REGIO- AND STEREOSELECTIVITY OF [2+3]CYCLOADDITION OF NITROETHENE TO (*Z*)-*N*-ARYL-*C*-PHENYLNITRONES+

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The cycloaddition reactions of nitroethene to (*Z*)-*N*-aryl-*C*-phenylnitrones lead to mixtures of stereoisomeric *cis*- and *trans*-2-aryl-4-nitro-3-phenylisoxazolidines. Regioselectivity of these reactions is determined by the character of nucleophile–electrophile interactions, while stereoselectivity is determined by the steric factors and the character of secondary orbital interactions.

Keywords: [2+3]Cycloadditions; Dipolar Cycloadditions; Nitrones; Isoxazolidines; Nitroethene; Regioselectivity; Stereoselectivity; DFT calculations.

Although [2+3]cycloaddition reactions of conjugated nitroalkenes have been the subject of many papers, the issues related to the reaction of the simplest representative of the conjugated nitroalkenes – nitroethene – are rarely discussed. Only a few reports refer to selectivity of cycloaddition of nitroethene to *N*-*tert*-butylnitrone[2], *N*-methyl-*C*-phenyl-, *N*-tert-butyl-*C*-phenyl- and *N*-benzyl-*C*-phenylnitrones[3], and *N*,*C*,*C*-triphenyl- and *N*-methyl-*C*,*C*-diphenylnitrones[4]. It is difficult to formulate general conclusions regarding regio- and stereoselectivity of nitroethene–nitrone reactions on the basis of the existing studies. This paper is a continuation of the systematic research[4a,5] aimed at comprehensive understanding of the regularities occurring in the course of these cycloadditions. Within the scope of the paper, regio- and stereoselectivity of [2+3]cycloaddition of nitroethene to a series of (*Z*)-*N*-aryl-*C*-phenylnitrones, containing different donor–acceptor substituents in the aryl ring, is explained and experimentally verified.

+ Part LXVII of the series Synthesis and Properties of Azoles and Their Derivatives; for Part LXVI, see ref.[1]

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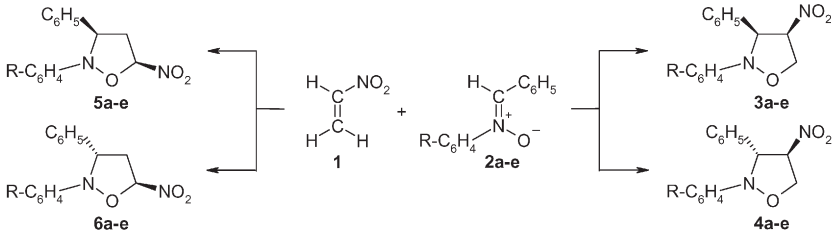
RESULTS AND DISCUSSION

The [2+3]cycloadditions in question could lead in principle, to mixtures of regio- and stereoisomeric nitroisoxazolidines **3a**–**3e**, **4a**–**4e**, **5a**–**5e** and **6a**–**6e** (Scheme 1).



R = 4-CH_3 (**a**), H (**b**), 4-Cl (**c**), 3-Cl (**d**), 4-$COOCH_3$ (**e**)

SCHEME 1

These reactions occurred easily even at room temperature. HPLC analysis showed that in all cases the conversion of nitrone was complete after 24 h and large amounts of two products with different retention times (R_T) appeared in the reaction mixture. After vacuum evaporation of the solvent and excess of unreacted nitroethene, the compounds were separated using semipreparative HPLC.

The constitution of the products was determined on the basis of elemental analysis and spectral data. In particular, in IR spectra of the products, the bands characteristic of nitro groups and isoxazolidines were observed. The fragmentation patterns of the parent ions upon electron impact are typical for 4-nitroisoxazolidines[6]. Information about regio- and stereochemistry of the compounds was provided by ^{1}H NMR spectroscopy. Multiplicity of the spin system confirms the location of the nitro group at the C4 position, while the magnitude of J(3,4) coupling constants indicates the relative positions of H3 and H4. In search for an experimental support of the structure assignment, NOESY measurements of compounds **3e** and **4e** were carried out. The spectrum of nitroisoxazolidine **3e** showed a correlation signal between H3 and H5 protons. The spectrum of nitroisoxazolidine **4e** showed a correlation signal between H3 and H5 and between H4 and Hα (Fig. 1). The analyses proved that in all cases the product with a lower R_T was *cis*-2-aryl-4-nitro-3-phenylisoxazolidine (major product), while the product at higher R_T was *trans*-2-aryl-4-nitro-3-phenylisoxazolidine (minor product).

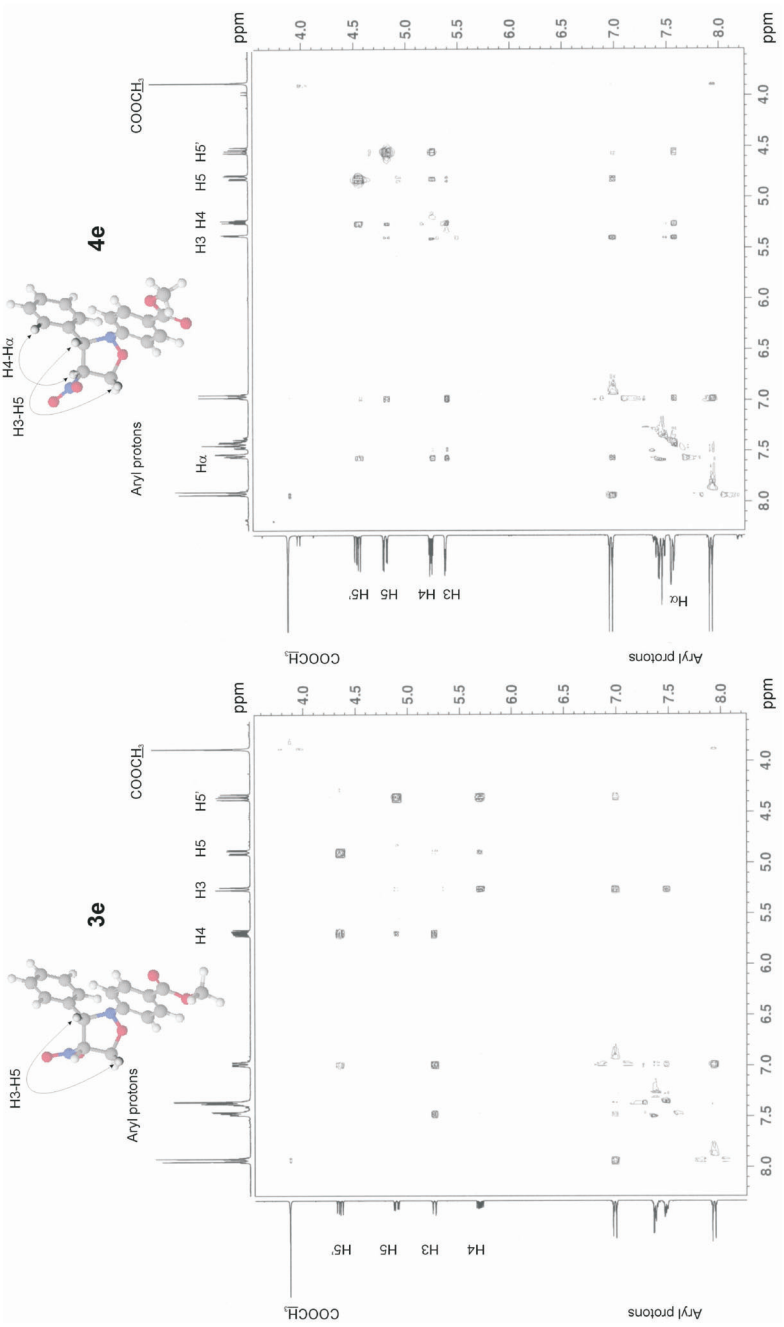


FIG. 1
The NOESY correlations for nitroisoxazolidines **3e** and **4e**. Geometry of **3e** and **4e** was taken from B3LYP/6-31G(d) (PCM) calculations

Regioselectivity of the [2+3]cycloaddition of nitroethene **1** to (*Z*)-*N*-aryl-*C*-phenylnitrones **2a**–**2e** can be explained by the HSAB theory[7]. Such an approach has recently been successfully applied *inter alia* to interpretation of the course of cycloaddition of (i) methyl acrylate to (*Z*)-*N*-methyl-*C*-(methoxycarbonyl)nitrone[8] or azomethine ylides[9], (ii) anthracene to 2,4,6-trimethylbenzonitrile *N*-oxide[10] and (iii) methyl propiolate to aryl azides[11]. The electron properties of the substrates were calculated by B3LYP/6-31G(d) method[12]. This algorithm has been successfully applied in recent years for calculations of the components of [4+2]-π-electron cycloadditions[13].

According to the HSAB theory, [2+3]cycloaddition can be treated as the process of transferring an electron pair from the addend donating the electrons (in this case nitrone) to the addend being the electron acceptor (in this case nitroethene). By treating the transition state as a donor–acceptor complex, it can be assumed that the transition state will be more stable when both constituents are soft or both are hard[7].

In order to predict regioselectivity of a cycloaddition reaction, not only the knowledge of the global softness index *S* of the addends is required, but also the knowledge of the local softness index *s* for the respective reaction centres is necessary. These indices were calculated from the equations[14] (see Tables I and II):

$$f^{+}_{i} = q_i(N + 1) - q_i(N)$$

$$f^{-}_{i} = q_i(N) - q_i(N - 1)$$

$$s^{+}_{k} = Sf^{+}_{k}$$

$$s^{-}_{k} = Sf^{-}_{k}$$

where $q_i(N)$ is electronic population of the site in neutral system, $q_i(N + 1)$ electronic population of the site in anionic system, $q_i(N - 1)$ electronic population of the site in cationic system, s^{+}_{k} local softness for nucleophilic attack and s^{-}_{k} local softness for electrophilic attack.

Having computed local softness indices, regioselectivity indices Δ, as proposed by Gazquez[15], were then calculated (Table III):

$$\Delta^{CO}_{\alpha\beta} = (s^{-}_{C} - s^{+}_{\alpha})^2 + (s^{-}_{O} - s^{+}_{\beta})^2$$

for reactions leading to 4-nitroisoxazolidines and

$$\Delta^{CO}_{\beta\alpha} = (s^{-}_{C} - s^{+}_{\beta})^2 + (s^{-}_{O} - s^{+}_{\alpha})^2$$

for reactions leading to 5-nitroisoxazolidines.

It appeared that independently of the character of the substituent in the nitrone molecule, the value of the index $\Delta^{CO}_{\alpha\beta}$ was always lower than the value of the index $\Delta^{CO}_{\beta\alpha}$. This means that the character of the nucleophile–electrophile interaction favours formation of isoxazolidines with nitro group in the C4 position, which were identified in the reaction mixtures.

Stereoselectivity of the reactions is determined by the balancing effect of the repulsive steric interactions, favouring *endo* transition states (path B) and the secondary orbital interactions[16], favouring *exo* transition states (path A) (Fig. 2). In particular, the exo transition states are stabilizing due to the overlaps of p_z orbitals located on oxygen atoms of nitro group with

TABLE I
Global and local softness of nitroethene **1**

S, a.u.	$H_2C=\underline{C}(H)NO_2$, ($s^+_\alpha$)	$H_2\underline{C}=C(H)NO_2$, ($s^+_\beta$)
4.993	0.030	0.514

TABLE II
Global and local softness of (*Z*)-*N*-aryl-*C*-phenylnitrones **2a**–**2e**

Compd.	*S*, a.u.	>$\underline{C}$=N(Ar)–O, (s^-_C)	>C=N(Ar)–$\underline{O}$, (s^-_O)
2a	6.988	1.076	1.733
2b	7.564	1.180	1.997
2c	7.221	1.090	1.805
2d	7.212	1.111	1.890
2e	7.634	1.054	1.886

TABLE III
Values of Δ indices for [2+3]cycloaddition of nitroethene **1** to arylnitrones **2a**–**2e**

Reaction	$\Delta^{CO}_{\alpha\beta}$	$\Delta^{CO}_{\beta\alpha}$	Reaction	$\Delta^{CO}_{\alpha\beta}$	$\Delta^{CO}_{\beta\alpha}$
1 + **2a**	2.580	3.216	**1** + **2d**	3.060	3.814
1 + **2b**	3.521	4.312	**1** + **2e**	2.929	3.735
1 + **2c**	2.791	3.483			

p_z orbitals located on carbon atoms of the phenyl ring bounded to the carbon atom of CNO nitrone fragment. These electronic effects are most probably slightly stronger than the steric interactions. Due to this, the amount of cycloadducts with 3,4-*cis* configuration is higher.

B3LYP/6-31G(d) calculations of the potential energy surface for the paths A and B proved that the transition states have asymmetric character (Fig. 2). Within the transition states the σ O1–C5 bond is formed substantially faster than σ C3–C4 bond. Detailed analysis of the critical structures on the reaction paths is the subject of a separate publication.

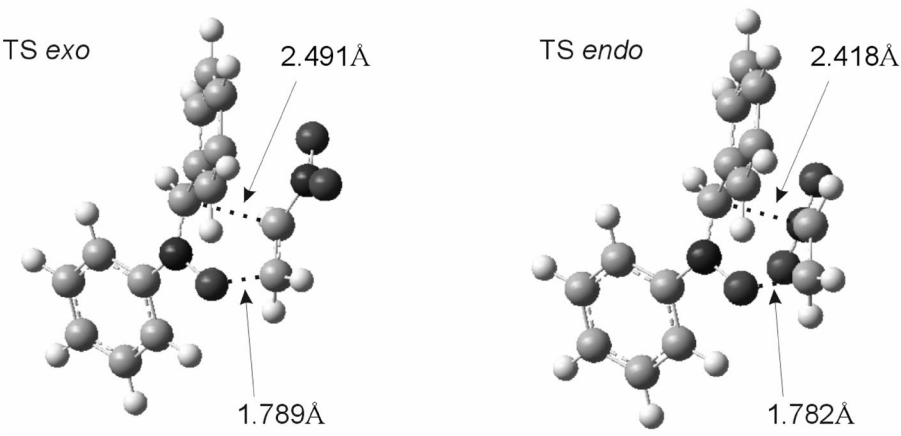


FIG. 2

Exo and *endo* transition structures approximated with B3LYP/6-31G(d) method for [2+3]-cycloaddition **1** + **2b** in toluene (for simulation of the solvent effect, the PCI approach was applied)

CONCLUSION

The cycloaddition reactions of nitroethene to (*Z*)-*N*-aryl-*C*-fenylnitrones lead to mixtures of stereoisomeric *cis*- and *trans*-2-aryl-3-phenyl-4-nitroisoxazolidines. Regioselectivity of these reactions can be explained by the HSAB theory. Stereoselectivity is influenced by repulsive steric interactions and secondary orbital interactions.

EXPERIMENTAL

General

Melting points were determined on a Boetius apparatus and are not corrected. ^{1}H NMR spectra were taken on a Bruker Avance (300 MHz) or Tesla BS-567C (80 MHz) spectrometer in

$CDCl_3$. Chemical shifts are expressed in ppm (δ-scale) downfield from TMS used as an internal standard, coupling constants, *J*, are given in Hz. IR spectra (ν, cm^{-1}) were recorded on a Bio-Rad 175 C spectrometer. Mass spectra (70 eV) were measured with a Finningan 955 spectrometer. HPLC analyses and separation of the cycloadducts were carried out using the Knauer apparatus analogously as it was recently reported[6a,17]. Elemental analyses were determined on a Perkin–Elmer PE-2400 CHN apparatus. The nitroethene and (*Z*)-*N*-aryl-*C*-phenylnitrones were prepared according to the method described in literature[18]. The quantum-chemical calculations were performed on a SGI-2800 computer at Cracow Computing Center 'Cyfronet'. Hybrid B3LYP functional and 6-31G(d) basis set included within Gaussian03 software were applied[12].

Synthesis of 2-Aryl-4-nitro-3-phenylisoxazolidines. General Procedure

A mixture of 5 mmol of nitroethene and 2.5 mmol of arylphenylnitrone in 5 ml of dry toluene was stirred in the dark at room temperature for 24 h. The solvent was evaporated in vacuo and the residue was separated by semipreparative HPLC. Evaporation of the eluent from the fractions gave stereoisomeric 4-nitroisoxazolidines.

cis-2-(4-Methylphenyl)-4-nitro-3-phenylisoxazolidine (**3a**). Yield 45%. M.p. 116–117 °C (ethanol). IR: 1566 s, 1374 m, 1181 w, 926 w. ^{1}H NMR: 7.43–6.97 m, 9 H (Ar-H); 5.65 ddd, 1 H, *J*(3,4) = 8.8, *J*(4,5) = 4.2, *J*(4,5′) = 6.7 (H4); 5.06 d, 1 H, *J*(3,4) = 8.8 (H3); 4.86 dd, 1 H, *J*(4,5) = 4.2, *J*(5,5′) = 10.2 (H5); 4.41 dd, 1 H, *J*(4,5′) = 6.7, *J*(5,5′) = 10.2 (H5′); 2.27 s, 3 H (CH_3). MS: 284 (45) [$M^{\bullet+}$], 195 (12), 194 (14), 105 (21). For $C_{16}H_{16}N_2O_3$ calculated: 67.59% C, 5.67% H, 9.85% N; found: 67.39% C, 5.90% H, 9.34% N.

trans-2-(4-Methylphenyl)-4-nitro-3-phenylisoxazolidine (**4a**). Yield 31%. Oil. IR: 1556 s, 1372 m, 1179 w, 919 w. ^{1}H NMR: 7.62–6.83 m, 9 H (Ar-H); 5.10 d, 1 H, *J*(3,4) = 3.7 (H3); 5.20 ddd, 1 H, *J*(3,4) = 3.7, *J*(4,5) = 2.4, *J*(4,5′) = 6.0 (H4); 4.78 dd, 1 H, *J*(4,5) = 2.4, *J*(5,5′) = 10.4 (H5); 4.48 dd, 1 H, *J*(4,5′) = 6.0, *J*(5,5′) = 10.4 (H5′); 2.26 s, 3 H (CH_3). MS: 284 (88) [$M^{\bullet+}$], 195 (10), 194 (16), 105 (27). For $C_{16}H_{16}N_2O_3$ calculated: 67.59% C, 5.67% H, 9.85% N; found: 67.44% C, 5.93% H, 9.36% N.

cis-4-Nitro-2,3-diphenylisoxazolidine (**3b**). Yield 46%. M.p. 112–113 °C (ethanol). IR: 1556 s, 1373 m, 1177 w, 929 w. ^{1}H NMR: 7.44–6.99 m, 10 H (Ar-H); 5.14 d, 1 H, *J*(3,4) = 8.5 (H3); 5.66 ddd, 1 H, *J*(3,4) = 8.5, *J*(4,5) = 3.8, *J*(4,5′) = 7.6 (H4); 4.95 dd, 1 H, *J*(4,5) = 3.8, *J*(5,5′) = 10.0 (H5); 4.43 dd, 1 H, *J*(4,5′) = 7.6, *J*(5,5′) = 10.0 (H5′). MS: 270 (83) [$M^{\bullet+}$], 181 (19), 180 (28), 91 (64). For $C_{15}H_{14}N_2O_3$ calculated: 66.66% C, 5.22% H, 10.36% N; found: 66.48% C, 5.21% H, 10.45% N.

trans-4-Nitro-2,3-diphenylisoxazolidine (**4b**). Yield 32%. M.p. 61–62 °C (cyclohexane). IR: 1556 s, 1367 m, 1177 w, 922 w. ^{1}H NMR: 7.57–6.97 m, 10 H (Ar-H); 5.24–5.19 m, 2 H (H3 + H4); 4.79 dd, 1 H, *J*(4,5) = 2.2, *J*(5,5′) = 10.5 (H5); 4.51 dd, 1 H, *J*(4,5′) = 5.8, *J*(5,5′) = 10.5 (H5′). MS: 270 (70) [$M^{\bullet+}$], 181 (18), 180 (31), 91 (65). For $C_{15}H_{14}N_2O_3$ calculated: 66.66% C, 5.22% H, 10.36% N; found: 66.58% C, 5.25% H, 10.32% N.

cis-2-(4-Chlorophenyl)-4-nitro-3-phenylisoxazolidine (**3c**). Yield 49%. M.p. 131–132 °C (ethanol). IR: 1557 s, 1364 m, 1178 w, 933 w. ^{1}H NMR: 7.50–6.86 m, 9 H (Ar-H); 5.03 d, 1 H, *J*(3,4) = 8.6 (H3); 5.65 ddd, 1 H, *J*(3,4) = 8.6, *J*(4,5) = 3.7, *J*(4,5′) = 6.5 (H4); 4.98 dd, 1 H, *J*(4,5) = 3.7, *J*(5,5′) = 10.0 (H5); 4.38 dd, 1 H, *J*(4,5′) = 6.5, *J*(5,5′) = 10.0 (H5′). MS: 304 (30) [$M^{\bullet+}$], 215 (5), 214 (5), 125 (12). For $C_{15}H_{13}ClN_2O_3$ calculated: 59.13% C, 4.30% H, 9.19% N; found: 58.23% C, 4.25% H, 9.01% N.

trans-2-(4-Chlorophenyl)-4-nitro-3-phenylisoxazolidine (**4c**). Yield 37%. Oil. IR: 1554 s, 1372 m, 1179 w, 919 w. ^{1}H NMR: 7.61–6.83 m, 9 H (Ar-H); 5.29–5.09 m, 2 H (H3 + H4); 4.79 dd, 1 H, *J*(4,5) = 2.4, *J*(5,5′) = 10.5 (H5); 4.48 dd, 1 H, *J*(4,5′) = 5.9, *J*(5,5′) = 10.5 (H5′). MS: 304 (82) [$M^{\bullet+}$], 215 (7), 214 (12), 125 (20). For $C_{15}H_{13}ClN_2O_3$ calculated: 59.13% C, 4.30% H, 9.19% N; found: 58.73% C, 4.22% H, 9.16% N.

cis-2-(3-Chlorophenyl)-4-nitro-3-phenylisoxazolidine (**3d**). Yield 48%. M.p. 123–127 °C (ethanol). IR: 1567 s, 1375 m, 1180 w, 927 w. ^{1}H NMR: 7.56–6.72 m, 9 H (Ar-H); 5.12 d, 1 H, *J*(3,4) = 8.6 (H3); 5.66 ddd, 1 H, *J*(3,4) = 8.6, *J*(4,5) = 4.1, *J*(4,5′) = 6.3 (H4); 4.86 dd, 1 H, *J*(4,5) = 4.1, *J*(5,5′) = 10.2 (H5); 4.34 dd, 1 H, *J*(4,5′) = 6.3, *J*(5,5′) = 10.2 (H5′). MS: 304 (70) [$M^{\bullet+}$], 215 (5), 214 (11), 125 (18). For $C_{15}H_{13}ClN_2O_3$ calculated: 59.13% C, 4.30% H, 9.19% N; found: 58.54% C, 4.29% H, 9.00% N.

trans-2-(3-Chlorophenyl)-4-nitro-3-phenylisoxazolidine (**4d**). Yield 40%. Oil. IR: 1554 s, 1372 m, 1176 w, 923 w. ^{1}H NMR: 7.62–6.68 m, 9 H (Ar-H); 5.13–5.28 m, 2 H (H3 + H4); 4.78 dd, 1 H, *J*(4,5) = 2.3, *J*(5,5′) = 10.6 (H5); 4.48 dd, 1 H, *J*(4,5′) = 6.0, *J*(5,5′) = 10.6 (H5′). MS: 304 (100) [$M^{\bullet+}$], 215 (5), 214 (11), 125 (17). For $C_{15}H_{13}ClN_2O_3$ calculated: 59.13% C, 4.30% H, 9.19% N; found: 59.12% C, 4.35% H, 9.00% N.

cis-2-(4-Carbomethoxyphenyl)-4-nitro-3-phenylisoxazolidine (**3e**). Yield 37%. M.p. 79–81 °C (ethanol). IR: 1560 s, 1373 m, 1177 w, 933 w. ^{1}H NMR: 8.00–6.93 m, 9 H (Ar-H); 5.25 d, 1 H, *J*(3,4) = 8.6 (H3); 5.68 ddd, 1 H, *J*(3,4) = 8.6, *J*(4,5) = 3.0, *J*(4,5′) = 6.3 (H4); 4.89 dd, 1 H, *J*(4,5) = 3.0, *J*(5,5′) = 10.2 (H5); 4.34 dd, 1 H, *J*(4,5′) = 6.3, *J*(5,5′) = 10.2 (H5′); 3.88 s, 3 H (CH_3). MS: 328 (100) [$M^{\bullet+}$], 239 (7), 238 (8), 149 (11). For $C_{17}H_{16}N_2O_5$ calculated: 62.18% C, 4.91% H, 8.53% N; found: 62.02% C, 4.77% H, 8.50% N.

trans-2-(4-Carbomethoxyphenyl)-4-nitro-3-phenylisoxazolidine (**4e**). Yield 45%. M.p. 104–105 °C (ethanol). IR: 1549 s, 1379 m, 1178 w, 929 w. ^{1}H NMR: 8.00–6.91 m, 9 H (Ar-H); 5.37 d, 1 H, *J*(3,4) = 2.7 (H3); 5.24 ddd, 1 H, *J*(3,4) = 2.7, *J*(4,5) = 2.9, *J*(4,5′) = 6.2 (H4); 4.81 dd, 1 H, *J*(4,5) = 2.9, *J*(5,5′) = 10.4 (H5); 4.52 dd, 1 H, *J*(4,5′) = 6.2, *J*(5,5′) = 10.4 (H5′); 3.87 s, 3 H (CH_3). MS: 328 (100) [$M^{\bullet+}$], 239 (12), 238 (11), 149 (20). For $C_{17}H_{16}N_2O_5$ calculated: 62.18% C, 4.91% H, 8.53% N; found: 61.97% C, 4.82% H, 8.53% N.

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