

Reactions of the amidines 11 with α-nitrosostyrenes 2

General procedure for the nitrones 12. A solution of compound **11** (4 mmol) and α-chloroacetophenone oxime (4.2 mmol) in dry CH_2Cl_2 (40 ml) was stirred at RT in the presence of sodium carbonate (6 mmol) for 40–52 h. Following an identical work-up with that described for the nitrones **6**, the crude product obtained was purified by column chromatography on silica gel [eluent: EtOAc–hexane (1 : 3)].

2-Dimethylamino-1,4-diphenyl-1,2-dihydro-5*H*-imidazole 3-oxide 12a. Yield 69%; mp 164.5–165.5 °C (Found: C, 72.64; H, 6.77; N, 14.89. $C_{17}H_{19}N_3O$ requires C, 72.57; H, 6.80; N, 14.93); ν_{max}/cm^{-1} (KBr) 1610, 1591 and 1220; δ_H(90 MHz) 2.67 [s, 6H, $N(CH_3)_2$], 4.52 (dd, *J* 14.0 and 2.0, 1H, CH_2), 4.83 (dd, *J* 14.0 and 4.5, 1H, CH_2), 5.76–5.88 (m, 1H, H-2), 6.81 (d, *J* 8.0, 2H, ArH), 7.20–7.60 (m, 6H, ArH) and 8.28–8.50 (m, 2H, ArH); *m*/*z* 281 (M^+) and 264 ($M^+ - 17$).

2-Dimethylamino-1-(*p*-tolyl)-4-phenyl-1,2-dihydro-5*H*-imidazole 3-oxide 12b. Yield 76%; mp 170–171 °C (Found: C, 73.09; H, 7.21; N, 14.27. $C_{18}H_{21}N_3O$ requires C, 73.19; H, 7.16; N, 14.22); ν_{max}/cm^{-1} (KBr) 1595, 1579 and 1223; δ_H(300 MHz) 2.28 (s, 3H, CH_3), 2.66 [s, 6H, $N(CH_3)_2$], 4.50 (dd, *J* 14.5 and 2.1, 1H, CH_2), 4.79 (dd, *J* 14.5 and 4.5, 1H, CH_2), 5.81 (dd, *J* 4.5 and 2.1, 1H, methine H-2), 6.75 (d, *J* 8.5, 2H, ArH), 7.12 (d, *J* 8.5, 2H, ArH), 7.45–7.52 (m, 3H, ArH) and 8.32–8.35 (m, 2H, ArH); δ_C(75.5 MHz) 20.4 (CH_3), 37.1 (CH_2), 50.8 [$N(CH_3)_2$], 101.9 (C-2), 112.7, 126.5, 126.7, 128.1, 128.6, 128.7, 129.2, 129.8, 130.7, 133.8 and 141.7 (C-4); *m*/*z* 295 (M^+) and 278 ($M^+ - 17$).

2-Dimethylamino-4-(*p*-tolyl)-1-phenyl-1,2-dihydro-5*H*-imidazole 3-oxide 12c. Yield 63%; mp 177–178 °C (Found: C, 73.05; H, 7.13; N, 14.29. $C_{18}H_{21}N_3O$ requires C, 73.19; H, 7.16; N, 14.22); ν_{max}/cm^{-1} (KBr) 1596, 1574 and 1224; δ_H(90 MHz) 2.41 (s, 3H, CH_3), 2.68 [s, 6H, $N(CH_3)_2$], 4.52 (dd, *J* 14.0 and 2.0, 1H, CH_2), 4.83 (dd, *J* 14.0 and 4.5, 1H, CH_2), 5.75–5.83 (m, 1H, H-2), 6.80–7.02 (m, 3H, ArH), 7.27–7.50 (m, 4H, ArH) and 8.33 (d, *J* 8.2, 2H, ArH); *m*/*z* 285 (M^+) and 268 ($M^+ - 17$).

1,2-Diphenyl-4-(*p*-tolyl)-2-pyrrolidin-1-yl-1,2-dihydro-5*H*-imidazole 3-oxide 12d. Yield 81%; mp 164–165 °C (Found: C, 78.69; H, 6.81; N, 10.49. $C_{26}H_{27}N_3O$ requires C, 78.56; H, 6.85; N, 10.57); ν_{max}/cm^{-1} (KBr) 1597, 1583 and 1223; δ_H(300 MHz) 1.88–1.92 (m, 4H, CH_2CH_2), 2.42 (s, 3H, CH_3), 3.00–3.08 (m, 2H, NCH_2), 3.44–3.49 (m, 2H, CH_2N), 4.41 (d, *J* 14.1, 1H, CH_2), 4.59 (d, *J* 14.1, 1H, CH_2), 6.82–6.87 (m, 1H, ArH), 7.16–7.27 (m, 7H, ArH), 7.32 (d, *J* 8.1, 2H, ArH), 7.45–7.50 (m, 2H, ArH) and 8.33 (d, *J* 8.3, 2H, ArH); δ_C(75.5 MHz) 21.7 (CH_3), 25.5 (CH_2CH_2), 47.7 (CH_2NCH_2), 48.4 (CH_2), 107.3 (C-2), 115.7, 119.7, 124.4, 126.7, 127.3, 128.1, 128.7, 128.9, 129.5, 133.8, 135.6, 141.1 and 142.9 (C-4); *m*/*z* 397 (M^+) and 381 ($M^+ - 16$).

2-Piperidino-1,2,4-triphenyl-1,2-dihydro-5*H*-imidazole 3-oxide 12e. Yield 75%; mp 148–149 °C (Found: C, 78.44; H, 6.90; N, 10.62. $C_{26}H_{27}N_3O$ requires C, 78.56; H, 6.84; N, 10.57); ν_{max}/cm^{-1} (KBr) 1652, 1599 and 1219; δ_H(90 MHz) 1.65 (br s, 6H, $CH_2CH_2CH_2$), 2.83–3.18 (m, 2H, NCH_2), 3.27–3.57 (m, 2H, CH_2N), 4.63 (br s, 2H, CH_2), 7.20–7.73 (m, 13H, ArH) and 8.45–8.65 (m, 2H, ArH); *m*/*z* 397 (M^+) and 381 ($M^+ - 16$).

1,2-Diphenyl-4-(*p*-tolyl)-2-piperidino-1,2-dihydro-5*H*-imidazole 3-oxide 12f. Yield 81%; mp 165–166 °C (Found: C, 78.69; H, 7.07; N, 10.30. $C_{27}H_{29}N_3O$ requires C, 78.80; H, 7.10; N, 10.21); ν_{max}/cm^{-1} (KBr) 1596, 1580 and 1226; δ_H(90 MHz) 1.64 (br s, 6H, $CH_2CH_2CH_2$), 2.42 (s, 3H, CH_3), 2.81–3.13 (m, 2H, NCH_2), 3.27–3.53 (m, 2H, CH_2N), 4.55 (s, 2H, CH_2), 7.13–7.50 (m, 12H, ArH) and 8.33 (d, *J* 8.0, 2H, ArH); *m*/*z* 411 (M^+) and 395 ($M^+ - 16$).

1,4-Diaryl-2-phenylimidazoles 13

(i) Thermolysis of the nitrones 3/12d–f. A solution of the nitrone **3/12d–f** (1.0 mmol) in dry benzene (8 ml) was heated in a sealed tube at 140–150 °C for 6–7 h. After solvent removal *in vacuo* the residue was purified by chromatography on silica gel (eluent: EtOAc–hexane, 1:9) to yield 69–74% of the corresponding imidazoles **13**.

(ii) Treatment of the nitrones 3/6 with $NaBH_4$. To a solution of the nitrone **3/6** (2.50 mmol) in methanol (50 ml) was added $NaBH_4$ (0.1 g, 2.70 mmol) and the reaction mixture was stirred at RT for 20–22 h. After solvent removal *in vacuo*, the residue was diluted with CH_2Cl_2 (35 ml) and the solution washed with water (4 × 50 ml), dried (Na_2SO_4) and evaporated under reduced pressure. The residue was purified by chromatography on silica gel (eluent: EtOAc–hexane, 1:9) to afford the products **13** (53–66%).

(iii) Reactions of *N*-arylbenzamidine 22 with α-nitrosostyrenes 2. A solution of the *N*-arylbenzamidine **22** (4.0 mmol) and α-chloroacetophenone oxime (4.2 mmol) in dry CH_2Cl_2 (20 ml) was stirred at RT in the presence of sodium carbonate for 2–3 h. Work-up identical with that employed for the nitrones **6** gave the crude product which was further purified by chromatography on silica gel (eluent: EtOAc–hexane, 1:9) to yield the corresponding products **13** (85–93%).

1,2,4-Triphenylimidazole 13a. Mp 92–94 °C (Found: C, 85.19; H, 5.41; N, 9.41. $C_{21}H_{16}N_2$ requires C, 85.12; H, 5.44; N, 9.45); ν_{max}/cm^{-1} (KBr) 1591 and 1205; δ_H(90 MHz) 7.20–7.61 (m, 14H; 13H, ArH and 1H, olefinic) and 7.92–8.11 (m, 2H, ArH); δ_C(75.5 MHz) 118.4 (C-5), 124.9, 125.7, 126.9, 128.1, 128.3, 128.5, 128.7, 129.9, 130.2, 133.8, 138.4, 141.6 and 146.9 (C-2); *m*/*z* 296 (M^+, 100%), 193 (63%), 165 (25%), 116 (3%), 103 (8%), 89 (32%) and 77 (28%).

2,4-Diphenyl-1-(*p*-tolyl)imidazole 13b. Mp 147–148 °C (Found: C, 85.05; H, 5.86; N, 9.07. $C_{22}H_{18}N_2$ requires C, 85.13; H, 5.84; N, 9.02); ν_{max}/cm^{-1} (KBr) 1602 and 1205; δ_H(300 MHz) 2.35 (s, 3H, CH_3), 7.09 (d, *J* 8.4, 2H, ArH), 7.15 (d, *J* 8.4, 2H, ArH), 7.20–7.26 (m, 4H, ArH), 7.35–7.40 (m, 3H, 2H, ArH and 1H, olefinic), 7.44–7.48 (m, 2H, ArH) and 7.86–7.90 (m, 2H, ArH); δ_C(75.5 MHz) 21.0 (CH_3), 118.5 (C-5), 124.9, 125.4, 126.8, 128.0, 128.2, 128.4, 128.6, 129.9, 130.3, 133.8, 135.8, 138.0, 141.4 and 146.8 (C-2); *m*/*z* 310 (M^+, 89%), 207 (100%), 165 (13%), 116 (10%), 103 (13%), 77 (33%) and 65 (13%).

1,2-Diphenyl-4-(*p*-tolyl)imidazole 13c. Mp 113.5–114.5 °C (Found: C, 85.17; H, 5.85; N, 9.07. $C_{22}H_{18}N_2$ requires C, 85.13; H, 5.84; N, 9.02; ν_{max}/cm^{-1} (KBr) 1600 and 1204; δ_H(90 MHz) 2.38 (s, 3H, CH_3), 7.18–7.57 (m, 13H; 12H, ArH and 1H, olefinic) and 7.83 (d, *J* 8.0, 2H, ArH); δ_C(75.5 MHz) 21.2 (CH_3), 118.0 (C-5), 124.9, 125.7, 128.0, 128.1, 128.3, 128.7, 129.2, 129.3, 130.3, 131.0, 136.5, 138.5, 141.7 and 146.7; *m*/*z* 310 (M^+).

Thermolysis of the nitrones 6

General procedure for 17. A solution of **6** (1.0 mmol) in benzene (8 ml) was heated in a sealed tube at 140–150 °C for 6–7 h. After solvent removal *in vacuo* the residue was purified by column chromatography on silica gel (eluent: EtOAc–hexane, 1:6).

3-(*N*,*N*-Dimethylcarbamoyl)-1-phenylbenzamidine 17a. Yield 73%; mp 125.5–126.5 °C (Found: C, 71.78; H, 6.45; N, 15.67. $C_{16}H_{17}N_3O$ requires C, 71.89; H, 6.41; N, 15.72); ν_{max}/cm^{-1} (KBr) 3422br, 1635 and 1602; δ_H(90 MHz) 3.05 (s, 3H, NCH_3), 3.32 (s, 3H, NCH_3), 6.80–7.77 (m, 10H, ArH) and 12.40 (br s, exchangeable with D_2O, 1H, NH); δ_C(75.5 MHz) 35.2 (NCH_3), 37.3 (CH_3N), 123.2, 124.3, 128.0, 128.6, 129.2, 130.2, 135.2, 139.1, 163.0 (C=N) and 164.7 (C=O); *m*/*z* 267 (M^+, 14%), 223 (100%), 180 (22%) and 77 (21%).

***N*-[*p*-Tolylamino(phenyl)methylene]morpholine-4-carboxamide 17b.** Yield 66%; mp 141–142.5 °C (Found: C, 70.69; H, 6.47; N, 12.91. $C_{19}H_{21}N_3O_2$ requires C, 70.56; H, 6.54; N, 12.99); ν_{max}/cm^{-1} (KBr) 3437br, 1625 and 1590; δ_H(90 MHz) 2.30 (s, 3H, CH_3), 3.70 (br s, 8H, morpholino), 6.83 (d, *J* 8.7, 2H, ArH), 7.08 (d, *J* 8.7, 2H, ArH), 7.23–7.67 (m, 5H, ArH) and 12.43 (br s, exchangeable with D_2O, 1H, NH); *m*/*z* 323 (M^+).

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