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Conjugated *Schiff*'s Bases, 19[1] Cycloaddition of Heterocumulenes to Sterically Congested 1,4-Diazabutadiene 4*N*-Oxides

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Reactions of aryl isocyanates with sterically congested 1,4-diazabutadiene 4*N*-oxides representing bifunctional nitrones, proved to be 1,3-dipolar cycloadditions in which the nitrone 1,3-dipol manifested its predominant reactivity in comparison with the 1,4-diazabutadiene system. 3-Substituted 5-oxadiazolidinones resulted from these cycloadditions. Acidic hydrolysis of these products was also investigated.

(Keywords: 1,3-Dipolar cycloaddition; 1,3-Heterodienes; Oxadiazolidinones; Bifunctional nitrones)

Konjugierte Schiff-Basen, 19. Mitt.: Cycloaddition von Heterokumulenen an sterisch gehinderten 1,4-Diazabutadien-4N-oxiden

Die Reaktionen von Arylisocyanaten mit sterisch gehinderten 1,4-Diazabutadien-4*N*-oxiden als Vertretern bifunktioneller Nitrone erwies sich als eine 1,3-dipolare Cycloaddition, bei der sich der Nitron-1,3-Dipol in seiner Reaktivität im Vergleich mit dem 1,4-Diazabutadiensystem bevorzugt zeigte. Es wurden bei diesen Cycloadditionen 3-substituierte 5-Oxadiazolidinone erhalten. Die saure Hydrolyse dieser Produkte wurde ebenfalls untersucht.

Introduction

Although interest of nitrones as useful reagents in organic synthesis has been distinctly augmented in recent years[2,3] it is still little known about the chemical behaviour of bifunctional nitrones which possess a nitrone functionality incorporated into a 1,3-heterodiene system[3,4,5]. The

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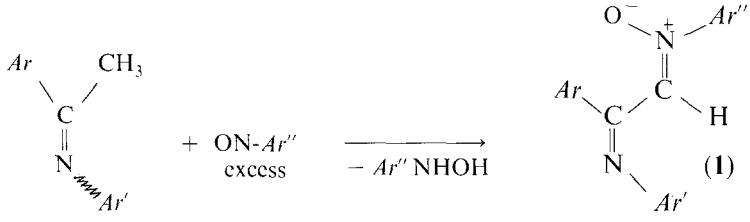
nitrone group itself is a well known 1,3-dipol yielding a number of heterocycles via dipolar cycloadditions[6]. On the other hand 1,3-heterodienes such as 1-oxa-4-azabutadienes[7] and 1,4-diazabutadienes[8,9] have been found as efficient "masked" 1,3-dipols prone to react with heterocumulenes[10,11].

Cycloadditions of the bifunctional nitrones derived from 1,3-heterodiene systems are hardly documented. *Utzinger* and *Regenass*[3] reported cycloaddition of a bifunctional nitrone containing the nitrone group as a part of an azabutadiene system with aryl isocyanates. This reaction yielded exclusively 5-oxazolidinones showing the predominant reactivity of the nitrone 1,3-dipol. Recently *Tacconi* and coworkers[4] described similar cycloadditions of bifunctional nitrones possessing the rigid, cisoid 1-oxa-4-azabutadiene 4*N*-oxide skeleton. Also these reactions revealed predominance of the nitrone group in comparison with the 1-oxa-4-azabutadiene system.

Sterically congested 1,4-diazabutadiene 4*N*-oxides (**1**) are representatives of bifunctional nitrones in which a nitrone group is a part of a 1,4-diazabutadiene relatively rigid system. This system itself manifested a distinct 1,3-dipolar reactivity in some reactions with aryl isocyanates[10], so it seemed interesting to compare potential competition or combination of these both 1,3-dipolar functionalities in cycloaddition. The 1,4-diazabutadiene 4*N*-oxides were easily obtainable by condensation of acetophenone anils with nitrosoarenes[12]:



(**1**)

The compounds **1** exist in relatively rigid, transoid *Z,Z*-configuration due to steric hindrance caused by bulky aryl substituents. This impedes to a high degree free rotation around the C2, C3 bond[8,12].

Results and Discussion

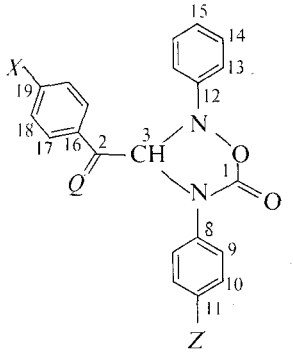
Aryl isocyanates were chosen as test dipolarophiles because of their sensitiveness towards both 1,3-dipolar functionalities present in the 1,4-diazabutadiene 4*N*-oxide molecule[2,10]. The cycloaddition process could proceed after three different routes. When, for instance, the

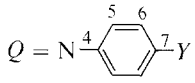
1,4-diazabutadiene system itself is involved in cycloaddition with aryl isocyanates Δ^2-imidazolines would be expected as a result of probable elimination of the nitrosoarene molecule[13] or 1,3-shift of the aldonitrone hydrogen[10]. Further, reactions employing the total bifunctional nitrone system would produce six-membered oxadiazine derivatives due to cyclization combined with a 1,2-migration of a substituent[11]. The predominant reactivity of the nitrone group itself would lead to some 5-oxadiazolidinone derivatives[2a].

The 1,4-diazabutadiene 4*N*-oxides (**1**) reacted smoothly with aryl isocyanates at room temperature yielding colourless crystalline products with satisfactory yields. Combustion analysis showed their composition as 1 : 1 adducts with regard to both reactants. The IR spectra revealed the sharp carbonyl absorption at approximately 1 770 cm^{-1} which was ascribed to the oxadiazolidinone carbonyl stretching vibrations[2,4,14]. The moderate absorption appearing between 1 640 and 1 650 cm^{-1} seemed to be from stretching vibrations of the C=N double bond and the sharp absorption at approximately 1 290 cm^{-1} reflected vibrations of the oxadiazolidinone C—O bond[15]. The ^1H NMR spectra showed a singulet ascribed to a methine proton at about 6.0 ppm and a complex multiplet of aromatic protons in the range from 6.5 to 8.5 ppm. The ^{13}C NMR spectra confirmed the oxadiazolidinone structure of the adducts. Thus the carbonyl carbon singulet appeared at approximately 164 ppm, azomethine carbon was responsible for a singulet at 153 ppm, and the methine group carbon produced a doublet at approximately 87 ppm with the coupling constant J_{CH} 156.6 Hz. Aromatic carbons caused a group of signals positioned from 111 to 149 ppm (see Table 1). The UV spectra contained two strong absorptions at approximately 210 and 230 ppm reflecting the $\pi \rightarrow \pi^*$ transitions within the aryl rings and the combined transitions including the anilo and oxadiazolidinone moiety, respectively. Introduction of a methoxyl or a nitro group to one of the aryl rings caused appearance of an additional longwave absorption. Generally absorption of the adducts was shifted hypsochromically about 30 to 40 nm compared with the absorption of the corresponding nitrones[6,11]. This reflected the disappearance of the conjugated system characterizing bifunctional nitrones.

As it was expected the mass spectra of the adducts did not show the molecular peaks but these related to the ions formed due to loss of carbon dioxide. The M-CO_2 ions, having probably the amidine-type structure, decomposed further splitting off either dehydrobenzylidene aniline or dehydroaniline ions which were responsible for relatively prominent peaks at m/z $178 + X + Y$ and $281 + X + Y$. Complementary carbodiimide ions were also observable by peaks at m/z $149 + Z$. The main fragmentation pathways are presented in Scheme 1.

Table 1. ^{13}C *NMR data (δ/ppm) of the representatively chosen compounds* **2** *and* **3**





2

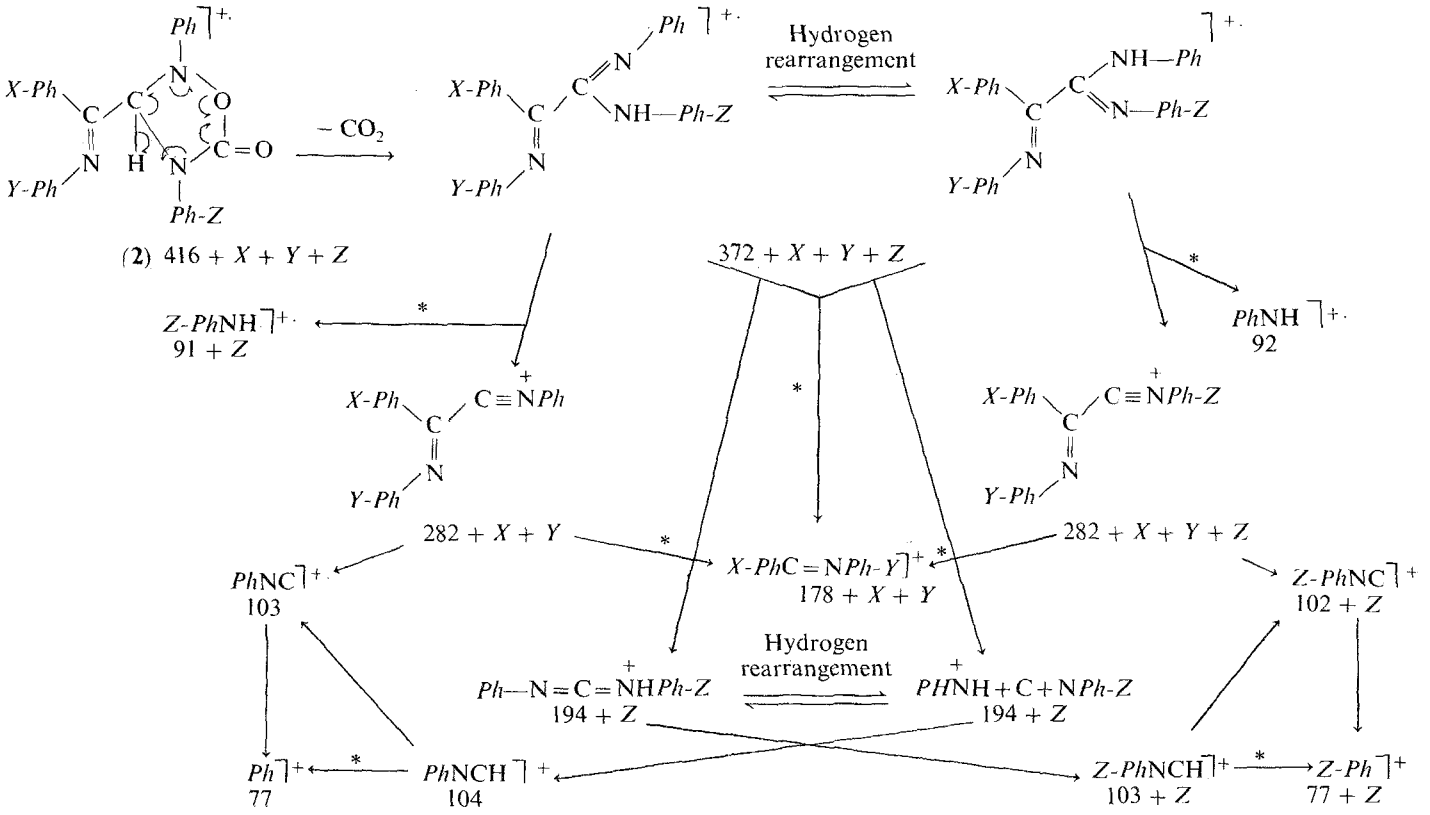
= O **3**

Carbon No.	**2d** ($X = Y = H$, $Z = Cl$)	**2h** ($X = H$, $Y = Z = Cl$)	**3d** ($X = Z = H$)
1	164.41, s,	165.15, s,	148.77, s,
2	153.30, s,	153.28, s,	189.49, s,
3	87.96, d, 156.19*	87.79, d, 156.41*	81.52, d, 151.77*
4	134.33, s,	134.34, s,	—
5	120.84, d, 162.00*	120.86, d, 162.50*	—
6	129.53, d, 162.00*	128.69, d, 162.80*	—
7	124.64, d, 162.00*	130.69, s,	—
8	148.17, s,	146.65, s,	133.49, s,
9	116.18, d, 161.71*	116.29, d, 162.50*	118.09, d, 162.50*
10	129.20, d, 162.00*	129.25, d, 162.50*	129.71, d, 162.50*
11	132.72, s,	132.54, s,	126.69, d, 162.60*
12	130.57, s,	130.21, s,	129.14, s**,
13	120.65, d, 162.10*	122.14, d, 162.50*	119.95, d, 162.10*
14	129.43, d, 162.00*	129.46, d, 162.50*	129.26, d, 162.00*
15	125.42, d, 162.10*	125.53, d, 162.20*	125.53, d, 162.10*
16	149.67, s,	149.65, s,	135.46, s,
17	128.00, d, 162.20*	127.92, d, 162.00*	129.14, d**, 162.20*
18	128.48, d, 162.10*	128.65, d, 162.80*	128.78, d, 162.20*
19	128.97, d, 162.10*	129.83, d, 162.10*	134.45, d, 162.10*

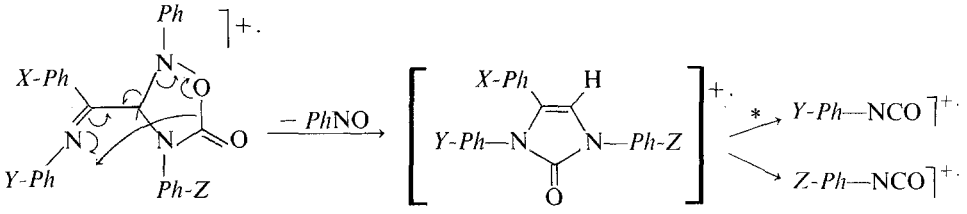
* Coupling constants J_{CH} in Hz.
** Overlapping signals.

The spectra were recorded on a Varian XL-100 spectrometer in deuterochloroform as solvent.

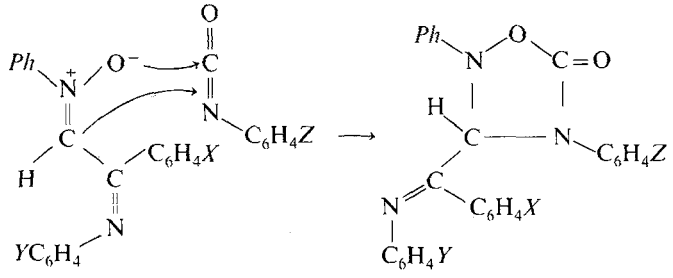
Scheme 1


Hydrogen rearrangement
(2) 416 + X + Y + Z
372 + X + Y + Z
91 + Z
92
282 + X + Y
282 + X + Y + Z
178 + X + Y
103
102 + Z
194 + Z
194 + Z
Hydrogen rearrangement
77
104
103 + Z
77 + Z

It is worth mentioning that the molecular ions (**2**) detached either the nitrosobenzene molecule. This minor fragmentation pathway was supported by the presence of the peaks corresponding to the *Y* substituted aryl isocyanate radical ions resulting from typical decomposition of the imidazolidine-type ions formed due to recyclization accompanying loss of nitrosobenzene[16]:



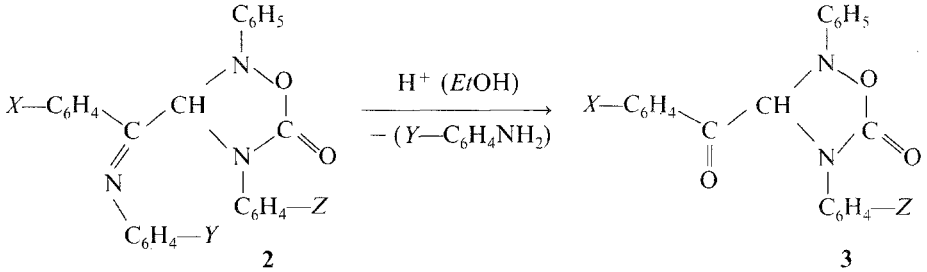
Then 5-oxadiazolidinones were obtained in cycloaddition of the 1,4-diazabutadiene 4*N*-oxides (**1**) with aryl isocyanates that reflected the same preference of the nitrone 1,3-dipol also in the competition with the 1,4-diazabutadiene system:



1 **2**

2	*X*	*Y*	*Z*	Yield (%)
a	H	H	H	84
b	H	H	*Me*	59
c	H	H	O*Me*	58
d	H	H	Cl	89
e	H	H	NO_2	92
f	H	O*Me*	Cl	76
g	H	*Me*	NO_2	92
h	H	Cl	Cl	68
i	O*Me*	H	NO_2	88
j	O*Me*	H	Cl	89
k	Cl	H	Cl	66
l	H	*Me*	H	92

The azomethine group of the 5-oxadiazolidinones **2** could be hydrolized to the corresponding aroyl group by diluted hydrochloric acid in ethanol under very mild conditions. In this way the 3-aroyl-5-oxadiazolidinones **3** were prepared:

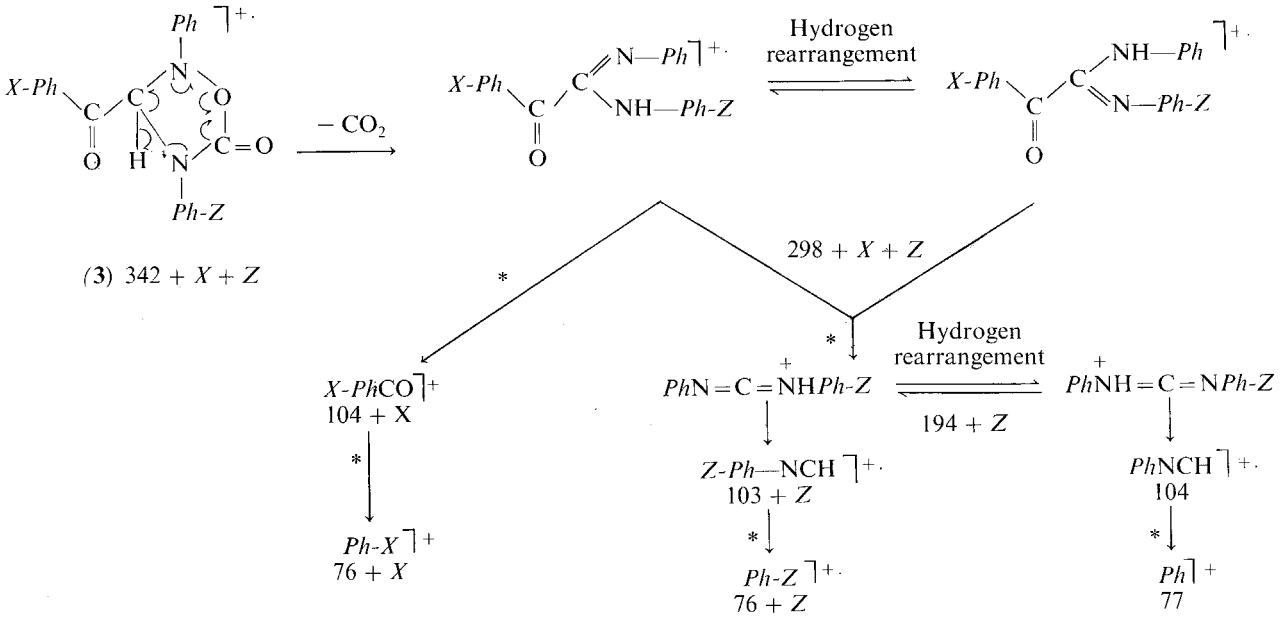


2 **3**

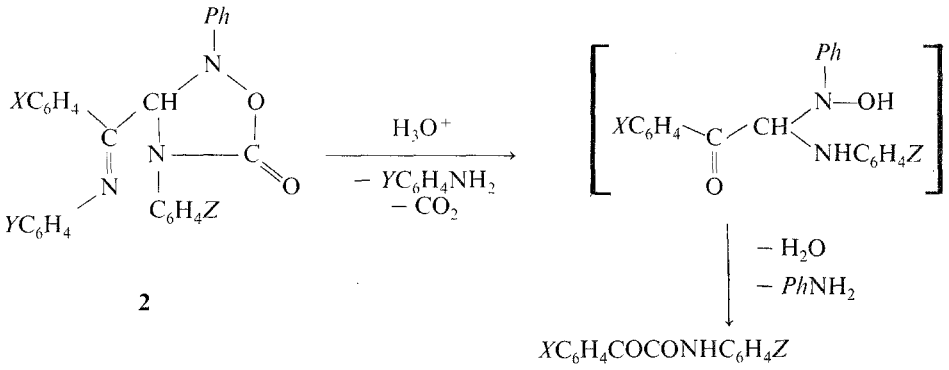
3	*X*	*Z*	Yield (%)
a	H	NO_2	94
b	H	Cl	96
c	Cl	Cl	96
d	H	H	93

The IR spectra of these 2,4-diaryl-3-aroyl-5-oxadiazolidinones (**3**) revealed relatively little changes compared with those determined for the initial compounds **2**. The new strong carbonyl absorption of the aroyl group appeared at approximately 1 690 cm^{-1}. Absorption characterizing the five-membered ring was practically as that determined for **2**, but absorption connected with stretching vibrations of the methine CH group was clearly seen as sharp, moderately intense band at approximately 2 930 cm^{-1}. The aroyl group affected very little the chemical shift of the methine group proton in the ^1H NMR spectra. It caused a lowfield shift of 0.5 ppm in relation to the values determined for compounds **2**. The ^{13}C NMR spectrum of the representatively chosen compound **3 d** showed an upfield shift of signals produced by the ring carbonyl and methine carbons because of the stronger inductive effect of the aroyl group. According to the expectations the mass spectra of the compounds **3** showed no peaks in the molecular region but the prominent peaks at *m/z* M—CO_2. The main fragmentation pathway was connected with loss of aroyl radicals and formation of carbodiimide-type ions:

Scheme 2


Ph
X-Ph
C
O
N
O
H
N
C=O
Ph-Z
(3) 342 + X + Z
− CO2
X-Ph
C
O
N—Ph
NH—Ph-Z
Hydrogen rearrangement
X-Ph
C
O
NH—Ph
N—Ph-Z
298 + X + Z
*
*
X-PhCO
104 + X
*
Ph-X
76 + X
PhN=C=NHPh-Z
Hydrogen rearrangement
194 + Z
Z-Ph—NCH
103 + Z
*
Ph-Z
76 + Z
PhNH=C=NPh-Z
PhNCH
104
*
Ph
77

Use of more concentrated acid for hydrolysis of the azomethine substituent caused total destruction of the heterocyclic ring and only arylglyoxalic acid anilide was isolated:



In conclusion, the nitrone group of 1,4-diazabutadiene 4*N*-oxides appeared to be more reactive towards polar double bonds of aryl isocyanates than the 1,4-diazabutadiene system itself and 5-oxadiazolidinone derivatives resulted exclusively from the cycloaddition. The careful acidic hydrolysis of an azomethine-type substituent permitted to obtain the corresponding ketones. Stronger acidic media for hydrolysis caused skeletal destruction of the compounds **2**.

Experimental

2,4-Diaryl-3-(1'-aryl)-arylimino-1-oxa-2,4-diazolidin-5-ones (**2**)

0.5 g of the corresponding 1,4-diazabutadiene 4*N*-oxide (**1**) were dissolved in the small amount of dichloromethane (usually 1 ml) and an equivalent molar amount of an aryl isocyanate in dichloromethane was added with gentle shaking. The mixture was allowed to stand over night at room temperature and then very carefully a few ml of *n*-hexane were added to turn it slightly turbid. The opaque mixture was then put in a refrigerator at − 15 °C for 2 h. The crystals were filtered off, washed with cold *n*-hexane and purified by crystallization from ethanol. Yields varied from 58 to 95%.

2,4-Diphenyl-3-(1'-phenyl)-phenylimino-1-oxa-2,4-diazolidin-5-one (**2a**)

M.p. 149–150 °C with decomposition; $C_{27}H_{21}N_3O_2$, m.w. 419.51, calc. % C 77.23 H 5.01 N 10.01, found % C 77.34 H 5.05 N 10.04. IR (cm^{-1}): 2962, m, CH; 1755, s, C=O; 1655, s, C=N; 1480, s, N—CO; 1390, s, oxadiazol. ring; 1190, s, N—O; 1130, s, C—O; 762, 695, s, aryl ring subst. ^{1}H NMR (ppm): 7.50–6.45, m, 20 H; 6.08, s, 1 H. UV (λ nm, ε_{max}): 208, 20500; 232, 18600. MS (*m/z*, % of the base peak): *M*-44, 375, 22.0; *M*-*Ph*NO, 312, 1.2; 284, 1.0; 283, 1.6; 180, 100; 104, 2.21; 92, 3.8; 77, 32.4.

2-Phenyl-4-p-methylophenyl-3-(1'-phenyl)-phenylimino-1-oxa-2,4-diazolidin-5-one (**2b**)

M.p. 137–138 °C with decomposition; $C_{28}H_{23}N_3O_2$, m.w. 433.54, calc. % C 77.50 H 5.31 N 9.69, found % C 77.56 H 5.34 N 9.72. IR (cm^{-1}): 2975, m, CH; 1755, s, C=O; 1652, m, C=N; 1525, s, N—CO; 1390, s, oxadiazol. ring; 1190, s, N—O; 1135, s, C—O; 812, 762, 695, s, aryl ring subst. ^{1}H NMR (ppm): 7.38–6.55, m, 19H; 6.05, s, 1H; 2.29, s, 3H. UV (λ nm, ε_{max}): 209, 23800; 232, 23800. MS (*m/z*, % of the base peak): *M*-44, 389, 25.2; 390, 7.3; *M*-*Ph*NO, 326, 3.1; 209, 14.6; 195, 6.3; 180, 100; 118, 3.7; 106, 4.2; 104, 2.6; 92, 12.5; 91, 30.8; 77, 36.4.

2-Phenyl-4-p-methoxyphenyl-3-(1'-phenyl)-phenylimino-1-oxa-2,4-diazolidin-5-one (**2c**)

M.p. 91–92 °C with decomposition; $C_{28}H_{23}N_3O_3$, m.w. 449.54, calc. % C 74.74 H 5.12 N 9.34, found % C 74.51 H 5.06 N 9.22. IR (cm^{-1}): 2980, w, CH; 2835, w, OCH_3; 1755, s, C=O; 1650, m, C=N; 1515, s, N—CO; 1390, s, oxadiazol. ring; 1190, m, N—O; 1145, s, C—O; 822, 765, 695, s, aryl ring subst. ^{1}H NMR (ppm): 7.40–6.55, m, 19H; 6.08, s, 1H; 3.87, s, 3H. UV (λ nm, ε_{max}): 209, 20000; 231, 17900. MS (*m/z*, % of the base peak): *M*-44, 405, 18.6; 406, 5.9; *M*-*Ph*NO, 342, 2.9; 225, 3.7; 195, 4.2; 180, 100; 134, 4.6; 121, 3.1; 118, 5.6; 106, 11.7; 104, 2.7; 92, 15.3; 77, 36.4.

2-Phenyl-4-p-chlorphenyl-3-(1'-phenyl)-phenylimino-1-oxa-2,4-diazolidin-5-one (**2d**)

M.p. 118–120 °C with decomposition; $C_{27}H_{20}ClN_3O_2$, m.w. 453.95, calc. % C 71.37 H 4.41 N 9.25 Cl 7.59, found % C 71.21 H 4.30 N 9.20 Cl 7.39. IR (cm^{-1}): 2975, w, CH; 1755, s, C=O; 1650, m, C=N; 1495, s, N—CO; 1392, s, oxadiazol. ring; 1198, m, NO; 1140, s, C—O; 825, 768, 698, s, aryl ring subst.; ^{1}H NMR (ppm): 7.35–6.50, m, 19H; 6.10, s, 1H. UV (λ nm, ε_{max}): 209, 22700; 238, 22300. MS (*m/z*, % of the base peak): *M*-44, 409, 6.7; 411, 2.5; *M*-*Ph*NO, 346, 2.1; 348, 0.8; 229, 3.7; 231, 1.4; 180, 100; 153, 21.8; 155, 7.3; 138, 1.3; 104, 5.9; 111, 5.3; 113, 1.4; 125, 6.6; 127, 2.5; 92, 4.6; 93, 9.1; 91, 9.7; 77, 85.0.

2-Phenyl-4-p-nitrophenyl-3-(1'-phenyl)-phenylimino-1-oxa-2,4-diazolidin-5-one (**2e**)

M.p. 126–127 °C with decomposition; $C_{27}H_{20}N_4O_4$, m.w. 464.51, calc. % C 69.75 H 4.31 N 12.06, found % C 69.71 H 4.33 N 12.08. IR (cm^{-1}): 2930, w, CH; 1770, s, C=O; 1645, m, C=N; 1512, s, asym. NO_2; 1485, s, N—CO; 1390, s, oxadiazol. ring; 1340, s, sym. NO_2; 1190, m, NO; 1139, s, C—O; 845, 751, 695, s, aryl ring subst.; ^{1}H NMR (ppm): 7.85, q_{AB}, 4H, J_{HH} = 9 Hz, $\Delta\nu$ = 30 Hz; 7.25–6.80, m, 13H; 6.60–6.41, m, 2H; 6.15, s, 1H. UV (λ nm, ε_{max}): 209, 20900; 222, 19700; 305, 11200. MS (*m/z*, % of the base peak): *M*-44, 420, 18.7; 421, 4.8; *M*-*Ph*NO, 357, 1.8; 240, 3.4; 180, 100; 149, 7.4; 104, 3.8; 194, 3.9; 122, 1.2; 92, 9.3; 77, 43.8.

2-Phenyl-4-p-chlorphenyl-3-(1'-phenyl)-p-methoxyphenylimino-1-oxa-2,4-diazolidin-5-one (**2f**)

M.p. 123–125 °C with decomposition; $C_{28}H_{22}N_3O_3Cl$, m.w., 483.98, calc. % C 69.42 H 4.55 N 8.69 Cl 7.12, found % C 69.40 H 4.54 N 8.70 Cl 7.10; IR (cm^{-1}): 2980, w, CH; 2838, m, OCH_3; 1770, s, C=O; 1648, m, C=N; 1485, s, N—CO; 1380, s, oxadiazol. ring; 1245, s, C—O*Me*; 1192, s, NO; 1134, s, C—O; 828, 760, 695, s, aryl ring subst. ^{1}H NMR (ppm): 7.50–6.90, m, 14H; 6.55, s, 4H; 6.03, s,

1 H; 3.66, s, 3 H. UV (λ nm, ε_{max}): 209, 23 000; 237, 22 000; 282, 10 800. MS (*m/z*, % of the base peak): *M*-44, 439, 13.5; 441, 4.9; *M*-*Ph*NO, 376, 2.8; 378, 0.9; 210, 100; 228, 2.4; 230, 1.1; 195, 3.0; 180, 24.1; 138, 1.2; 104, 1.7; 111, 2.6; 113, 0.9; 92, 11.0; 126, 1.32; 77, 26.4.

2-Phenyl-4-p-nitrophenyl-3-(1'-phenyl)-p-methylphenylimino-1-oxa-2,4-diazolidin-5-one (**2g**)

M.p. 143–144 °C with decomposition; $C_{28}H_{22}N_4O_4$, m.w., 478.54, calc. % C 70.26 H 4.63 N 11.70, found % C 70.37 H 4.70 N 11.70. IR (cm^{-1}): 2 940, w, CH; 1 765, s, C=O; 1 652, m, C=N; 1 512, s, asym. NO_2; 1 488, s, N—CO; 1 378, s, oxadiazol. ring; 1 342, s, sym. NO_2; 1 190, s, NO; 1 135, s, C—O; 842, 815, 760, 692, s, aryl ring subst. ^{1}H NMR (ppm): 7.86, q_{AB}, 4 H, J_{HH} = 9 Hz, $\Delta\nu$ = 28 Hz; 7.28–6.95, m, 10 H; 6.60, q_{AB}, 4 H, J_{HH} = 8 Hz, $\Delta\nu$ = 24 Hz; 6.11, s, 1 H; 2.14, s, 3 H. UV (λ nm, ε_{max}): 210, 23 700; 224, 21 900, 307, 12 750. MS (*m/z*, % of the base peak): *M*-44, 434, 18.2; 434, 5.5; *M*-*Ph*NO, 371, 9.1; 240, 1.3; 225, 2.7; 194, 100; 180, 26.1; 105, 2.5; 104, 2.7; 92, 2.7; 91, 19.2; 77, 9.8.

2-Phenyl-4-p-chlorphenyl-3-(1'-phenyl)-p-chlorphenylimino-1-oxa-2,4-diazolidin-5-one (**2h**)

M.p. 153–154 °C with decomposition; $C_{27}H_{19}N_3O_2Cl_2$, m.w., 488.06, calc. % C 66.38 H 3.92 N 8.60 Cl 14.12, found % C 66.20 H 3.83 N 8.63 Cl 14.08. IR (cm^{-1}): 2 980, w, CH; 1 785, s, C=O; 1 660, m, C=N; 1 503, s, N—CO; 1 390, s, oxadiazol. ring; 1 190, s, NO; 835, 830, 765, 695, s, aryl ring subst. ^{1}H NMR (ppm): 7.50–6.85, m, 14 H; 6.75, q_{AB}, 4 H, J_{HH} = 8 Hz, $\Delta\nu$ = 28 Hz; 6.07, s, 1 H. UV (λ nm, ε_{max}): 211, 19 700; 235, 25 600. MS (*m/z*, % of the base peak): *M*-44, 443, 11.4; 445, 7.60; 447, 1.4; *M*-*Ph*NO, 380, 0.9; 231, 4.7; 230, 4.7; 214, 100; 216, 32.4; 139, 14.8; 127, 4.8; 119, 3.6; 111, 8.9; 113, 2.8; 92, 5.8; 77, 69.5.

2-Phenyl-4-p-nitrophenyl-3-(1'-p-methoxyphenyl)-phenylimino-1-oxa-2,4-diazolidin-5-one (**2i**)

M.p. 107–109 °C with decomposition; $C_{28}H_{22}N_4O_5$, m.w., 494.54, calc. % C 67.94 H 4.45 N 11.32, found % C 67.78 H 4.38 N 11.26. IR (cm^{-1}): 2 950, w, CH; 2 828, m, OCH_3; 1 780, s, C=O; 1 655, m, C=N; 1 515, s, asym. NO_2; 1 500, s, N—CO; 1 380, s, oxadiazol. ring; 1 345, s, sym. NO_2; 1 240, s, C—OCH_3; 1 190, s, NO; 1 140, s, C—O; 845, 825, 780, 765, 695, 690, s, aryl ring subst. ^{1}H NMR (ppm): 7.86, q_{AB}, 4 H, J_{HH} = 9 Hz, $\Delta\nu$ = 30 Hz; 7.35–6.40, m, 14 H; 6.13, s, 1 H; 3.71, s, 3 H. UV (λ nm, ε_{max}): 218, 20 100; 293, 14 300. MS (*m/z*, % of the base peak): *M*-44, 450, 16.5; 451, 3.9; 435, 3.0; 359, 1.9; 240, 2.7; 194, 4.9; 210, 100; 195, 39.8; 179, 4.9; 149, 3.1; 104, 1.2; 107, 8.3; 92, 27.8, 77, 34.6; *M*-*Ph*NO, 387, 1.

2-Phenyl-4-p-chlorphenyl-3-(1'-p-methoxyphenyl)-phenylimino-1-oxa-2,4-diazolidin-5-one (**2j**)

M.p. 70–71 °C with decomposition; $C_{28}H_{22}N_3O_3Cl$, m.w., 483.98, calc. % C 69.42 H 4.55 N 8.69 Cl 7.12, found % C 69.36 H 4.50 N 8.70 Cl 7.08. IR (cm^{-1}): 2 958, w, CH; 2 840, w, OCH_3; 1 770, s, C=O; 1 640, s, C=N; 1 492, s, N—CO; 1 382, s, oxadiazol. ring; 1 255, s, C—OCH_3; 1 178, m, NO; 1 135, s, C—O; 830, 815, 765, 695, 690, s, aryl ring subst. ^{1}H NMR (ppm): 7.50–6.42, m, 18 H; 6.05, s, 1 H; 3.69, s, 3 H. UV (λ nm, ε_{max}): 213, 19 000; 229, 19 700; 276, 10 700. MS (*m/z*, % of the base peak): *M*-44, 439, 27.5; 441, 9.4; *M*-*Ph*NO, 376, 1.3; 348, 2.7; 350, 0.9; 229, 4.6; 231, 1.8; 210, 100; 195, 49.6; 194, 3.9; 138, 5.8; 140, 2.6; 126, 3.9; 128, 1.3; 149, 2.6; 111, 17.2; 113, 5.7; 107, 8.9; 92, 15.3; 77, 39.9.

2-Phenyl-4-p-chlorphenyl-3-(1'-p-chlorphenyl)-phenylimino-1-oxa-2,4-diazolidin-5-one (**2k**)

M.p. 141–142 °C with decomposition; $C_{27}H_{19}N_3O_2Cl$, m.w., 488.06, calc. % C 66.38 H 3.92 N 8.60 Cl 14.12, found % C 66.33 H 4.18 N 8.61 Cl 14.22. IR (cm^{-1}): 2985, w, CH; 1760, s, C=O; 1650, s, C=N; 1487, s, N—CO; 1385, s, oxadiazol. ring; 1185, s, NO; 1145, s, C—O; 828, 810, 770, 760, 695, s, aryl ring subst. ^{1}H NMR (ppm): 7.50–6.80, m, 16H; 6.60–6.38, m, 2H; 6.05, s, 1H. UV (λ nm, ε_{max}): 209, 21100; 238, 21500. MS (*m/z*, % of the base peak): *M*-44, 443, 28.4; 445, 18.9; *M-Ph*NO, 380, 3.0; 382, 2.0; 352, 1.9; 354, 1.2; 229, 3.7; 231, 1.3; 214, 100; 216, 33.6; 128, 1.7; 111, 39.4; 113, 13.2; 126, 3.0; 128, 1.0; 104, 3.1; 194, 2.7; 77, 30.9; 92, 9.0.

2,4-Diphenyl-3-(1'-p-methylphenyl)-phenylimino-1-oxa-2,4-diazolidin-5-one (**2l**)

M.p. 151–152 °C with decomposition; $C_{28}H_{23}N_3O_2$, m.w., 433.54, calc. % C 77.50 H 5.31 N 9.69, found % C 77.52 H 5.28 N 9.73. IR (cm^{-1}): 2985, w, CH; 1755, s, C=O; 1650, m, C=N; 1500, s, N—CO; 1390, s, oxadiazol. ring; 1190, m, NO; 1130, s, C—O; 825, 762, 760, 698, 694, s, aryl ring subst. ^{1}H NMR (ppm): 7.55–6.95, m, 15H; 6.62, q_{AB}, 4H, J_{HH} = 8 Hz, $\Delta\nu$ = 22 Hz; 6.08, s, 1H, 2.18, s, 3H. UV (λ nm, ε_{max}): 210, 19700; 230, 19300. MS (*m/z*, % of the base peak): *M*-44, 389, 29.3; 390, 8.7; *M-Ph*NO, 326, 1.6; 298, 3.7; 195, 16.2; 194, 100; 104, 4.3; 91, 30.2; 92, 11.8; 77, 39.2.

2,4-Diaryl-3-aroyl-1-oxa-2,4-diazolidin-5-ones (**3**)

0.5 g of the corresponding 2,4-diaryl-3-(1'-aryl)-arylimino-1-oxa-2,4-diazolidin-5-one (**2**) were suspended in 15 ml of ethanol and one drop of concentrated hydrochloric acid was added. The mixture was warmed to get a transparent solution. Crystals appeared after addition of a few ml of water and cooling to 0 °C. Crystals were filtered off, washed carefully with water and dried on air. Crystallization from ethanol gave analytically pure compounds **3**. Yields from 86 to 96%.

2-Phenyl-4-p-nitrophenyl-3-benzoyl-1-oxa-2,4-diazolidin-5-one (**3a**)

M.p. 136–137 °C with decomposition; $C_{21}H_{15}N_3O_5$, m.w., 389.12, calc. % C 64.76 H 3.86 N 10.80, found % C 64.71 H 3.84 N 10.80. IR (cm^{-1}): 3000, m, CH; 1765, s, C=O ring; 1690, s, C=O; 1520, s, asym. NO_2; 1500, s, N—CO; 1388, s, oxadiazol. ring; 1340, s, sym NO_2; 1190, s, NO; 1140, s, C—O; 812, 762, 685, aryl ring subst. ^{1}H NMR (ppm): 8.03, d, 2H, J_{HH} = 1.5 Hz; 7.88, d, 2H, J_{HH} = 1.5 Hz; 7.59, q_{AB}, 4H, J_{HH} = 9 Hz, $\Delta\nu$ = 40.4 Hz; 7.55–7.18, m, 3H; 7.30, s, 5H; 6.58, s, 1H. MS (*m/z*, % of the base peak): *M*-44, 345, 28.8; 346, 7.3; 240, 100; 105, 57.4; 118, 2.3; 104, 3.1; 103, 1.7; 92, 12.4; 91, 2.5; 77, 47.4.

2-Phenyl-4-p-chlorphenyl-3-benzoyl-1-oxa-2,4-diazolidin-5-one (**3b**)

M.p. 143–145 °C with decomposition; $C_{21}H_{15}N_2O_3Cl$, m.w., 378.57, calc. % C 66.57 H 3.99 N 7.40 Cl 9.36, found % C 66.50 H 3.96 N 7.43 Cl 9.30. IR (cm^{-1}): 3000, m, CH; 1765, s, C=O ring; 1693, s, C=O; 1490, s, N—CO; 1390, s, oxadiazol. ring; 1200, s, NO; 1138, s, C—O; 830, 760, 690, s, aryl ring subst., ^{1}H NMR (ppm): 6.80–7.85, m, 14H; 6.35, s, 1H. MS (*m/z*, % of the base peak): *M*-44, 334, 26.5; 336, 8.6; 229, 100; 231, 33.7; 105, 53.9; 138, 5.7; 140, 1.8; 104, 4.6; 111, 8.3; 113, 2.6; 92, 8.5; 91, 3.7; 77, 51.3.

2-Phenyl-4-p-chlorphenyl-3-p-chlorbenzoyl-1-oxa-2,4-diazolidin-5-one (**3c**)

M.p. 135–136 °C with decomposition; $C_{21}H_{14}N_2O_3Cl_2$, m.w., 413.02, calc. % C 61.01 H 3.42 N 6.78 Cl 17.17, found % C 61.12 H 3.45 N 6.70 Cl 17.17. IR (cm^{-1}): 2995, m, CH; 1763, s, C=O ring; 1685, s, C=O; 1590, s, N—CO; 1390, s, oxadiazol. ring, 1190, m, NO; 1140, s, C—O; 825, 762, 692, s, aryl ring subst., ^{1}H NMR (ppm): 8.00, d, 1H, J_{HH} = 1.5 Hz; 7.86, d, 1H, J_{HH} = 1.5 Hz; 7.55–7.08, m, 6H; 7.25, s, 5H; 6.98, s, 1H. MS (*m/z*, % of the base peak): *M*-44, 368, 29.3; 370, 19.5; 229, 100; 231, 33.4; 139, 60.3; 141, 20.1; 111, 39.8; 113, 13.3; 138, 17.6; 140, 5.9; 126, 7.9; 128, 2.7; 76, 14.3.

2,4-Diphenyl-3-benzoyl-1-oxa-2,4-diazolidin-5-one (**3d**)

M.p. 128–129 °C with decomposition; $C_{21}H_{16}N_2O_3$, m.w., 344.13, calc. % C 73.21 H 4.69 N 8.14, found % C 73.19 H 4.67 N 8.10. IR (cm^{-1}): 2995, m, CH; 1755, s, C=O ring; 1690, s, C=O; 1595, s, N—CO; 1395, s, oxadiazol. ring, 1210, s, NO; 1125, s, C—O; 750, 685, s, aryl ring subst. ^{1}H NMR (ppm): 7.95, d, 1H, J_{HH} = 1.6 Hz; 7.83, d, 1H, J_{HH} = 1.6 Hz; 7.50–6.90, m, 8H; 7.23, s, 5H; 6.35, s, 1H. MS (*m/z*, % of the base peak): *M*-44, 300, 36.4; 301, 7.9; 195, 100; 105, 63.2; 104, 13.6; 92, 27.2; 91, 8.3; 77, 59.5.

IR spectra were recorded on a Perkin-Elmer 257 spectrophotometer in KBr pills. ^{1}H NMR spectra were determined on an Hitachi-Perkin Elmer 24B spectrometer in $CDCl_3$ using *TMS* as internal standard. UV spectra were recorded on a 2P-VSU Zeiss, Jena, Spectrophotometer in 96% ethanol using 1 cm silica transmission cells. MS spectra were made on a MICROMAS spectrometer using a direct inlet system under the following conditions: 70 eV, accelerating voltage 8 kV, D.I. temp. 80 to 120 °C, I.S. temp. 120 °.

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