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An in-depth analysis of the effect of substituents on imines in cycloaddition reactions with nitrosoalkenes

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Abstract—An in-depth experimental and theoretical analysis of the reactions of simple acyclic imines with nitrosoalkenes is reported. The effect of the substituents on nitrogen as well as carbon atom of imines on the cycloaddition pathways followed is systematically explored. The reactions of various functionalized imines with nitrosoalkenes leading to the formation of imidazoles and imidazole-*N*-oxides have also been explored. The plausible mechanisms leading to various heterocycles have been proposed.

1. Introduction

The C-nitroso group of arylnitroso, α-chloronitroso, cyano–nitroso, C-nitroso sugar derivatives, and acylnitroso compounds is known to effectively participate as a 2π component in hetero Diels–Alder reactions.[1] Of these, the acylnitroso species has been exploited much more extensively than the other dienophiles.[2] On the other hand, α-nitrosostyrenes have been known to participate as 4π components in Diels–Alder reactions with various polarized and unpolarized alkenes,[3a,b,c] allenes,[3d] all carbon dienes,[3e] enamines,[3f,g,h] and enol ethers.[3i] In contrast, there are not many such reports of the cycloadditions of nitrosoalkenes with carbon–nitrogen double bond.[4] Mackay et al.[5] reported an unusual [3+2] cycloaddition of α-nitrosoalkenes with carbon–nitrogen double bonds of oxazines and failed to observe such a reaction of nitrosoalkenes with various other cyclic and acyclic compounds bearing a carbon–nitrogen double bond.

Subsequent disclosures from our laboratory have shown a generalized and unusual [3+2] cycloaddition mode with various polarized 1,3-diazabuta-1,3-dienes[6] resulting in an easy access to synthetically and biologically significant imidazoline *N*-oxides. Few generalizations have been enunciated to account for the nature and preponderance of cycloadducts formed in such reactions. Mackay et al.[5] proposed that the electronic nature of the α-substituents on nitrosoalkenes determine their preferred conformations, which in turn become instrumental in controlling the distribution of products in these reactions. However, in recent reports by Tahdi et al.,[7] the effect of substituents present on α-carbon atom of nitrosoalkenes on the cycloaddition pathways followed is not generalized.[7] In view of these contradictions and in order to have a deeper insight regarding the key factors influencing the [3+2] versus [4+2] cycloaddition reactions, we examined the reactions of various imines with α-substituted nitrosoalkenes.

The treatment of benzylidene-phenyl-amine with α-phenyl nitrosoalkenes (entry a; Scheme 1), generated in situ from the corresponding α-bromooxime and sodium bicarbonate, in methylene chloride resulted in the exclusive formation of **3a**, a [3+2] cycloadduct. In order to scrutinize the effect of the electronic nature of α-substituents on nitrosoalkenes, the reactions of benzylidene-phenyl-amine were repeated with other nitrosoalkenes viz. *p*-tolyl and *p*-nitrophenyl substituted nitrosoalkenes (entry b and c; Scheme 1). These reactions also led to the exclusive formation of nitrones **3b** and **3c**. This observation got generalized by the sole formation of nitrones **3** in the reactions of other *N*-aryl imines with nitrosoalkenes (Scheme 1). The presence of oxazines **4** even in traces was excluded by analysis of the crude product with the help of high-resolution ^{1}H NMR spectroscopy. These experiments indicated that the nature of substituents on the nitrosoalkenes do not play any significant role in influencing the competitive [3+2] versus [4+2] cycloaddition pathways as proposed earlier.[5] It was felt that the substituents on imines might be crucial in influencing the pathways followed and the distribution of the products formed in their reactions with nitrosoalkenes. In order to substantiate this proposition, we considered it worthwhile to examine the reactions of *N*-alkyl imines with nitrosoalkenes. Interestingly, the reactions of benzylidene-cyclohexyl-amine with all the

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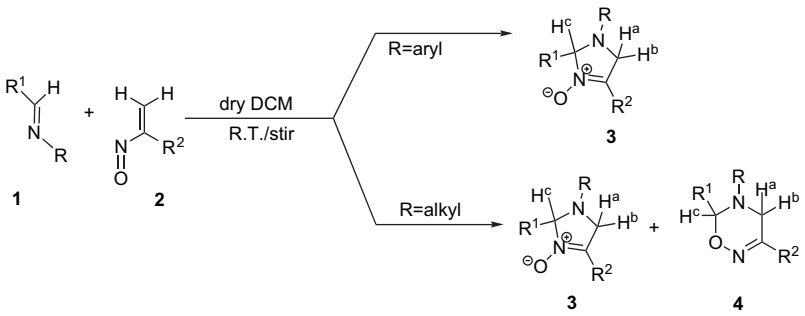


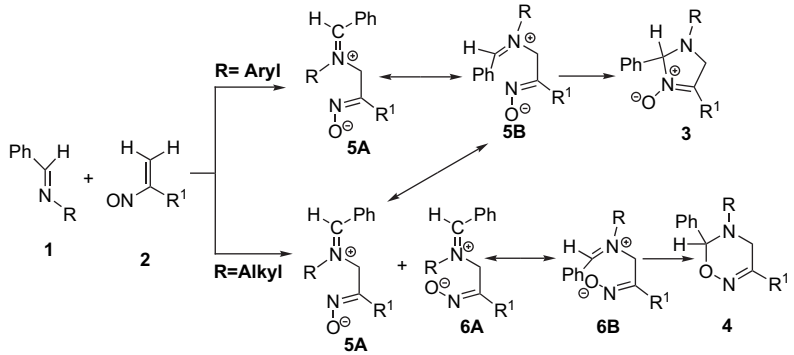
a. R=C_6H_5,R^1=C_6H_5,R^2=C_6H_4-CH_3(*p*)
b. R=C_6H_5,R^1=C_6H_5,R^2=C_6H_5
c. R=C_6H_5,R^1=C_6H_5,R^2=C_6H_4-NO_2(*p*)
d. R=cyclohexyl,R^1=C_6H_5,R^2=C_6H_5
e. R=cyclohexyl,R^1=C_6H_5,R^2=C_6H_4-CH_3(*p*)
f. R=cyclohexyl,R^1=C_6H_5,R^2=C_6H_4-NO_2(*p*)
g. R=C_6H_4-CH_3(*p*),R^1=C_6H_5,R^2=C_6H_5
h. R=C_6H_4-CH_3(*p*),R^1=C_6H_5,R^2=C_6H_4-CH_3(*p*)
i. R=C_6H_4-CH_3(*p*),R^1=C_6H_5,R^2=C_6H_4-NO_2(*p*)
j. R=C_6H_4-OCH_3(*p*),R^1=C_6H_4-NMe_2(*p*),R^2=C_6H_5
k. R=C_6H_4-OCH_3(*p*),R^1=C_6H_4-NMe_2(*p*),R^2=C_6H_4-CH_3(*p*)
l. R=C_6H_4-OCH_3(*p*),R^1=C_6H_4-NMe_2(*p*),R^2=C_6H_4-NO_2(*p*)
m. R=benzyl,R^1=C_6H_4-NMe_2(*p*),R^2=C_6H_5
n. R=benzyl,R^1=C_6H_4-NMe_2(*p*),R^2=C_6H_4-CH_3(*p*)
o. R=benzyl,R^1=C_6H_4-NMe_2(*p*),R^2=C_6H_4-NO_2(*p*)
p. R=n-butyl,R^1=C_6H_5,R^2=C_6H_5
q. R=n-butyl,R^1=C_6H_5,R^2=C_6H_4-CH_3(*p*)
r. R=n-butyl,R^1=C_6H_5,R^2=C_6H_4-NO_2(*p*)
s. R=iso-propyl,R^1=C_6H_5,R^2=C_6H_5
t. R=iso-propyl,R^1=C_6H_5,R^2=C_6H_4-CH_3(*p*)
u. R=iso-propyl,R^1=C_6H_5,R^2=C_6H_4-NO_2(*p*)
v. R=furyl,R^1=C_6H_5,R^2=C_6H_5
w. R=furyl,R^1=C_6H_5,R^2=C_6H_4-CH_3(*p*)
x. R=furyl,R^1=C_6H_5,R^2=C_6H_4-NO_2(*p*)

Scheme 1.

forementioned nitrosoalkenes (entry d, e, f) resulted in the isolation of a mixture of nitrones **3** and oxazines **4** in good yields; oxazines obtained in higher proportions (40:60). The reproducible formation of similar mixtures of nitrones and oxazines in the reactions of other *N*-alkyl imines with nitrosoalkenes once again supported the deliberation regarding the decisive role of iminic substituents in the product distribution. Accordingly, the present manuscript is a generalized and consummate account of our earlier communication[8] on the effect of substituents on various imines on the mode of cycloadditions followed in their reactions with nitrosoalkenes.

The structures **3** and **4** have been assigned to [3+2] and [4+2] cycloadducts on the basis of analytical data and spectral evidences. The products **3m** and **4m**, for example, were characterized as [4-(1-benzyl-3-oxy-4-phenyl-2,5-dihydro-1*H*-imidazol-2-yl)-phenyl]-dimethyl-amine and [4-(5-benzyl-3-phenyl-5,6-dihydro-4*H*-[1,2,5]oxadiazin-6-yl)-phenyl]-dimethyl-amine. The mass spectrum of product **3m**, for example, analyzed for $C_{24}H_{25}N_3O$, exhibited an intense M-16 peak (*m*/*z*=355) diagnostic of nitrone,[3a] while the mass spectrum of **4m** exhibited a molecular ion peak at *m*/*z*=371 for $C_{24}H_{25}N_3O$. In the ^{1}H NMR of **3m**, the methylene protons exhibited two doublets of doublets at δ 3.92, 4.35 (J=14.1 and 4.2 Hz, H^a) and 4.35 (J=14.2 and 3.6 Hz, H^b) corresponding to a CH_2 of a nitrone, downfield from the position δ 3.95 in case of oxazine **4m**. A doublet of doublet (J=4.2 and 3.6 Hz, H^c) corresponding to the CH of nitrone **3f** appeared at δ 5.49, while that for oxazine **4m** appeared as a singlet at δ 6.00. The ^{13}C NMR spectra were also in agreement with the nitrone and oxazine structures assigned above to **3m** and **4m**.

The nitrones **3** and oxazines **4** are formed in competition and are not in equilibrium, these were separately shown to be stable to the reaction conditions, though rearrangements of oxazines to nitrones[9] and nitrones to oxazines[10] are well documented in the literature. The plausible mechanism for the formation of nitrones and oxazines is illustrated in Scheme 2. The addition of nitrosoalkene to a C=N bond is less likely to proceed via a concerted single step as reported earlier.[3,11] The reaction presumably proceeds through



Scheme 2.

zwitterionic intermediates, **5A** and **6A**, which are formed from the *cisoid* and *transoid* conformations of the nitrosoalkenes. These intermediates are interconvertible to other intermediates **5B** and **6B**, respectively.

However, the interconversion between sets of **5A** and **6A** and **5B** and **6B** does not seem to be credible as suggested earlier,[10,3,4] since this requires rotation around a C=N–O bond, which becomes stronger after nucleophilic attack, i.e., changes from a partial double bond in the nitrosoalkene to a typical double bond in the zwitterionic intermediate. Finally, the intermediates **5B** and **6B** cyclize to form the nitrones **3** and oxazines **4**, respectively. It seems that formation of the intermediate **6A** is discouraged in the case of aryl-substituted imines because of the steric repulsions between the oxygen lone pairs and the π electron cloud on the aryl substituent. In the case of alkyl-substituted imines; the formation of both intermediates **5A** and **6A** is possible because of the reduced steric repulsion between the alkyl group and the nitrogen or oxygen of the nitrosoalkenes. The above mechanistic rationale is in agreement with the formation of both [4+2] and [3+2] cycloadducts in the case of alkyl imines and exclusively [3+2] adduct in the case of aryl imines.

The experimental observations and the mechanism proposed above have been supported by the theoretical calculations at semi-empirical AM1 and ab initio[12] HF/6-31G* levels of computational analysis implemented in Gaussian series of programs.[13] The schematic representation of the reaction mechanism studied theoretically is shown in Figure 1.

The schematic representation of the conformations of optimized structures of the intermediates is shown in Figure 2. The optimized parameters like bond lengths, bond angles, and dihedral angles of the intermediates are characterized in Figure 3. The activation energies of the various reactants, products, and the transition states were estimated from HF/6-31G* point energy calculations on the structures previously optimized (Table 1). The relative energies (kcal/mol) of various intermediates and products bearing *N*-alkyl and *N*-aryl substituents using HF theoretical methods at room temperature using 6-31+G* basis sets are given in Table 2. All attempts to locate a transition state for a concerted process, as proposed by Gilchrist[3] for the formation of six-membered ring, between H_2C=NH and H_2C=CH–N=O at AM1 and HF/6-31+G* level calculations have revealed that the only pathway operative in this reaction involves the initial nucleophilic attack of iminic nitrogen on the terminal carbon of nitrosoethylene. Complete optimizations carried out at HF/6-31+G* theory level on the reaction path involving

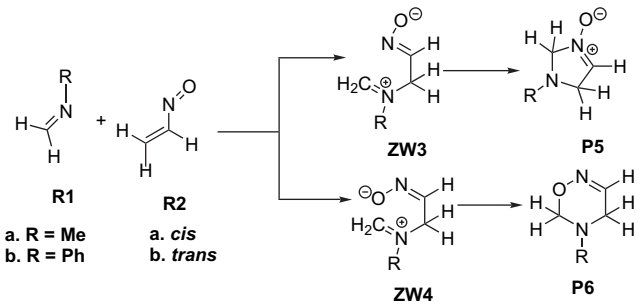


Figure 1.

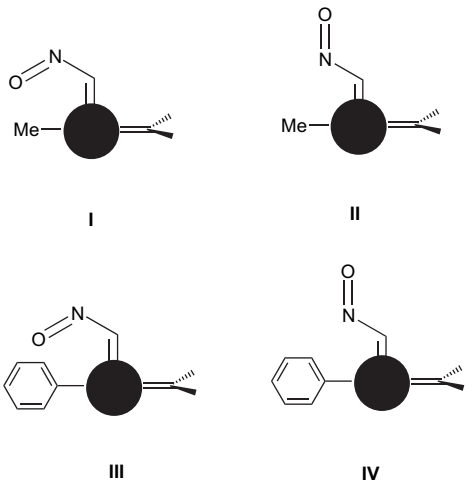
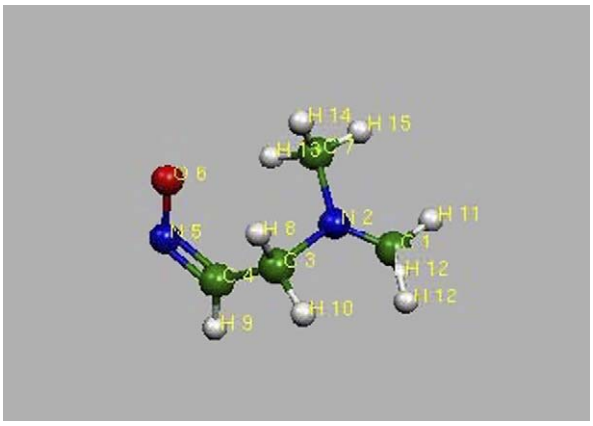


Figure 2. Schematic representation of the conformations of the intermediates on the reaction path between nitrosoalkenes and imines.

H_2C=NMe and *cis*- and *trans*-conformers of H_2C=CH–N=O have exhibited that the initial nucleophilic attack occurs in such a way so as to form intermediates **I** and **II**, respectively. The intermediates **I** and **II** have been found to be 17.6 and 27.6 kcal/mol higher in energy than the corresponding starting materials. The corresponding final products are stable by −37.6 and −20.2 kcal/mol as compared to the starting materials (Fig. 3) indicating that the formation of six-membered ring, in the subsequent ring closure step, is more favorable from kinetic as well as thermodynamic aspects.

Further, HF/6-31+G* calculations for the reaction path involving H_2C=N–Ph and H_2C=CH–N=O indicated that the formation of a zwitterionic intermediate is feasible for the *s-trans* arrangement of nitrosoethylene. However, such an intermediate could not be located for the *s-cis* arrangement. This may be due to the repulsive interactions operating between the approaching phenyl (π-electrons) and oxygen (non-bonding electrons) during the initial nucleophilic attack. Due to these repulsive forces, the formation of the corresponding zwitterionic intermediate is avoided. However, in the case of *s-trans* of nitrosoethylene, the formation of intermediate **IV** is conceivable after a twist in the C–C–N–C angle probably because of the decreased repulsive interactions. The relative energies of the intermediate **IV** and the nitrone are 28.6 and −21.1 kcal/mol with respect to the corresponding starting materials. Thus, the presence of a phenyl group on nitrogen does not allow the formation of zwitterionic intermediate **6**, thereby justifying the absence of the six-membered oxazine in the title reactions of imines bearing *N*-aryl substituents. This rationale is further substantiated by the formation of nitrones and oxazines in the reactions of benzylidene-benzyl-amine (entry m, n, o) and benzylidene-furyl-amine (entry v, x, y) with nitrosoalkenes **2**, where the above referred electronic repulsions and steric interactions are supposedly decreased, the phenyl ring being one carbon atom away from the nitrogen of imine due to the insertion of a methylene group (Fig. 4).

Solvent effects have not been taken into account in our study. However, solvents of different polarities might also change the chemoselectivity of the reaction. However, the solvent used experimentally, dichloromethane, a non-polar solvent,



I

C1-N2=1.253924 ; C3-N2-C1=121.6523538

N2-C3=1.518186 ; C4-C3-N2=112.238191

C4-C3=1.4871451; N5-C4-C3=120.9890215

N5-C4=1.2968952; O6-N5-C4=117.6119068

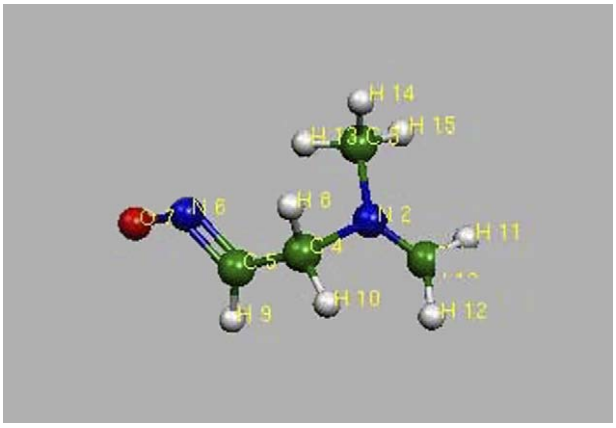
O6-N5=1.2646881; C7-N2-C3=116.6974679

C7-N2=1.4734058; C4-C3-N2-C1=-111.0999956

C7-N2-C3=116.697468; N5-C4-C3-N2=-88.4786299

N2-C3-C4=112.238191;O6-N5-C4-C3=6.0749739

O6-N5-C4-C3=6.0749739;C7-N2-N3-C4=66.1768982



II

N2-C1=1.252758; C5-C4-N2=111.492389

C3-N2=1.4656284; N6-C5-C4=116.6413079

C4-N2=1.558485; O7-N6-C5=119.2266812

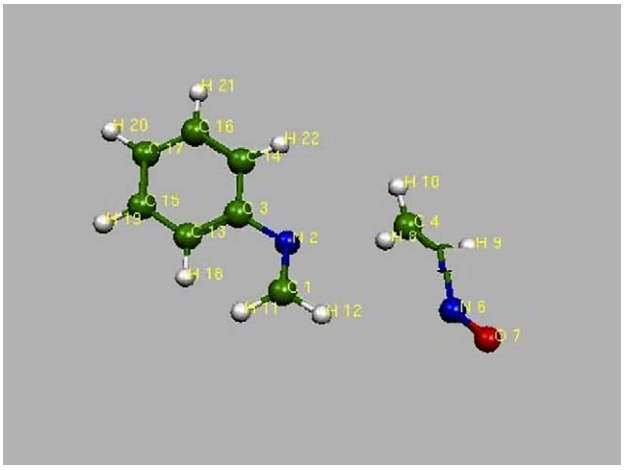
C5-C4=1.4636224; C4-N2-C3-C1=-175.1989112

N6-C5=1.3089472; C5-C4-N2-C3=69.9372295

O7-N6=1.2393158; N6-C5-C4-N2=-93.2134719

C3-N2-C1=122.39158; O7-N6-C5-C4=177.5004877

C4-N2-C3=115.4419577



IV

N2-C1=1.2564137; C15-C13=1.3874312

C3-N2=1.4378906; C16-C14=1.3863046

C4-N2=1.6058972; C17-C15=1.3867999

C5-C4=1.4519722; C3-N2-C1=121.538060

N6-C5=1.3147996; C4-N2-C3=117.348833

O7-N6=1.2357110; C5-C4-N2=113.606416

C13-C3=1.3849957; N6-C5-C4=116.527161

C14-C3=1.3856619; O7-N6-C5=119.1016681

C4-N2-C3-C1=-176.3054821;C13-C3-N2-C1=83.3302754

C5-C4-N2-C3=-173.3125322;C16-C14-C3-N2=1.3863045

N6-C5-C4-N2=-86.9930372; C17-C15-C13-C3=-0.4286934

O7-N6-C5-C4=177.5699184

Figure 3. Three dimensional representation of the geometries of the intermediates **I**, **II**, and **IV** (**III** does not exist) optimized at HF/6-31+G* theory level.

Table 1. Yields of nitrones **3** and oxazines **4** in Scheme 1

Entry no.	**3** (Yield %)	**4** (Yield %)	Entry no.	**3** (Yield %)	**4** (Yield %)
a	79	—	m	37	55
b	78	—	n	30	50
c	73	—	o	36	54
d	35	53	p	34	56
e	32	48	q	30	50
f	34	51	r	31	53
g	75	—	s	35	47
h	80	—	t	37	48
i	78	—	u	31	52
j	85	—	v	34	49
k	81	—	w	31	54
l	88	—	x	34	50

would not have any significant influence on the activation energies (Table 3).

The results presented above are in agreement with the earlier report regarding the exclusive formation of nitrones, i.e., [3+2] adducts in the reactions of nitrosoalkenes with *N*-aryl-formamidines.[6a]

In continuation of these studies, it was felt worthwhile to examine the effect of substituents on carbon of imines in such reactions. In this series, the reactions of *N*-aryl-benzamidines with nitrosoalkenes yielding imidazoles have already been studied in our laboratory. In-depth study of these reactions has been explored by investigating these reactions with

Table 2. Absolute energies (ZPE corrected values that has been scaled by a factor of 0.9153 for HF level) of various reactants, intermediates and products at rt

Strs	HF/6-31+G*	ZPVE	Scaling factor (0.9153)	Total energy
R1a	−133.0655661	0.073537	0.067308416	−132.9982577
R1b	−323.5871725	0.130540	0.119483262	−323.4676892
R2a	−206.6777504	0.052863	0.048385504	−206.629402
R2b	−206.6857993	0.053289	0.048775422	−206.6364239
ZW3a	−339.7067992	0.132047	0.12086219	−339.5859366
ZW3b	−530.2269237	0.187762	0.171858559	−530.0550651
ZW4a	—	—	—	—
ZW4b	−339.7152183	0.133285	0.121995761	−339.5932225
P5a	−339.7829033	0.136773	0.125188327	−339.657715
P5b	−530.3061588	0.193126	0.176768228	−530.1293906
P6a	−339.8031696	0.137465	0.125821715	−339.6773479
P6b	−530.3208283	0.193775	0.177362258	−530.143466

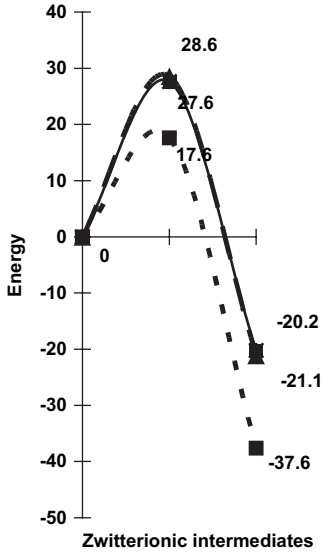
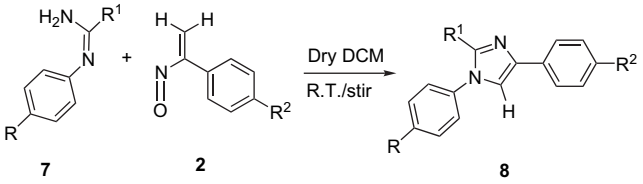


Figure 4. Potential energy surface showing the relative energy of zwitterionic intermediates on the reaction path between nitrosoalkene and imine. The path involving intermediate **I** leads to the formation of oxazine, the path involving intermediates **II** and **IV** lead to the formation of nitrones. Path involving **III**, which should have led to an oxazine, could not be traced due of the instability of intermediate **III** on PE surface.



a. R = H, R^1 = SCH_3, R^2 = CH_3
b. R = CH_3, R^1 = SCH_3, R^2 = CH_3
c. R = CH_3, R^1 = SCH_3, R^2 = NO_2
d. R = CH_3, R^1 = Piperidine, R^2 = NO_2
e. R = H, R^1 = morpholine, R^2 = NO_2
f. R = CH_3, R^1 = pyrrollidine, R^2 = CH_3

Scheme 3.

Table 4. Yields of imidazoles **8** in Scheme 3

Entry no.	Yield %
8a	78
8b	80
8c	81
8d	80
8e	81
8f	85

imines bearing polar donating amines and thiomethyl at carbon of imines, i.e., *N*-aryl-secondary amine-carboxamidines commonly known as guanidines and 2-methyl-1-aryl-isothioureas **7**.

Interestingly, these reactions also resulted in the exclusive isolation of imidazoles **8** in very good yields (Scheme 3, Table 4), characterized on the basis of spectral and analytical evidences (Table 4).

The one pot synthesis of imidazoles reported here assumes significance because:

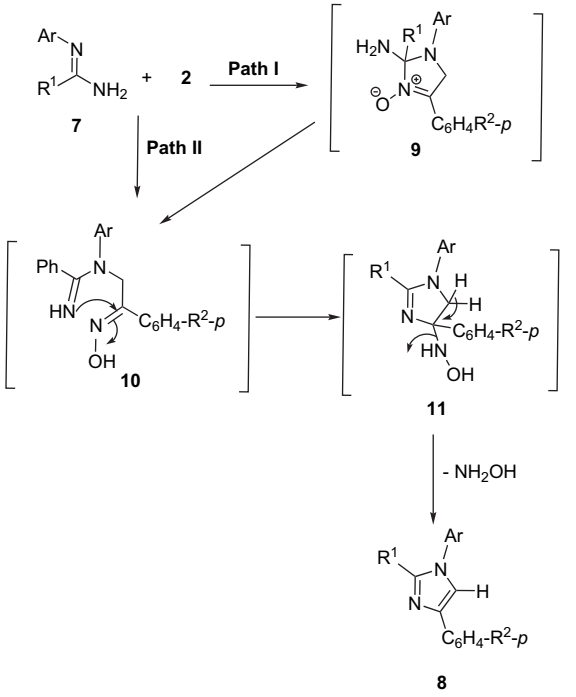
1. These observations are at variance with the earlier reports by Mackay et al. that nitrosoalkenes did not react with the carbon–nitrogen double bonds of *N*,*N*-dimethyl-*N*′-phenyl-benzamidine and 1-phenyl-ethanone *O*-methyl-oxime.
2. The earlier reported reactions of *N*-aryl-benzamidines with nitrosoalkenes leading to the formation of imidazoles involve very cumbersome experimental procedures and the use of iron carbonyls.[10]

It is possible to discern various possible mechanistic pathways to the formation of imidazoles in this case. The

Table 3. Relative energies (kcal/mol) of various intermediates and products bearing alkyl and aryl substituents using HF theoretical methods at rt using 6-31+G* basis sets

Reaction	Relative energies of zwitterionic intermediates		Relative energies of products formed	
	Before adding ZPVE	After adding ZPVE	Before adding ZPVE	After adding ZPVE
Me–N=CH_2+*cis* H_2C=CH–N=O	17.6 (**I**)	21.6 (**I**)	−37.6 (**I**)	−31.2 (**I**)
Me–N=CH_2+*trans* H_2C=CH–N=O	27.6 (**II**)	30.78 (**II**)	−20.2 (**II**)	−15.86 (**II**)
Ph–N=CH_2+*trans* H_2C=CH–N=O	28.6 (**IV**)	30.59 (**IV**)	−21.1 (**IV**)	−14.45 (**IV**)

plausible mechanism, consistent with the one prescribed earlier for the reaction of benzamidines with nitrosoalkenes,[6a,b] is depicted in Scheme 4.

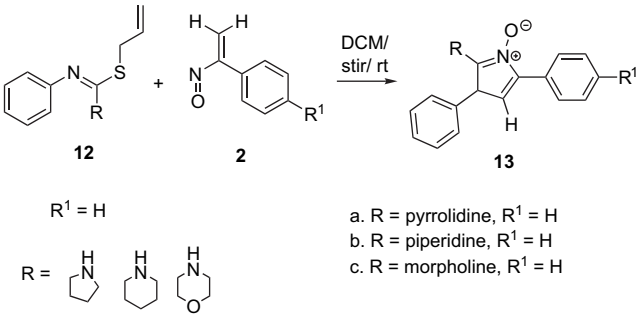


Scheme 4.

The reaction may lead to the initial formation of 2-amino-*N*-oxide intermediate **9**, which probably being unstable is transformed to another intermediate **10**. The intermediate **10** then cyclizes, as shown, to yield another intermediate **11**, which ultimately undergoes elimination of NH_2OH to yield the imidazoles **8**. The formation of **8** in this case could also be explained via initial displacement of halide from α-chlorooxime leading to the intermediate **10**, which as described above then yields **8** via **11**.

In order to authenticate the synthetic versatility of these reactions, it was felt that the presence of a suitably disposed dipolarophile in the molecular structure might result in intramolecular 1,3-dipolar cycloadditions of the generated nitrone. Keeping this in view, we have examined the reactions of *S*-allylated imines **12** with nitrosoalkenes. Interestingly, the reactions of *N*-phenyl-secondaryamino-1-carboximidothioic acid allyl ester **12a–d** with nitrosoalkenes **2** following the procedure described earlier resulted in the formation of imidazole-*N*-oxides **13** in good yields (Table 5), instead of the expected dipolar adducts (Scheme 5). The formation of the imidazole-*N*-oxides **13** in these reactions is at odds with our earlier assumption that the allylated nitrones **15** formed above will be stable enough so as to follow intramolecular 1,3-dipolar cycloadditions utilizing the *S*-allyl moiety thus leading to the formation of tricyclic heterocycle **16** (Table 5).

The products formed **13** were characterized as imidazoles on the basis of spectral and analytical data. The ^{1}H NMR spectrum of the products showed the absence of allylic function as well as the methylene protons and the presence of a characteristic olefenic proton. The compound **13a**, for example, characterized as 1,4-diphenyl-2-pyrrolidin-1-yl-1*H*-imidazole and analyzed for $C_{19}H_{19}N_3O$ exhibited two multiplets at δ 1.79 and 3.30 corresponding to the pyrrolidine protons. A characteristic singlet corresponding to olefenic proton appeared at δ 6.88. The ^{13}C NMR spectral data is in perfect consistent with the suggested structure. The mass spectra of the compound showed a molecular ion peak (M^+) at *m/z*: 305.

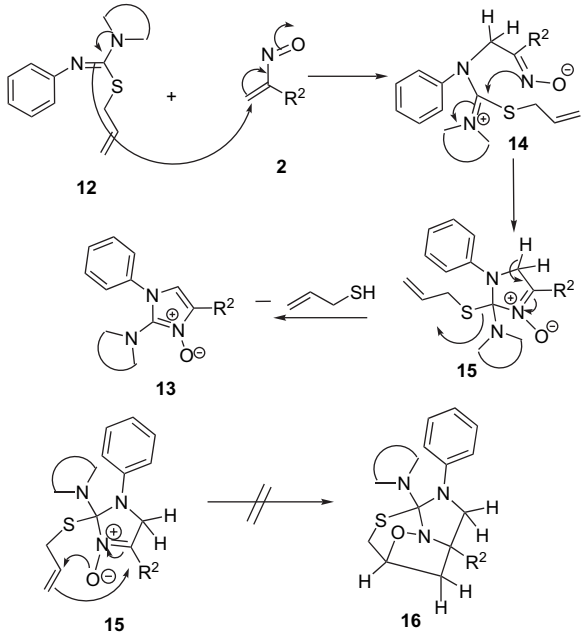


Scheme 5.

Table 5. Yields of imidazole-*N*-oxides **16** in Scheme 5

Entry no.	Yield %
16a	77
16b	80
16c	79

The most plausible mechanism for the formation of imidazole-*N*-oxides **13** has been depicted in Scheme 6. It is assumed that the nitrogen atom of the *S*-allylated imine **12** attacks the electrophilic carbon of nitrosoalkene **2**, as expected, to form an intermediate **14**, which then cyclizes to form another intermediate **15**. This intermediate **15** after the elimination of a molecule of allyl thiol leads to the formation of **13**.



Scheme 6.

In view of the above observations, it is generalized that the aryl imines cycloaddition to nitrosoalkenes in a [3+2] manner, while alkyl imines cycloaddition to nitrosoalkenes in competitive [3+2] and [4+2] manner. It may be inferred that the substituents on nitrogen as well as carbon atoms of simple and functionalized imines play a pivotal role in determining the mechanistic pathways and products formed in their reactions with nitrosoalkenes.

These cycloaddition reactions offer a remarkable practical ingress to a diversity of functional and synthetically flexible nitrogen containing molecular assemblies having biological and pharmacological significance.[14]

2. Experimental

2.1. 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) and AC-E 300 (300 MHz) spectrometers using TMS as internal standard. Chemical shift values are expressed as δ (parts per million) downfield from TMS and J values are in hertz. 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) or Brucker AC-300E (75.0 MHz) spectrometers in a 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 Analyzer.

2.2. Starting materials

All the acyclic imines (Schiff's bases)[15a] 1,2-methyl-1-aryl-isothioureas **7a**–**c**,[15b] *N*-aryl-secondary amine-carboxamidines **7d**–**f**,[15b] *S*-allylated imines **12**, and bromooximes of acetophenone, *p*-nitroacetophenone and *p*-methylacetophenone **2**[15c] were prepared by reported procedures.

2.3. Reactions of acyclic imines (Schiff's bases) with α-nitrosoalkenes. General procedure for nitrones 3 and oxazines 4

A solution of Schiff's base **1** (4 mmol) and α-bromooxime **2** (4.2 mmol) in dry CH_2Cl_2 was stirred at rt in the presence of anhydrous sodium bicarbonate (6 mmol) for 24–25 h. The deposited salt and the excess of sodium bicarbonate were filtered off and washed with small portions (2×10 ml) of CH_2Cl_2. The combined filtrates were washed with water, extracted with dichloromethane, dried over Na_2SO_4, and concentrated under reduced pressure. The nitrones **3** and oxazines **4** were isolated and purified with the help of column chromatography on 60–120 mesh silica gel. The nitrones and oxazines were recrystallized from benzene–hexane (2:1) and EtOAc–hexane (1:5), respectively.

2.3.1. 1,2-Diphenyl-4-*p*-tolyl-2,5-dihydro-1*H*-imidazole 3-oxide (3a). White crystalline solid; yield 79%; mp 165–166 °C; [Found: C, 80.49; H, 6.21; N, 11.62. $C_{22}H_{20}N_2O$ requires C, 80.46; H, 6.14; N, 11.69%]; ν_{max}/cm^{-1} (KBr): 1218 (N–O), 1545, 1595 (C═N); δ_H (200 MHz): δ 2.28 (s, 3H, –CH_3), 4.93 (dd, J=14.1 and 2.4 Hz, 1H, –CH_2), 5.17 (dd, J=14.1 and 5.2 Hz, 1H, –CH_2), 6.20 (dd, J=2.4 and 5.2 Hz, 1H, methine), 6.60 (d, J=8.2 Hz, 2H, ArH), 7.13 (d, J=8.2 Hz, 2H, ArH), 7.49–7.65 (m, 6H, ArH), 8.25–8.43 (m, 4H, ArH); ^{13}C NMR: 21.1 (CH_3), 57.4 (CH_2), 94.3 (methine), 118.9, 122.1, 124.2, 125.7, 127.9, 133.5, 134.1, 134.9, 136.3, 139.1, 141.8, 148.2, and 153.1; *m*/*z*: 328 (M^+) and 312 (M^+-16).

2.3.2. 1,2,4-Triphenyl-2,5-dihydro-1*H*-imidazole 3-oxide (3b). White crystalline solid; yield 78%; mp 140–141 °C; [Found: C, 80.18; H, 5.80; N, 8.98. $C_{21}H_{18}N_2O$ requires C, 80.23; H, 5.77; N, 8.91%]; ν_{max}/cm^{-1} (KBr): 1219 (N–O), 1547 (C═N), 1589 (C═N); δ_H (200 MHz): δ 4.88 (dd, J=14.2 and 2.4 Hz, 1H, –CH_2), 5.16 (dd, J=14.2 and 5.2 Hz, 1H, –CH_2), 6.18 (dd, J=2.4 and 5.3 Hz, 1H, methine), 6.56–6.84 (m, 3H, ArH), 7.18–7.47 (m, 6H, ArH), 7.60–7.62 (m, 3H, ArH), 8.32–8.35 (m, 3H, ArH); ^{13}C NMR: 58.1 (CH_2), 89.3 (CH), 120.2, 121.1, 123.2, 124.7, 126.8, 128.5, 134.2, 135.2, 136.3, 138.3, 140.2, 147.2, and 152.1; *m*/*z*: 314 (M^+) and 298 (M^+-16).

2.3.3. 4-(4-Nitro-phenyl)-1,2-diphenyl-2,5-dihydro-1*H*-imidazole 3-oxide (3c). White crystalline solid; yield 73%; mp 181–182 °C; [Found: C, 70.22; H, 4.84; N, 11.62. $C_{21}H_{17}N_3O_3$ requires C, 70.18; H, 4.77; N, 11.69%]; ν_{max}/cm^{-1} (KBr): 1219 (N–O), 1545, 1592 (C═N); δ_H (200 MHz): δ 5.18 (dd, J=14.4 and 2.9 Hz, 1H, –CH_2), 5.46 (dd, J=14.4 and 5.4 Hz, 1H, –CH_2), 6.49 (dd, J=2.9 and 5.4 Hz, 1H, methine), 7.05–7.52 (m, 5H, ArH), 7.65–7.88 (m, 5H, ArH), 8.54 (d, J=9.0 Hz, 2H, ArH), 8.74 (d, J=9.0 Hz, 2H, ArH); ^{13}C NMR: 56.3 (CH_2), 94.4 (methine), 118.2, 120.9, 123.3, 125.1, 125.9, 133.2, 133.8, 134.4, 135.1, 137.6, 140.5, 145.2, and 152.2; *m*/*z*: 359 (M^+) and 343 (M^+-16).

2.3.4. 1-Cyclohexyl-2,4-diphenyl-2,5-dihydro-1*H*-imidazole 3-oxide (3d). White crystalline solid; yield 35%; mp 165–166 °C; [Found: C, 78.78; H, 7.50; N, 8.71. $C_{21}H_{24}N_2O$ requires C, 78.71; H, 7.55; N, 8.74%]; ν_{max}/cm^{-1} (KBr): 1218 (N–O), 1525, 1598 (C═N); δ_H (200 MHz): δ 1.26–2.03 (m, 10H, cyclohexyl), 2.71–2.73 (m, 1H, –CH, cyclohexyl), 4.32 (dd, J=14.7 and 3.6 Hz, 1H, –CH_2), 4.66 (dd, J=14.4 and 4.2 Hz, 1H, –CH_2), 5.78 (dd, J=3.6 and 4.2 Hz, 1H, methine), 7.36–7.53 (m, 6H, ArH), 7.69–7.74 (m, 2H, ArH), 8.33–8.37 (m, 2H, ArH); ^{13}C NMR: 25.5, 25.7, 30.7, 31.2, 31.9, 37.8, 52.9 (CH_2), 90.7 (methine), 122.5, 126.3, 129.1, 129.9, 132.7, 136.8, 139.0, 142.9, and 163.8; *m*/*z*: 320 (M^+) and 304 (M^+-16).

2.3.5. 5-Cyclohexyl-3,6-diphenyl-5,6-dihydro-4*H*-[1,2,5]oxadiazine (4d). White crystalline solid; yield 53%; mp 141–142 °C; [Found: C, 78.76; H, 7.48; N, 8.76. $C_{21}H_{24}N_2O$ requires C, 78.71; H, 7.55; N, 8.74%]; ν_{max}/cm^{-1} (KBr): 1620 (C═N); δ_H (200 MHz): δ 1.21–2.03 (m, 10H, cyclohexyl), 2.82–2.85 (m, 1H, –CH, cyclohexyl), 3.59 (s, 2H, –CH_2), 6.00 (s, 1H, methine), 7.21–7.52 (m, 5H, ArH), 7.73–8.10 (m, 5H, ArH); ^{13}C NMR: 25.6, 25.7, 25.8, 31.1, 31.9, 38.2, 61.7 (CH_2), 89.2 (methine), 123.7, 124.9,

126.2, 127.8, 128.4, 137.7, 140.2, 147.7, and 153.5; *m/z*: 334 (M^+).

2.3.6. 1-Cyclohexyl-2-phenyl-4-*p*-tolyl-2,5-dihydro-1*H*-imidazole 3-oxide (3e). White crystalline solid; yield 32%; mp 175–176 °C; [C, 79.05; H, 7.90; N, 8.29. $C_{22}H_{26}N_2O$ requires C, 79.00; H, 7.84; N, 8.38%]; ν_{max}/cm^{-1} (KBr): 1220 (N–O), 1545, 1591 (C═N); δ_H (200 MHz): δ 1.15–1.89 (m, 10H, cyclohexyl), 2.43 (s, 3H, CH_3), 2.83–2.86 (m, 1H, –CH, cyclohexyl), 3.95 (dd, J=14.1 and 3.2 Hz, 1H, –CH_2), 4.61 (dd, J=14.1 and 4.5 Hz, 1H, –CH_2), 5.70 (dd, J=3.2 and 4.5 Hz, 1H, methine), 6.59 (d, J=8.1 Hz, 2H, ArH), 7.03 (d, J=8.1 Hz, 2H, ArH), 7.12–7.52 (m, 5H, ArH); ^{13}C NMR: 20.9, 25.1, 25.4, 25.8, 30.7, 31.1, 38.7, 52.9 (CH_2), 89.1 (CH), 120.6, 124.2, 126.1, 127.3, 128.1, 132.2, 134.3, 139.4, and 161.7; *m/z*: 334 (M^+) and 318 (M^+-16).

2.3.7. 5-Cyclohexyl-6-phenyl-3-*p*-tolyl-5,6-dihydro-4*H*-[1,2,5]oxadiazine (4e). White crystalline solid; yield 48%; mp 153–154 °C; [Found C, 78.97; H, 7.91; N, 8.45. $C_{22}H_{26}N_2O$ requires C, 79.00; H, 7.84; N, 8.38%]; ν_{max}/cm^{-1} (KBr): 1621 (C═N); δ_H (200 MHz): δ 1.21–2.07 (m, 10H, cyclohexyl), 2.39 (s, 3H, CH_3), 2.84–2.87 (m, 1H, –CH, cyclohexyl), 3.61 (s, 2H, –CH_2), 5.99 (s, 1H, methine), 6.58 (d, J=8.2 Hz, 2H, ArH), 7.01 (d, J=8.0 Hz, 2H, ArH), 7.10–7.46 (m, 5H, ArH); ^{13}C NMR: 21.0, 25.4, 25.7, 25.8, 30.9, 31.2, 38.3, 61.4 (CH_2), 89.3 (CH), 121.1, 123.9, 126.0, 127.8, 128.3, 133.0, 134.5, 138.3, and 153.6; *m/z*: 334 (M^+).

2.3.8. 1-Cyclohexyl-4-(4-nitro-phenyl)-2-phenyl-2,5-dihydro-1*H*-imidazole 3-oxide (3f). White crystalline solid; yield 34%; mp 169–170 °C; [Found C, 69.08; H, 6.31; N, 11.52. $C_{21}H_{23}N_3O_3$ requires C, 69.02; H, 6.34; N, 11.50%]; ν_{max}/cm^{-1} (KBr): 1221 (N–O), 1547, 1595 (C═N); δ_H (200 MHz): δ 1.18–1.95 (m, 10H, cyclohexyl), 2.65–2.66 (m, 1H, –CH, cyclohexyl), 3.98 (dd, J=14.7 and 3.6 Hz, 1H, –CH_2), 4.62 (dd, J=14.7 and 4.2 Hz, 1H, –CH_2), 5.72 (dd, J=3.6 and 4.2 Hz, 1H, methine), 7.43–7.61 (m, 5H, ArH), 8.27 (d, J=8.6 Hz, 2H, ArH), 8.42 (d, J=8.6 Hz, 2H, ArH); ^{13}C NMR: 25.3, 25.5, 25.8, 30.9, 31.4, 38.8, 53.1 (CH_2), 89.9 (methine), 123.7, 127.2, 128.5, 129.8, 133.1, 136.7, 138.0, 148.1, and 161.9; *m/z*: 365 (M^+) and 349 (M^+-16).

2.3.9. 5-Cyclohexyl-3-(4-nitro-phenyl)-6-phenyl-5,6-dihydro-4*H*-[1,2,5]oxadiazine (4f). White crystalline solid; yield 51%; mp 153–154 °C; [Found: C, 69.10; H, 6.30; N, 11.55. $C_{21}H_{23}N_3O_3$ requires C, 69.02; H, 6.34; N, 11.50%]; ν_{max}/cm^{-1} (KBr): 1620 (C═N); δ_H (200 MHz): δ 1.21–2.05 (m, 10H, cyclohexyl), 2.85–2.87 (m, 1H, –CH, cyclohexyl), 3.62 (s, 2H, –CH_2), 6.00 (s, 1H, methine), 7.30–7.57 (m, 5H, ArH), 7.73 (d, J=8.5 Hz, 2H, ArH), 8.19 (d, J=8.5 Hz, 2H, ArH); ^{13}C NMR: 25.5, 25.6, 25.7, 31.1, 31.4, 38.9 (–CH, cyclohexyl), 61.6 (–CH_2), 89.4 (methine), 123.6, 125.2, 126.5, 128.2, 128.5, 138.0, 140.1, 148.2, and 153.5; *m/z*: 365 (M^+).

2.3.10. 2,4-Diphenyl-1-*p*-tolyl-2,5-dihydro-1*H*-imidazole 3-oxide (3g). White crystalline solid; yield 75%; mp 175–176 °C; [Found: C, 80.50; H, 6.16; N, 8.48. $C_{22}H_{20}N_2O$ requires C, 80.46; H, 6.14; N, 8.53%]; ν_{max}/cm^{-1} (KBr): 1221 (N–O), 1545, 1600 (C═N); δ_H (200 MHz): δ 2.25 (s, 3H, –CH_3), 4.88 (dd, J=14.1 and 3.2 Hz, 1H, –CH_2), 5.14 (dd, J=14.1 and 5.0 Hz, 1H, –CH_2), 6.20 (dd, J=3.2 and 5.0 Hz, 1H, methine), 6.52 (d, J=8.4 Hz, 2H, ArH), 7.04 (d, J=8.4 Hz, 2H, ArH), 7.42–7.48 (m, 6H, ArH), 7.62–7.63 (m, 2H, ArH), 8.34–8.35 (m, 2H, ArH); ^{13}C NMR: 24.9, 55.1 (CH_2), 89.2 (methine), 118.2, 121.2, 122.9, 123.6, 126.2, 133.1, 133.9, 134.1, 135.2, 137.5, 141.1, 147.2, and 152.1; *m/z*: 328 (M^+) and 312 (M^+-16).

2.3.11. 2-Phenyl-1,4-di-*p*-tolyl-2,5-dihydro-1*H*-imidazole 3-oxide (3h). White crystalline solid; yield 80%; mp 135–136 °C; [Found: C, 80.72; H, 6.40; N, 8.22. $C_{23}H_{22}N_2O$ requires C, 80.67; H, 6.48; N, 8.18%]; ν_{max}/cm^{-1} (KBr): 1220 (N–O), 1545, 1601 (C═N); δ_H (200 MHz): δ 2.21 (s, 3H, –CH_3), 2.25 (s, 3H, CH_3), 4.91 (dd, J=14.1 and 3.2 Hz, 1H, –CH_2), 5.17 (dd, J=14.1 and 5.2 Hz, 1H, –CH_2), 6.22 (dd, J=3.2 and 5.2 Hz, 1H, methine), 6.48 (d, J=8.6 Hz, 2H, ArH), 7.02 (d, J=8.6 Hz, 2H, ArH), 7.35–7.51 (m, 9H, ArH); ^{13}C NMR: 24.5, 25.1, 55.2 (CH_2), 90.1 (methine), 118.7, 120.5, 123.2, 123.8, 124.5, 125.9, 134.1, 134.9, 136.4, 139.1, 140.1, 146.5, and 153.1; *m/z*: 342 (M^+) and 326 (M^+-16).

2.3.12. 4-(4-Nitro-phenyl)-2-phenyl-1-*p*-tolyl-2,5-dihydro-1*H*-imidazole 3-oxide (3i). White crystalline solid; yield 78%; mp 160–161 °C; [Found: C, 70.82; H, 5.16; N, 11.29. $C_{22}H_{19}N_3O_3$ requires C, 70.76; H, 5.13; N, 11.25%]; ν_{max}/cm^{-1} (KBr): 1221 (N–O), 1547, 1597 (C═N); δ_H (200 MHz): δ 2.20 (s, 3H, –CH_3), 5.02 (dd, J=14.1 and 2.8 Hz, 1H, –CH_2), 5.27 (dd, J=14.1 and 5.4 Hz, 1H, –CH_2), 6.30 (dd, J=2.8 and 5.4 Hz, 1H, methine), 6.61 (d, J=8.4 Hz, 2H, ArH), 7.13 (d, J=8.4 Hz, 2H, ArH), 7.50–7.70 (m, 5H, ArH), 8.39 (d, J=8.9 Hz, 2H, ArH), 8.59 (d, J=8.9 Hz, 2H, ArH); ^{13}C NMR: 20.1 (CH_3), 52.5 (CH_2), 90.1 (methine), 112.9, 117.3, 123.6, 127.2, 127.8, 127.9, 128.6, 129.7, 129.9, 132.5, 141.3, 147.7, and 152.2; *m/z*: 373 (M^+) and 357 (M^+-16).

2.3.13. {4-[1-(4-Methoxy-phenyl)-3-oxy-4-phenyl-2,5-dihydro-1*H*-imidazol-2-yl]-phenyl}-dimethyl-amine (3j). Yellow crystalline solid; yield 85%; mp 139–140 °C; [Found: C, 74.45; H, 6.45; N, 10.82. $C_{24}H_{25}N_3O_2$ requires C, 74.39; H, 6.50; N, 10.84%]; ν_{max}/cm^{-1} (KBr): 1223 (N–O), 1546, 1589 (C═N); δ_H (200 MHz): δ 2.91 [(s, 6H, –$N(CH_3)_2$], 3.72 (s, 3H, –OCH_3), 4.76 (dd, J=14.1 and 3.2 Hz, 1H, –CH_2), 5.05 (dd, J=14.1 and 5.5 Hz, 1H, –CH_2), 6.00 (dd, J=3.2 and 5.5 Hz, 1H, methine), 6.53 (d, J=8.8 Hz, 2H, ArH), 6.69 (d, J=8.7 Hz, 2H, ArH), 6.79 (d, J=8.8 Hz, 2H, ArH), 7.20–8.24 (m, 7H, ArH); ^{13}C NMR: 40.4 (NMe_2), 52.5 (–CH_2–), 55.6 (OCH_3), 90.6 (methine), 112.1, 113.8, 115.0, 122.2, 124.1, 128.1, 128.9, 133.2, 135.8, 138.5, 148.9, 152.1, and 153.5; *m/z*: 387 (M^+) and 371 (M^+-16).

2.3.14. {4-[1-(4-Methoxy-phenyl)-3-oxy-4-*p*-tolyl-2,5-dihydro-1*H*-imidazol-2-yl]-phenyl}-dimethyl-amine (3k). Yellow crystalline solid; yield 81%; mp 177–178 °C; [Found: C, 74.84; H, 6.75; N, 10.45. $C_{25}H_{27}N_3O_2$ requires C, 74.79; H, 6.78; N, 10.47%]; ν_{max}/cm^{-1} (KBr): 1225 (N–O), 1547, 1595 (C═N); δ_H (200 MHz): δ 2.35 (s, 3H, CH_3), 2.91 [(s, 6H, –$N(CH_3)_2$], 3.72 (s, 3H, –OCH_3), 4.71 (dd, J=14.2 and 3.2 Hz, 1H, –CH_2), 5.10 (dd, J=14.2 and 5.4 Hz, 1H, –CH_2), 6.03 (dd, J=3.2 and 5.4 Hz, 1H, methine), 6.62 (d, J=8.8 Hz, 2H, ArH), 6.71 (d, J=8.8 Hz,

2H, ArH), 6.91 (d, J=8.8 Hz, 2H, ArH), 6.99 (d, J=8.8 Hz, 2H, ArH), 7.27 (d, J=8.8 Hz, 2H, ArH), 7.43 (d, J=8.8 Hz, 2H, ArH); ^{13}C NMR: 21.6 (CH_3), 40.3 (NMe_2), 52.8 (–CH_2–), 55.5 (OCH_3), 90.6 (methine), 113.9, 114.3, 115.2, 122.3, 126.9, 127.5, 128.1, 129.1, 134.6, 135.7, 140.2, 146.1, and 153.1; *m/z*: 401 (M^+) and 385 (M^+-16).

2.3.15. {4-[1-(4-Methoxy-phenyl)-4-(4-nitro-phenyl)-3-oxy-2,5-dihydro-1*H*-imidazol-2-yl]-phenyl}-dimethyl-amine (3l). Red crystalline solid; yield 88%; mp 166–167 °C; [Found: C, 66.63; H, 5.52; N, 12.99. $C_{24}H_{24}N_4O_4$ requires C, 66.69; H, 5.59; N, 12.96%]; ν_{max}/cm^{-1} (KBr): 1220 (N–O), 1542, 1591 (C═N); δ_H (200 MHz): δ 2.96 [(s, 6H, –$N(CH_3)_2$], 3.73 (s, 3H, –OCH_3), 4.79 (dd, J=14.1 and 3.1 Hz, 1H, –CH_2), 5.15 (dd, J=14.1 and 5.4 Hz, 1H, –CH_2), 6.08 (dd, J=3.1 and 5.4 Hz, 1H, methine), 6.59 (d, J=8.8 Hz, 2H, ArH), 6.70 (d, J=8.7 Hz, 2H, ArH), 6.81 (d, J=8.8 Hz, 2H, ArH), 7.44 (d, J=8.7 Hz, 2H, ArH), 8.29 (d, J=8.8 Hz, 2H, ArH), 8.49 (d, J=8.8 Hz, 2H, ArH); ^{13}C NMR: 40.3 (NMe_2), 52.7 (–CH_2–), 55.5 (OCH_3), 90.7 (methine), 112.1, 113.7, 114.9, 122.2, 123.9, 127.2, 128.8, 132.9, 135.2, 138.3, 147.8, 151.7, and 152.8; *m/z*: 432 (M^+) and 416 (M^+-16).

2.3.16. [4-(1-Benzyl-3-oxy-4-phenyl-2,5-dihydro-1*H*-imidazol-2-yl)-phenyl]-dimethyl-amine (3m). Creamish crystalline solid; yield 37%; mp 178–179 °C; [Found: C, 77.57; H, 6.82; N, 11.33. $C_{24}H_{25}N_3O$ requires C, 77.60; H, 6.78; N, 11.37%]; ν_{max}/cm^{-1} (KBr): 1221 (N–O), 1547, 1600 (C═N); δ_H (200 MHz): δ 2.90 [(s, 6H, –$N(CH_3)_2$], 3.21 (d, J=13.5 Hz, 1H, benzylic), 3.92 (dd, J=14.1 and 4.2 Hz, 1H, CH_2), 4.05 (d, J=13.5 Hz, 1H, benzylic), 4.35 (dd, J=14.2 and 3.6 Hz, 1H, CH_2), 5.49 (dd, J=4.2 and 3.6 Hz, 1H, methine), 6.81 (d, J=8.5 Hz, 2H, ArH), 7.31–7.57 (m, 5H, ArH), 7.62 (d, J=8.5 Hz, 2H, ArH), 7.95–8.10 (m, 5H, ArH); ^{13}C NMR: 41.1 (NMe_2), 52.7 (CH_2, benzylic), 56.1 (CH_2), 94.3 (methine), 112.1, 121.2, 123.6, 126.7, 128.1, 128.7, 129.9, 132.5, 134.1, 136.9, 148.1, 152.1, and 153.2; *m/z*: 371 (M^+) and 355 (M^+-16).

2.3.17. [4-(5-Benzyl-3-phenyl-5,6-dihydro-4*H*-[1,2,5]oxadiazin-6-yl)-phenyl]-dimethyl-amine (4m). White crystalline solid; yield 55%; mp 172–173 °C; [Found: C, 77.68; H, 6.82; N, 11.33. $C_{24}H_{25}N_3O$ requires C, 77.60; H, 6.78; N, 11.37%]; ν_{max}/cm^{-1} (KBr): 1621 (C═N); δ_H (200 MHz): δ 2.92 [(s, 6H, –$N(CH_3)_2$], 3.25 (d, J=13.6 Hz, 1H, benzylic CH_2), 3.95 (s, 2H, CH_2, oxazine), 4.09 (d, J=13.6 Hz, 1H, benzylic –CH_2), 6.00 (s, 1H, methine), 6.78 (d, J=8.5 Hz, 2H, ArH), 7.15–7.32 (m, 5H, ArH), 7.48 (d, J=8.5 Hz, 2H, ArH), 7.65–7.98 (m, 5H, ArH); ^{13}C NMR: 40.2 (NMe_2), 52.1 (CH_2, oxazine), 53.6 (CH_2, benzylic), 92.9 (methine), 112.2, 122.7, 123.9, 127.5, 128.3, 129.0, 130.9, 135.5, 137.1, 138.2, 147.1, 152.5, and 153.5; *m/z*: 371 (M^+).

2.3.18. [4-(1-Benzyl-3-oxy-4-*p*-tolyl-2,5-dihydro-1*H*-imidazol-2-yl)-phenyl]-dimethyl-amine (3n). Yellow crystalline solid; yield 30%; mp 161–162 °C; [Found: C, 77.94; H, 7.02; N, 10.87. $C_{25}H_{27}N_3O$ requires C, 77.89; H, 7.06; N, 10.90%]; ν_{max}/cm^{-1} (KBr): 1225 (N–O), 1548, 1601 (C═N); δ_H (200 MHz): δ 2.32 (s, 3H, CH_3), 2.91 [(s, 6H, –$N(CH_3)_2$], 3.56 (d, J=13.0 Hz, 1H, benzylic), 3.82 (dd, J=14.2 and 4.2 Hz, 1H, CH_2), 4.06 (d, J=13.0 Hz, 1H, benzylic), 4.32 (dd, J=14.2 and 3.6 Hz, 1H, CH_2), 5.49 (dd, J=4.1 and 3.5 Hz, 1H, methine), 6.78 (d, J=8.4 Hz, 2H, ArH), 6.88 (d, J=8.6 Hz, 2H, ArH), 6.99 (d, J=8.6 Hz, 2H, ArH), 7.12–7.89 (m, 7H, ArH); ^{13}C NMR: 20.9 (CH_3), 41.1 (NMe_2), 52.9 (CH_2, benzylic), 56.1 (CH_2), 94.1 (methine), 112.5, 120.9, 122.5, 125.5, 128.1, 128.8, 131.2, 134.1, 134.7, 138.2, 146.1, 151.9, and 152.9; *m/z*: 385 (M^+) and 369 (M^+-16).

2.3.19. [4-(5-Benzyl-3-*p*-tolyl-5,6-dihydro-4*H*-[1,2,5]oxadiazin-6-yl)-phenyl]-dimethyl-amine (4n). White crystalline solid; yield 50%; mp 142–143 °C; [Found: C, 77.92; H, 7.02; N, 10.93. $C_{25}H_{27}N_3O$ requires C, 77.89; H, 7.06; N, 10.90%]; ν_{max}/cm^{-1} (KBr): 1624 (C═N); δ_H (200 MHz): δ 2.32 (s, 3H, CH_3), 2.90 [(s, 6H, –$N(CH_3)_2$], 3.23 (d, J=13.8 Hz, 1H, benzylic), 3.95 (s, 2H, CH_2, oxazine), 4.15 (d, J=13.8 Hz, 1H, benzylic), 5.98 (s, 1H, methine), 6.75 (d, J=8.0 Hz, 2H, ArH), 6.95 (d, J=8.0 Hz, 2H, ArH), 7.18 (d, J=8.5 Hz, 2H, ArH), 7.21–7.40 (m, 5H, ArH), 7.48 (d, J=8.5 Hz, 2H, ArH); ^{13}C NMR: 20.9 (CH_3), 40.3 (NMe_2), 52.5 (CH_2, oxazine), 54.3 (CH_2, benzylic), 93.1 (methine), 114.1, 119.1, 123.5, 126.2, 129.1, 129.9, 132.2, 134.1, 135.2, 137.7, 146.1, 152.1, and 153.5; *m/z*: 385 (M^+).

2.3.20. {4-[1-Benzyl-4-(4-nitro-phenyl)-3-oxy-2,5-dihydro-1*H*-imidazol-2-yl]-phenyl}-dimethyl-amine (3o). White crystalline solid; yield 36%; mp 147–148 °C; [Found: C, 69.26; H, 5.85; N, 13.39. $C_{24}H_{24}N_4O_3$ requires C, 69.21; H, 5.81; N, 13.45%]; ν_{max}/cm^{-1} (KBr): 1219 (N–O), 1547, 1595 (C═N); δ_H (200 MHz): δ 2.90 [(s, 6H, –$N(CH_3)_2$], 3.62 (d, J=13.0 Hz, 1H, benzylic), 3.87 (dd, J=14.0 and 4.6 Hz, 1H, CH_2), 4.08 (d, J=13.0 Hz, 1H, benzylic), 4.36 (dd, J=14.0 and 3.2 Hz, 1H, CH_2), 5.46 (dd, J=4.6 and 3.2 Hz, 1H, methine), 6.80 (d, J=8.4 Hz, 2H, ArH), 7.25–7.36 (m, 5H, ArH), 7.54 (d, J=8.4 Hz, 2H, ArH), 8.21 (d, J=9.0 Hz, 2H, ArH), 8.35 (d, J=9.0 Hz, 2H, ArH); ^{13}C NMR: 40.3 (NMe_2), 53.9 (–CH_2–, benzylic), 56.3 (–CH_2); 94.6 (methine), 112.1, 121.2, 123.6, 126.9, 127.7, 128.6, 130.0, 133.3, 133.6, 136.5, 147.6, 151.8, and 152.9; *m/z*: 416 (M^+) and 400 (M^+-16).

2.3.21. {4-[5-Benzyl-3-(4-nitro-phenyl)-5,6-dihydro-4*H*-[1,2,5]oxadiazin-6-yl]-phenyl}-dimethyl-amine (4o). Yellow crystalline solid; yield 54%; mp 115–117 °C; [Found: C, 69.27; H, 5.86; N, 13.39. $C_{24}H_{24}N_4O_3$ requires C, 69.21; H, 5.81; N, 13.45%]; ν_{max}/cm^{-1} (KBr): 1625 (C═N); δ_H (200 MHz): δ 2.95 [(s, 6H, –$N(CH_3)_2$], 3.47 (d, J=14.0 Hz, 1H, benzylic), 3.49 (d, J=13.9 Hz, 1H, benzylic), 3.62 (d, J=5.0 Hz, 1H, –CH_2), 3.87 (d, 1H, J=5.1 Hz), 5.76 (s, 1H, methine), 6.73 (d, J=8.8 Hz, 2H, ArH), 7.27–7.41 (m, 5H, ArH), 7.47 (d, J=8.7 Hz, 2H, ArH), 7.70 (d, J=8.9 Hz, 2H, ArH), 8.17 (d, J=8.9 Hz, 2H, ArH); ^{13}C NMR: 40.3 (NMe_2), 52.1 (CH_2, benzylic), 56.1 (–CH_2), 91.3 (methine), 112.4, 122.5, 124.1, 127.3, 128.1, 129.1, 131.5, 134.2, 134.8, 137.1, 148.5, 152.5, and 153.2; *m/z*: 416 (M^+).

2.3.22. 1-Butyl-2,4-diphenyl-2,5-dihydro-1*H*-imidazole 3-oxide (3p). White crystalline solid; yield 34%; mp 146–147 °C; [Found: C, 77.60; H, 7.45; N, 9.48. $C_{19}H_{22}N_2O$ requires C, 77.52; H, 7.53; N, 9.52%]; ν_{max}/cm^{-1} (KBr): 1221 (N–O), 1545, 1594 (C═N); δ_H (200 MHz): δ 0.92 (t, J=7.4 Hz, 3H, CH_3), 1.37–1.65 (m, 4H, 2×CH_2), 2.72–2.81 (m, 2H, CH_2), 4.32 (dd, J=14.7 and 3.6 Hz, 1H,

CH_2), 4.71 (dd, J=14.7 and 4.2 Hz, 1H, CH_2), 5.85 (dd, J=3.5 and 4.1 Hz, 1H, methine), 6.99–7.32 (m, 6H, ArH), 7.42–7.59 (m, 4H, ArH); ^{13}C NMR: 14.3, 21.7, 23.9, 45.2, 53.1, 91.2, 122.9, 123.5, 125.9, 127.9, 129.7, 137.9, 141.7, 150.2, and 153.2; *m/z*: 294 (M^+) and 278 (M^+-16).

2.3.23. 5-Butyl-3,6-diphenyl-5,6-dihydro-4*H*-[1,2,5]oxadiazine (4p). White crystalline solid; yield 56%; mp 129–130 °C; [Found: C, 77.55; H, 7.48; N, 9.47. $C_{19}H_{22}N_2O$ requires C, 77.52; H, 7.53; N, 9.52%]; ν_{max}/cm^{-1} (KBr): 1621 (C=N); δ_H (200 MHz): δ 0.95 (t, 3H, CH_3), 1.39–1.63 (m, 4H, 2×CH_2), 2.71–2.84 (m, 2H, CH_2), 3.89 (AB quartet, J=7.7 Hz, 2H, CH_2), 5.99 (s, 1H, methine), 6.95–7.32 (m, 5H, ArH), 7.45–7.98 (m, 5H, ArH); ^{13}C NMR: 13.7, 20.2, 32.1, 46.6, 52.1, 91.5, 125.7, 121.9, 124.3, 126.9, 129.9, 140.2, 143.9, 151.1, and 153.1; *m/z*: 294 (M^+).

2.3.24. 1-Butyl-2-phenyl-4-*p*-tolyl-2,5-dihydro-1H-imidazole 3-oxide (3q). White crystalline solid; yield 30%; mp 155–156 °C; [Found: C, 77.82; H, 7.81; N, 9.13. $C_{20}H_{24}N_2O$ requires C, 77.89; H, 7.84; N, 9.08%]; ν_{max}/cm^{-1} (KBr): 1220 (N–O), 1547, 1596 (C=N); δ_H (200 MHz): δ 0.92 (t, J=7.5 Hz, 3H, CH_3), 1.38–1.62 (m, 4H, 2×CH_2), 2.32 (s, 3H, CH_3), 2.73–2.81 (m, 2H, CH_2), 4.40 (dd, J=14.7 and 3.6 Hz, 1H, CH_2), 4.79 (dd, J=14.7 and 4.2 Hz, 1H, CH_2), 5.79 (dd, J=3.6 and 4.2 Hz, 1H, methine), 6.60 (d, J=8.5 Hz, 2H, ArH), 7.02 (d, J=8.5 Hz, 2H, ArH), 7.35–7.61 (m, 5H, ArH); ^{13}C NMR: 14.1, 21.2, 23.5, 46.1, 55.3, 94.3, 121.1, 122.4, 126.3, 128.1, 129.2, 138.7, 142.2, 148.5, and 152.9; *m/z*: 308 (M^+) and 292 (M^+-16).

2.3.25. 5-Butyl-6-phenyl-3-*p*-tolyl-5,6-dihydro-4*H*-[1,2,5]oxadiazine (4q). White crystalline solid; yield 50%; mp 140–141 °C; [Found: C, 77.89; H, 7.80; N, 9.14. $C_{20}H_{24}N_2O$ requires C, 77.89; H, 7.84; N, 9.08%]; ν_{max}/cm^{-1} (KBr): 1625 (C=N); δ_H (200 MHz): δ 0.94 (t, J=7.2 Hz, 3H, CH_3), 1.38–1.62 (m, 4H, 2×CH_2), 2.35 (s, 3H, CH_3), 2.73–2.81 (m, 2H, CH_2), 3.62 (AB quartet, J=7.6 Hz, 2H, CH_2, oxazine), 5.80 (s, 1H, methine), 6.58 (d, J=8.2 Hz, 2H, ArH), 6.98 (d, J=8.2 Hz, 2H, ArH), 7.07–7.42 (m, 5H, ArH); ^{13}C NMR: 13.7, 20.2, 21.2, 30.2, 45.1, 52.0, 91.1, 121.1, 122.8, 123.9, 126.2, 128.9, 139.1, 141.4, 149.1, and 153.1; *m/z*: 308.42 (M^+).

2.3.26. 1-Butyl-4-(4-nitro-phenyl)-2-phenyl-2,5-dihydro-1*H*-imidazole 3-oxide (3r). White crystalline solid; yield 31%; mp 125–126 °C; [Found: C, 67.29; H, 6.20; N, 12.35. $C_{19}H_{21}N_3O_3$ requires C, 67.24; H, 6.24; N, 12.38%]; ν_{max}/cm^{-1} (KBr): 1219 (N–O), 1549, 1600 (C=N); δ_H (200 MHz): δ 0.92 (t, J=7.4 Hz, 3H, CH_3), 1.38–1.63 (m, 4H, 2×CH_2), 2.75–2.85 (m, 2H, CH_2), 4.35 (dd, J=14.7 and 3.6 Hz, 1H, CH_2), 4.75 (dd, J=14.7 and 4.2 Hz, 1H, CH_2), 5.75 (dd, J=3.2 and 4.5 Hz, 1H, methine), 7.41–7.68 (m, 5H, ArH), 7.91 (d, J=8.8 Hz, 2H, ArH), 8.32 (d, J=8.7 Hz, 2H, ArH); ^{13}C NMR: 13.5, 21.2, 28.9, 45.3, 51.4, 93.8, 122.7, 123.5, 127.1, 129.4, 129.9, 139.4, 143.1, 150.2, and 153.2; *m/z*: 339 (M^+) and 326 (M^+-16).

2.3.27. 5-Butyl-3-(4-nitro-phenyl)-6-phenyl-5,6-dihydro-4*H*-[1,2,5]oxadiazine (4r). White crystalline solid; yield 53%; mp 105–106 °C; [Found: C, 67.29; H, 6.20; N, 12.35. $C_{19}H_{21}N_3O_3$ requires C, 67.24; H, 6.24; N, 12.38%]; ν_{max}/cm^{-1} (KBr): 1620 (C=N); δ_H (200 MHz): δ 0.94 (t, J=7.2 Hz, 3H, CH_3), 1.39–1.63 (m, 4H, 2×CH_2), 2.74–2.82 (m, 2H, CH_2), 3.65 (AB quartet, J=7.7 Hz, 2H, CH_2, oxazine), 5.79 (s, 1H, methine), 7.28–7.59 (m, 5H, ArH), 7.78 (d, J=8.8 Hz, 2H, ArH), 8.23 (d, J=8.8 Hz, 2H, ArH); ^{13}C NMR: 13.8, 20.2, 29.9, 43.8, 51.5, 91.0, 123.7, 125.4, 126.6, 128.5, 128.6, 137.1, 140.3, 148.3, and 152.1; *m/z*: 339 (M^+).

2.3.28. 1-Isopropyl-2,4-diphenyl-2,5-dihydro-1*H*-imidazole 3-oxide (3s). White crystalline solid; yield 35%; mp 120–121 °C; [Found: C, 77.19; H, 7.12; N, 10.05. $C_{18}H_{22}N_2O$ requires C, 77.11; H, 7.19; N, 9.99%]; ν_{max}/cm^{-1} (KBr): 1225 (N–O), 1545, 1599 (C=N); δ_H (200 MHz): δ 1.15–1.21 (m, 6H, 2×CH_3), 3.19–3.45 (m, 1H, –CH, isopropyl), 4.32 (dd, J=14.7 and 3.6 Hz, 1H, CH_2), 4.72 (dd, J=14.7 and 4.2 Hz, 1H, CH_2), 5.79 (dd, J=3.6 and 4.2 Hz, 1H, methine), 6.82–7.35 (m, 6H, ArH), 7.51–7.69 (m, 2H, ArH), 7.92–8.05 (m, 2H, ArH); ^{13}C NMR: 12.3, 22.4, 49.1, 89.7, 127.5, 129.1, 130.2, 130.8, 131.7, 133.5, 134.7, 142.1, and 153.9; *m/z*: 280 (M^+) and 264 (M^+-16).

2.3.29. 5-Isopropyl-3,6-diphenyl-5,6-dihydro-4*H*-[1,2,5]-oxadiazine (4s). White crystalline solid; yield 47%; mp 101–102 °C; [Found: C, 77.08; H, 7.12; N, 10.06. $C_{18}H_{22}N_2O$ requires C, 77.14; H, 7.19; N, 9.99%]; ν_{max}/cm^{-1} (KBr): 1623 (C=N); δ_H (200 MHz): δ 1.15–1.23 (m, 6H, 2×CH_3), 3.21–3.48 (m, 1H, –CH, isopropyl), 3.69 (s, 2H, –CH_2, oxazine), 5.99 (s, 1H, methine), 6.75–7.10 (m, 5H, ArH), 7.25–7.95 (m, 5H, ArH); ^{13}C NMR: 11.8, 21.9, 48.8, 89.8, 129.1, 129.7, 130.2, 132.1, 132.9, 134.1, 134.7, 140.7, and 152.1; *m/z*: 280 (M^+).

2.3.30. 1-Isopropyl-2-phenyl-4-*p*-tolyl-2,5-dihydro-1*H*-imidazole 3-oxide (3t). White crystalline solid; yield 37%; mp 133–134 °C; [Found: C, 77.58; H, 7.50; N, 9.48. $C_{19}H_{22}N_2O$ requires C, 77.52; H, 7.53; N, 9.52%]; ν_{max}/cm^{-1} (KBr): 1221 (N–O), 1547, 1595 (C=N); δ_H (200 MHz): δ 1.13–1.21 (m, 6H, 2×CH_3), 2.32 (s, 3H, CH_3), 3.15–3.42 (m, 1H, –CH, isopropyl), 4.35 (dd, J=14.2 and 4.2 Hz, 1H, CH_2), 4.62 (dd, J=14.2 and 4.2 Hz, 1H, CH_2), 5.75 (dd, J=3.7 and 4.1 Hz, 1H, methine), 6.65 (d, J=8.5 Hz, 2H, ArH), 6.99 (d, J=8.5 Hz, 2H, ArH), 7.10–7.49 (m, 5H, ArH); ^{13}C NMR: 11.6, 20.6 (CH_3), 21.4 (CH), 44.1 (CH_2), 90.1 (methine), 127.8, 128.1, 129.5, 130.1, 130.9, 131.2, 134.1, 140.1, and 153.1; *m/z*: 294 (M^+) and 278 (M^+-16).

2.3.31. 5-Isopropyl-6-phenyl-3-*p*-tolyl-5,6-dihydro-4*H*-[1,2,5]oxadiazine (4t). White crystalline solid; yield 48%; mp 105–106 °C; [Found: C, 77.59; H, 7.48; N, 9.58. $C_{19}H_{22}N_2O$ requires C, 77.52; H, 7.53; N, 9.52%]; ν_{max}/cm^{-1} (KBr): 1620 (C=N); δ_H (200 MHz): δ 1.15–1.22 (m, 6H, 2×CH_3), 2.32 (s, 3H, CH_3), 3.25–3.50 (m, 1H, –CH, isopropyl), 3.95 (s, 2H, oxazine CH_2), 5.98 (s, 1H, methine), 6.94 (d, J=8.6 Hz, 2H, ArH), 7.02 (d, J=8.6 Hz, 2H, ArH), 7.12–7.45 (m, 5H, ArH); ^{13}C NMR: 11.4, 20.5 (CH_3), 22.0 (CH), 45.4 (CH_2), 93.1 (methine), 128.1, 129.2, 129.9, 131.1, 132.8, 133.2, 134.1, 137.4, and 152.5; *m/z*: 294 (M^+) and 278 (M^+-16).

2.3.32. 1-Isopropyl-4-(4-nitro-phenyl)-2-phenyl-2,5-dihydro-1*H*-imidazole 3-oxide (3u). White crystalline solid; yield 31%; mp 111–112 °C; [Found: C, 66.51; H, 5.85; N, 12.94. $C_{18}H_{19}N_3O_3$ requires C, 66.45; H, 5.89; N, 12.91%];

ν_{max}/cm^{-1} (KBr): 1219 (N–O), 1545, 1596 (C═N); δ_H (200 MHz): δ 1.15–1.22 (m, 6H, 2×CH_3), 3.21–3.48 (m, 1H, –CH, isopropyl), 4.22 (dd, J=14.7 and 3.6 Hz, 1H, CH_2), 4.68 (dd, J=14.7 and 4.2 Hz, 1H, CH_2), 5.72 (dd, J=3.6 and 4.2 Hz, 1H, methine), 7.35–7.61 (m, 5H, ArH), 7.82 (d, J=8.7 Hz, 2H, ArH), 8.27 (d, J=8.7 Hz, 2H, ArH); ^{13}C NMR: 11.4, 21.3 (CH, isopropyl), 43.5 (CH_2), 90.1 (methine), 127.2, 127.9, 128.4, 129.1, 130.5, 130.7, 132.4, 133.9, and 154.2; m/z: 325 (M^+) and 309 (M^+-16).

2.3.33. 5-Isopropyl-3-(4-nitro-phenyl)-6-phenyl-5,6-dihydro-4*H*-[1,2,5]oxadiazine (4u). White crystalline solid; yield 52%; mp 98–99 °C; [Found: C, 66.50; H, 5.85; N, 12.98. $C_{18}H_{19}N_3O_3$ requires C, 66.45; H, 5.89; N, 12.91%]; ν_{max}/cm^{-1} (KBr): 1621 (C═N); δ_H (200 MHz): δ 1.17–1.25 (m, 6H, 2×CH_3), 3.25–3.51 (m, 1H, –CH, isopropyl), 3.61 (s, 2H, –CH_2, oxazine), 5.91 (s, 1H, methine), 7.29–7.55 (m, 5H, ArH), 7.73 (d, J=8.7 Hz, 2H, ArH), 8.19 (d, J=8.7 Hz, 2H, ArH); ^{13}C NMR: 11.2, 21.2, 42.4, 94.8, 127.5, 128.2, 128.7, 128.9, 130.1, 130.5, 132.1, 134.2, and 153.5; m/z: 325 (M^+); Anal. Calcd for: C, 66.45; H, 5.89; N, 12.91.

2.3.34. 1-Furan-2-ylmethyl-2,4-diphenyl-2,5-dihydro-1*H*-imidazole 3-oxide (3v). White crystalline solid; yield 34%; mp 138–139 °C. [Found: C, 66.50; H, 5.85; N, 12.98. $C_{18}H_{19}N_3O_3$ requires C, 66.45; H, 5.89; N, 12.91%]; ν_{max}/cm^{-1} (KBr): 1219 (N–O), 1545, 1597 (C═N); δ_H (200 MHz): δ 3.81 (d, J=14.6 Hz, 1H, furyl), 3.92 (d, J=14.6 Hz, 1H, furyl), 4.2 (dd, J=14.2 and 4.5 Hz, 1H, –CH_2–), 4.56 (dd, J=14.2 and 3.3 Hz, 1H, –CH_2–), 5.62 (dd, J=4.5 and 3.3 Hz, 1H, methine), 6.23–6.32 (m, 2H, H_b and H_c), 6.42–7.53 (m, 11H, 10ArH and 1H, H_a); ^{13}C NMR: 54.2, 56.5, 94.5 (methine), 111.8, 119.3, 122.4, 126.8, 127.5, 129.2, 132.6, 134.3, 137.5, 139.2, 148.2, 152.2, and 154.1; m/z: 318 (M^+) and 302 (M^+-16); Anal. Calcd for $C_{20}H_{18}N_2O_2$: C, 75.45; H, 5.70; N, 8.80; Found: C, 75.50; H, 5.76; N, 8.82.

2.3.35. 5-Furan-2-ylmethyl-3,6-diphenyl-5,6-dihydro-4*H*-[1,2,5]oxadiazine (4v). White crystalline solid; yield 49%; mp 121–122 °C. [Found: C, 75.51; H, 5.78; N, 8.85. $C_{20}H_{18}N_2O_2$ requires C, 75.45; H, 5.70; N, 8.80%]; ν_{max}/cm^{-1} (KBr): 1625 (C═N); δ_H (200 MHz): δ 3.62 (s, 2H, CH_2), 3.82 (d, J=14.7 Hz, 1H, furyl), 3.91 (d, J=14.7 Hz, 1H, furyl), 5.78 (s, 1H, methine), 6.26–6.33 (m, 2H, H_b and H_c), 6.78–7.32 (m, 5H, 4ArH and 1H, H_a), 7.34–7.48 (m, 6H, ArH); ^{13}C NMR: 53.8, 56.5, 94.5, 112.0, 117.9, 120.8, 121.3, 125.7, 126.5, 127.3, 130.5, 132.6, 135.4, 146.9, 151.2, and 153.1; m/z: 318 (M^+).

2.3.36. 1-Furan-2-ylmethyl-2-phenyl-4-*p*-tolyl-2,5-dihydro-1*H*-imidazole 3-oxide (3w). White crystalline solid; yield 31%; mp 145–146 °C. [Found: C, 75.93; H, 6.12; N, 8.45. $C_{21}H_{20}N_2O_2$ requires C, 75.88; H, 6.06; N, 8.43%]; ν_{max}/cm^{-1} (KBr): 1219 (N–O), 1550, 1595 (C═N); δ_H (200 MHz): δ 2.39 (s, 3H, CH_3), 3.83 (d, J=14.7 Hz, 1H, furyl), 3.94 (d, J=14.7 Hz, 1H, furyl), 4.24 (dd, J=14.1 and 4.4 Hz, 1H, –CH_2–), 4.54 (dd, J=14.1 and 3.5 Hz, 1H, –CH_2–), 5.60 (dd, J=4.4 and 3.5 Hz, 1H, methine), 6.29–6.31 (m, 2H, H_b and H_c), 6.99–7.01 (d, J=8.4 Hz, 2H, ArH), 7.03–7.06 (d, J=8.4 Hz, 2H, ArH), 7.17–7.45 (m, 6H, 5ArH and 1H, H_a); ^{13}C NMR: 21.5 (CH_3), 54.0, 56.4, 94.6 (methine), 112.4, 120.9, 124.0, 127.0, 128.1, 128.8, 131.1, 133.4, 134.2, 137.3, 147.4, 152.1, and 152.9; m/z: 332 (M^+) and 316 (M^+-16).

2.3.37. 5-Furan-2-ylmethyl-6-phenyl-3-*p*-tolyl-5,6-dihydro-4*H*-[1,2,5]oxadiazine (4w). White crystalline solid; yield 54%; mp 130–131 °C. [Found: C, 75.92; H, 6.10; N, 8.45. $C_{21}H_{20}N_2O_2$ requires C, 75.88; H, 6.06; N, 8.43%]; ν_{max}/cm^{-1} (KBr): 1621 (C═N); δ_H (200 MHz): δ 2.35 (s, 3H, CH_3), 3.63 (s, 2H, CH_2), 3.83 (d, J=14.7 Hz, 1H, furyl), 3.94 (d, J=14.7 Hz, 1H, furyl), 5.78 (s, 1H, methine), 6.27–6.33 (m, 2H, H_b and H_c), 6.99–7.02 (d, J=8.2 Hz, 2H, ArH), 7.13–7.80 (m, 8H, 7ArH and 1H, H_a); ^{13}C NMR: 20.9, 53.7, 56.4, 94.4, 111.8, 118.3, 120.8, 121.9, 122.8, 124.6, 127.0, 129.2, 130.1, 133.2, 147.5, 151.4, and 153.0; m/z: 332 (M^+).

2.3.38. 1-Furan-3-ylmethyl-4-(4-nitro-phenyl)-2-phenyl-2,5-dihydro-1*H*-imidazole 3-oxide (3x). Bright yellow crystalline solid; yield 30%; mp 155–156 °C. [Found: C, 66.16; H, 4.76; N, 11.59. $C_{20}H_{17}N_3O_4$ requires C, 66.11; H, 4.72; N, 11.56%]; ν_{max}/cm^{-1} (KBr): 1220 (N–O), 1551, 1589 (C═N); δ_H (200 MHz): δ 3.84 (d, J=14.8 Hz, 1H, furyl CH_2), 3.98 (d, J=14.8 Hz, 1H, furyl), 4.26 (dd, J=14.1 and 4.5 Hz, 1H, –CH_2–), 4.56 (dd, J=14.1 and 3.7 Hz, 1H, –CH_2–), 5.61 (dd, J=4.4 and 3.5 Hz, 1H, methine), 6.27–6.36 (m, 2H, H_b and H_c), 7.27–7.62 (m, 6H, 5ArH and H_a), 8.26 (d, J=8.9 Hz, 2H, ArH), 8.39 (d, J=8.9 Hz, 2H, ArH); ^{13}C NMR: 53.9 (–CH_2–), 56.3 (–CH_2), 94.6 (methine), 112.1, 121.2, 123.6, 126.9, 127.7, 128.6, 130.0, 133.3, 133.6, 136.5, 147.6, 151.8, and 152.9; m/z: 363 (M^+) and 347 (M^+-16).

2.3.39. 5-Furan-2-ylmethyl-3-(4-nitro-phenyl)-6-phenyl-5,6-dihydro-4*H*-[1,2,5]oxadiazine (4x). Yellow crystalline solid; yield 50%; mp 126–127 °C. [Found: C, 66.15; H, 4.76; N, 11.58. $C_{20}H_{17}N_3O_4$ requires C, 66.11; H, 4.72; N, 11.56%]; ν_{max}/cm^{-1} (KBr): 1625 (C═N); δ_H (200 MHz): δ 3.65 (s, 2H, CH_2), 3.82 (d, J=14.6 Hz, 1H, furyl), 3.93 (d, J=14.6 Hz, 1H, furyl), 5.77 (s, 1H, methine), 6.28–6.33 (m, 2H, H_b and H_c), 7.26–7.56 (m, 6H, 5ArH and 1H, H_a), 7.74 (d, J=8.8 Hz, 2H, ArH), 8.23 (d, J=8.8 Hz, 2H, ArH); ^{13}C NMR: 53.8 (–CH_2–), 56.3, 94.5 (methine), 111.9, 118.2, 121.3, 122.3, 123.7, 125.9, 127.8, 129.1, 130.5, 133.4, 147.5, 151.5, and 153.1; m/z: 363 (M^+).

2.4. Reactions of 2-methyl-1-aryl-isothioureas 7a–c and *N*-aryl-secondary amine-carboxamidines 7d–f with α-nitrosoalkenes

A solution of carboxamidines or isothioureas **7** (4 mmol) and α-bromooxime **2** (4.2 mmol) in dry CH_2Cl_2 (20 ml) was stirred at rt in the presence of sodium bicarbonate for 2–3 h. Work up identical with that employed for the nitrone **3** gave the crude products **8**, which were purified by column chromatography on silica gel (EtOAc–hexane :: 1:9) to yield the corresponding imidazoles **8** (75–85%).

2.4.1. 2-Methylsulfanyl-1-phenyl-4-*p*-tolyl-1*H*-imidazole (8a). Mp 145–146 °C; yield 78%; [Found: C, 72.85; H, 5.73; N, 10.01. $C_{17}H_{16}N_2S$ requires C, 72.82; H, 5.75; N, 9.99%]; ν_{max}/cm^{-1} (KBr): 1592 (C═N); δ_H (200 MHz): δ 2.35 (s, 3H, CH_3), 2.47 (s, 3H, SCH_3), 6.51 (d, J=8.2 Hz, 2H, ArH), 7.21 (d, J=8.2 Hz, 2H, ArH), 7.45

(s, 1H, H_a), 7.47–7.52 (m, 5H, ArH); δ_C (200 MHz): δ 18.9 (SCH_3); 20.9 (CH_3); 121.0, 123.1, 125.2, 126.9, 128.0, 129.4, 129.7, 133.5, 136.7, and 137.7; *m/z*: 280.39 (M^+), 280.10 (100%), 281.11 (19.1%), and 282.10 (4.6%).

2.4.2. 4-[4-(4-Nitro-phenyl)-1-phenyl-1*H*-imidazol-2-yl]-morpholine (8e). Mp 165–166 °C; yield 81%; [Found: C, 65.14; H, 5.20; N, 15.97. $C_{19}H_{18}N_4O_3$ requires C, 65.13; H, 5.18; N, 15.99%]; ν_{max}/cm^{-1} (KBr): 1595 (C=N); δ_H (200 MHz): δ 2.92 (m, 4H, $-CH_2-N-CH_2-$), 3.67 (m, 4H, $-CH_2-O-CH_2-$), 7.19–7.32 (m, 6H, 5 aromatic+1 olefenic), 8.24 (d, 2H, *J*=8.0 Hz, arom), 8.40 (d, 2H, *J*=8.0 Hz, arom); δ_C (200 MHz): δ 58.9 ($-CH_2-N-CH_2-$), 71.4 ($-CH_2-O-CH_2-$), 121.0, 123.2, 124.1, 125.0, 127.9, 128.0, 129.4, 136.7, 137.0, 142.6, and 148.4; *m/z*: 350.37 (M^+), 350.14 (100%), 351.14 (21.5%), and 352.14 (3.1%).

2.4.3. 2-Pyrrolidin-1-yl-1, 4-di-*p*-tolyl-1*H*-imidazole (8f). Mp 132–133 °C; yield 85%; [Found: C, 79.49; H, 7.31; N, 13.21. $C_{21}H_{23}N_3$ requires C, 79.46; H, 7.30; N, 13.24%]; ν_{max}/cm^{-1} (KBr): 1601 (C=N); δ_H (200 MHz): δ 1.59 (m, 4H, $-CH_2-CH_2-$), 2.32 (s, 3H, CH_3), 2.81 (m, 4H, $-CH_2-N-CH_2-$), 6.79 (d, *J*=8.0 Hz, 2H, ArH), 7.05 (m, 3H, 2 aromatic+1 olefenic), 7.12 (d, 2H, *J*=8.0 Hz, arom), 7.36 (d, 2H, *J*=8.0 Hz, arom); δ_C (200 MHz): δ 20.5 (CH_3), 20.9 (CH_3), 25.1 ($-CH_2-CH_2-$), 47.7 ($-CH_2-N-CH_2-$), 120.9, 123.0, 125.2, 126.9, 129.7, 130.1, 133.5, 133.7, 137.0, 137.2, and 137.7; *m/z*: 317.43 (M^+), 317.19 (100%), 318.19 (24.5%), and 319.20 (2.7%).

2.5. Reactions of *N*-phenyl-secondaryamino-1-carboximidothioic acid allyl ester 15a–d and 2-allyl-1,1-dimethyl-3-phenyl-isothiourea 15e–f with α-nitrosoalkenes

A solution of *S*-allylated imines **15** (4 mmol) and α-bromooxime **2** (4.2 mmol) in dry CH_2Cl_2 (20 ml) was stirred at rt in the presence of sodium bicarbonate for 2–3 h. Work up identical with that employed for the nitrones **3** and **8** gave the crude products, which were purified by column chromatography on silica gel (EtOAc–hexane:: 1:10) to yield the corresponding products **16** (70–80%).

2.5.1. 1,4-Diphenyl-2-pyrrolidin-1-yl-1*H*-imidazole 3-oxide (16a). Mp 142–143 °C; yield 77%; [Found: C, 74.76; H, 6.20; N, 13.75. $C_{19}H_{19}N_3O$ requires C, 74.73; H, 6.27; N, 13.76%]; ν_{max}/cm^{-1} (KBr): 1223 (N–O), 1583, 1596 (C=N); δ_H (200 MHz): δ 1.79 (m, 4H, $-CH_2-CH_2-$), 3.30 (m, 4H, $-CH_2-N-CH_2-$), 6.88 (m, 1H, olefenic), 7.08–7.32 (m, 10H, ArH); δ_C (200 MHz): δ 22.6, 45.7, 69.2, 119.6, 122.7, 125.2, 126.5, 127.1, 128.7, 130.2, 132.5, 139.1, and 154.2; *m/z*: 305 (M^+).

2.5.2. 1-(3-Oxy-1,4-diphenyl-1*H*-imidazol-2-yl)-piperidine (16b). Mp 153–154 °C; yield 80%; [Found: C, 75.24; H, 6.62; N, 13.17. $C_{20}H_{21}N_3O$ requires C, 75.21; H, 6.63; N, 13.16%]; ν_{max}/cm^{-1} (KBr): 1219 (N–O), 1599, 1652 (C=N); δ_H (200 MHz): δ 1.58 (m, 6H, $-CH_2-CH_2-CH_2-$), 2.83 (m, 2H, $-N-CH_2-$), 3.42 (m, 2H, $-N-CH_2-$), 6.49 (m, 1H, olefenic), 6.83–7.45 (m, 10H, ArH); δ_C (200 MHz): δ 25.2 ($-CH_2-CH_2-$), 26.2 (CH_2), 55.1 ($-CH_2-N-CH_2-$), 70.1, 119.8, 123.2, 125.9, 126.2, 127.5, 128.5, 130.0, 140.2, and 153.2; *m/z*: 319 (M^+).

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