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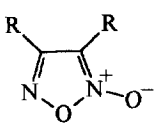
Cycloadditions of Nitrile Oxides to Amidoximes. A General Synthesis of 3,5-Disubstituted 1,2,4-Oxadiazole-4-oxides.(*)

Paolo Quadrelli, Anna Gamba Invernizzi, Mario Falzoni and Pierluigi Caramella

Dipartimento di Chimica Organica, Università degli Studi di Pavia; Viale Taramelli, 10 I-27100 Pavia, Italy

Abstract. The cycloaddition of nitrile oxides to amidoximes is a general method for the sinthesis of 3,5-disubstituted 1,2,4-oxadiazole-4-oxides with the same or different substituents. The yields are only moderate since an equivalent amount of the nitrile oxide is consumed by reaction with the amine released in the fragmentation of the primary cycloadducts and reforms the amidoxime. With excess nitrile oxides the 1,2,4-oxadiazole-4-oxides undergo a disproportionation reaction to yield nitroso carbonyl intermediates and 1,2,4-oxadiazoles.

Nitrile oxides are highly reactive 1,3-dipoles and, in the absence of dipolarophiles, dimerize by cycloaddition to the CN bond of the nitrile oxides affording furoxans, the 1,2,5-oxadiazole-2-oxides **1**. The isomeric dimers **2** and **3** are not normally formed under the mild conditions in which cycloaddition reactions are usually performed. However they can be obtained under appropriate and specific acid or base catalysis.[1] The 1,4,2,5-dioxadiazines **2** were isolated by exposing nitrile oxides to excess BF_3 in hexane or benzene[2] or by the pyridine catalyzed dimerization of nitrile oxides in ethanol.[3] The 1,2,4-oxadiazole-4-oxides **3** are formed in the presence of dry HCl in benzene[4] or BF_3 (0.5 equivs.) in a non-coordinating solvent (hexane or benzene)[4] or by trimethylamine catalyzed dimerization in ethanol.[5]



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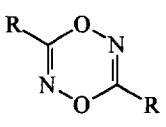

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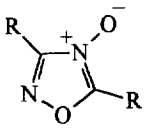


3

Some years ago we reported the formation of 3,5-diphenyl-1,2,4-oxadiazole-4-oxide **3** (R=C_6H_5) in the cycloaddition of benzonitrile oxide (BNO) to N,N-dimethyl benzamidoxime.[6,7] The following is a more detailed study of the scope and limitations of the cycloadditions of nitrile oxides to amidoximes. From a synthetic point of view this reaction provides the only general route for the synthesis of 1,2,4-oxadiazole-4-oxides **3** with different 3- and 5- substituents.

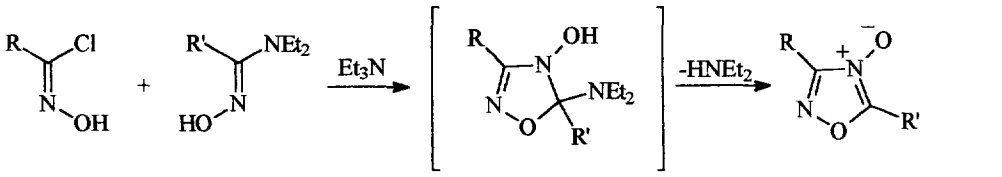
(*). Dedicated to Prof. Gianfranco Bettinetti on the occasion of his 72nd birthday and his retirement from teaching duties.

RESULTS

Cycloadditions.

The nitrile oxides were generated *in situ* by adding the hydroximoyl chlorides **4** to a stirred solution of (E)-N,N-diethylamidoximes **5** (1 equiv.) and triethylamine in benzene (Scheme 1). The primary cycloadducts **6** spontaneously aromatize with loss of diethylamine affording the 1,2,4-oxadiazole-4-oxides **7**. We have recovered the unreacted (and reformed, *vide infra*) amidoximes by extraction with 5% HCl. Separation of the oxides **7** from minor amounts of by-products and the furoxans, which derive from the competing dimerization of the nitrile oxides and are significantly faster running in tlc, could be easily achieved by column chromatography (method A). Since in some cases the reagents have only a low solubility in benzene, the reactions were performed in methanol, too (method B) and this procedure gave invariably better yields.

The yields and the physical constants of the 1,2,4-oxadiazole-4-oxides **7** are gathered in Table 1. The isolated oxides are all crystalline compounds and their structures have been confirmed by their smooth deoxygenation with trimethylphosphite in boiling benzene affording quantitatively the oxadiazoles **8**, which are known compounds or easily prepared[8] by acylation of amidoximes and thermal cyclization of their O-acyl derivatives **9**.

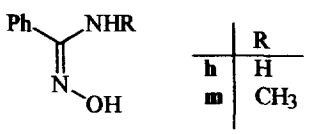


4A-F **5a-e** **6** **7** **8** **9**

	R		R'
A	Ph	**a**	Ph
B	*p*.MePh	**b**	*p*.MePh
C	*p*.MeOPh	**c**	*p*.MeOPh
D	*p*.ClPh	**d**	*p*.ClPh
E	*p*.NO_2Ph	**e**	*p*.NO_2Ph
F	CH_3		

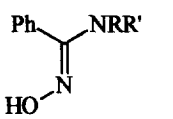
Scheme 1

In the case of the oxide **7Aa**, the influence of the substitution and the configuration[9] of the amidoxime in the synthesis was investigated. The benzamidoximes (Z)-**10 h-m** or (E)-**11x-z** behave however like the N,N-diethylamino benzamidoxime **5a** in the cycloadditions giving **7Aa** in yields similar to those reported in Table 1.



10h-m

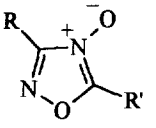
	R
h	H
m	CH_3



11x-z

	NR_2
x	NMe_2
y	morpholino
z	pyrrolidino

Table 1. Yields and physical constants of 1,2,4-oxadiazole-4-oxides **7**.

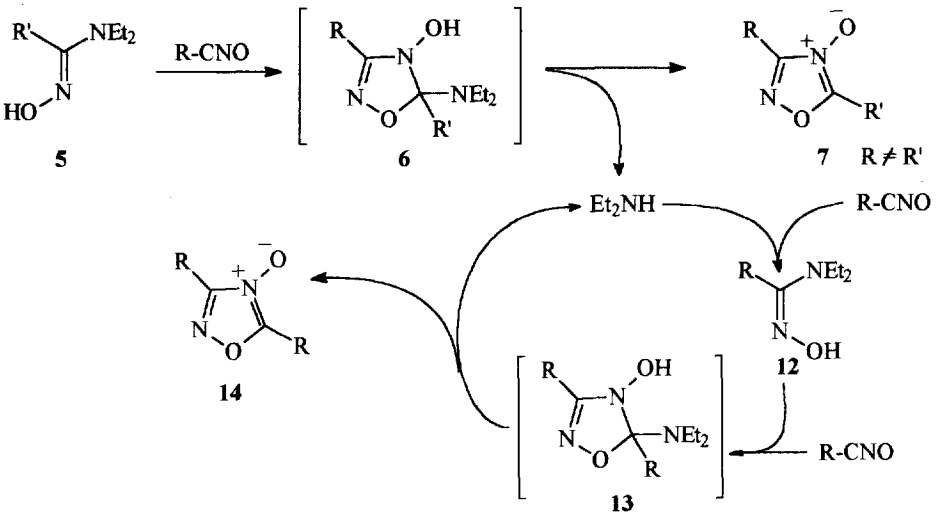


Entry	7	R	R'	mp °C[a]	Method A yield %	Method B yield %
1	**Aa**	Ph	Ph	134 (134)[b]	28	43
2	**Bb**	*p*.MePh	*p*.MePh	173-5 (165-7)[b]	25	52
3	**Cc**	*p*.MeOPh	*p*.MeOPh	176-8 (180)[b]	19	42
4	**Dd**	*p*.ClPh	*p*.ClPh	189-190 (194)[b]	23	33
5	**Ee**	*p*.NO_2Ph	*p*.NO_2Ph	195-7 (200)[b]	19	28
6	**Ab**	Ph	*p*.MePh	132-4	25	27
7	**Ac**	Ph	*p*.MeOPh	167-8	27	33
8	**Ad**	Ph	*p*.ClPh	160-1	28	33
9	**Ae**	Ph	*p*.NO_2Ph	119-121	/	45
10	**Ba**	*p*.MePh	Ph	142-3	24	34
11	**Ca**	*p*.MeOPh	Ph	163-5	15	26
12	**Da**	*p*.ClPh	Ph	171-3	/	24
13	**Ea**	*p*.NO_2Ph	Ph	201-2	19	30
14	**Fd**	CH_3	*p*.ClPh	140-1	/	20
15	**Fe**	CH_3	*p*.NO_2Ph	177-9	/	23

(a) Crystals from ethanol, melting with decomposition; (b) ref. 5.

The crossed oxides **7** (Table 1, entry 6-13), derived by combining nitrile oxides and amidoximes with different R,R' substituents, could still be obtained in fair yields, along with minor amounts (2-15%) of the oxides **14** with same substituents R and identical to the nitrile oxide substituent (Scheme 2).

In these cycloadditions the diethylamine, formed in the elimination of the primary cycloadduct **6**, competes with amidoxime **5** for the nitrile oxide and forms the isomeric amidoxime **12**. The latter adds further nitrile oxide giving the primary cycloadduct **13**, which fragments to the oxides **14** and regenerates diethylamine, which re-enters into the cyclic process.

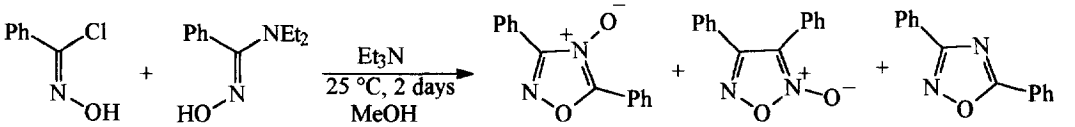


5 **6** **7** R≠R' **12** **13** **14**

Scheme 2

The catalytic cycle.

The cyclic mechanism of Scheme 2 points out a possible catalytic role of the amidoxime in the conversion of nitrile oxides to 1,2,4-oxadiazole-4-oxides and in order to get more insights on the mechanism we have investigated the product distribution in cycloadditions performed in the presence of excess nitrile oxide. As a model reaction we chose the reaction of N,N-diethylbenzamidoxime **5a** with excess BNO (1-9 equivs.) in methanol at 25 °C and the product distribution was determined quantitatively by hplc analysis. The main products detected in the reaction mixtures were the oxide **7Aa**, the 3,4-diphenyl-furoxan **15** as well as the oxadiazole **8Aa** (Scheme 3).



4A **5a** **7Aa** **15** **8Aa**

Scheme 3

In Figure 1 the yields of the three products are expressed as mmoles of product formed by reacting 1 mmole amidoxime and are plotted against the equivalents of BNO used. The plot shows that the yields of the oxide **7Aa** (squares) increase as expected and reach a limiting value of 1.4 mmoles with 6-9 equivs. of BNO but

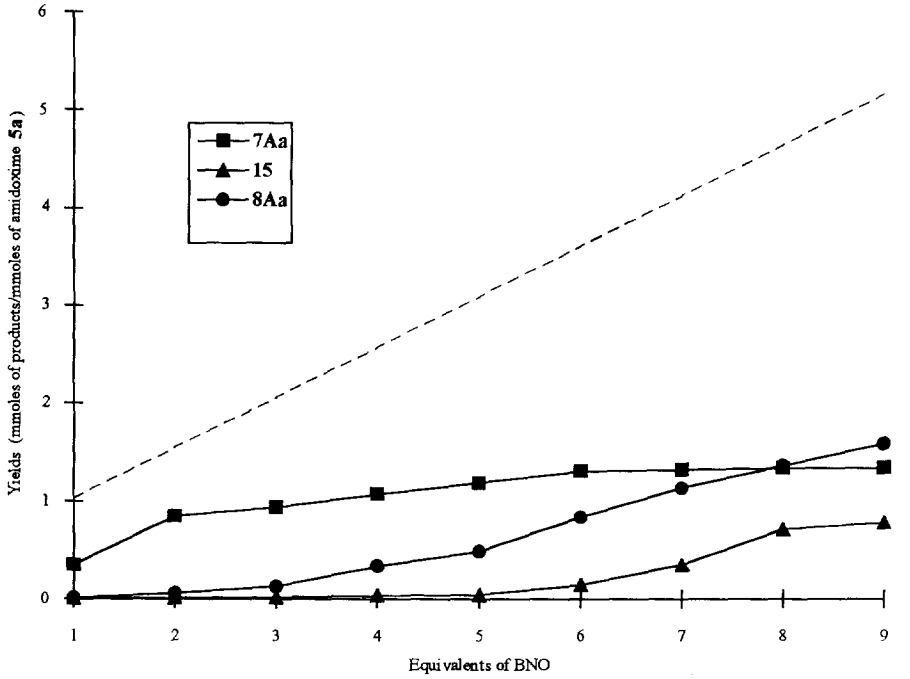


Figure 1. Product distribution in the cycloaddition of excess BNO to benzamidoxime **5a** in MeOH at 25 °C.

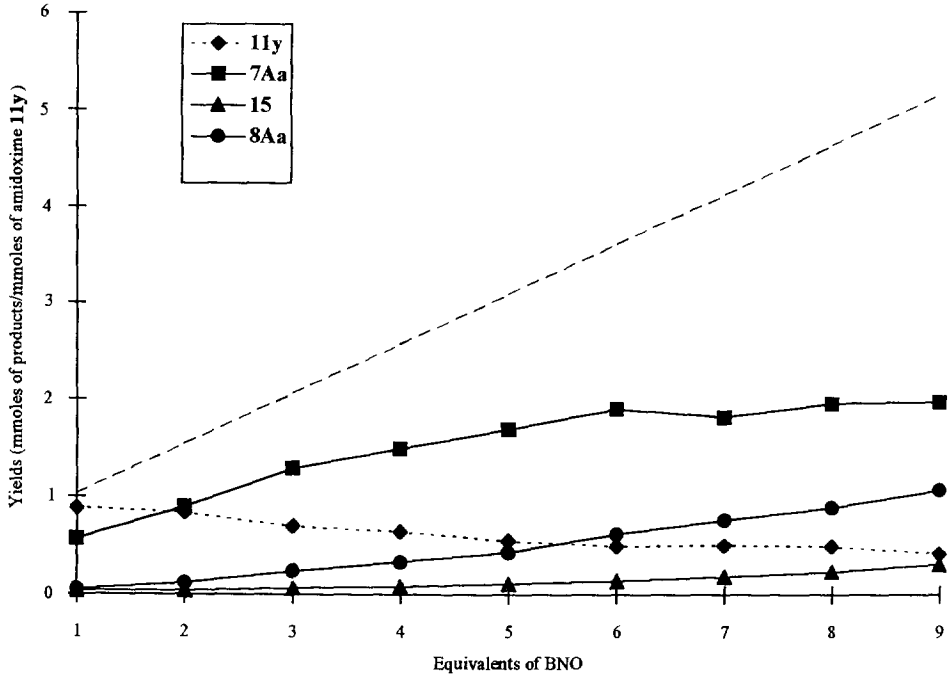


Figure 2. Product distribution in the cycloaddition of excess BNO to benzamidoxime **11y** in MeOH at 25 °C.

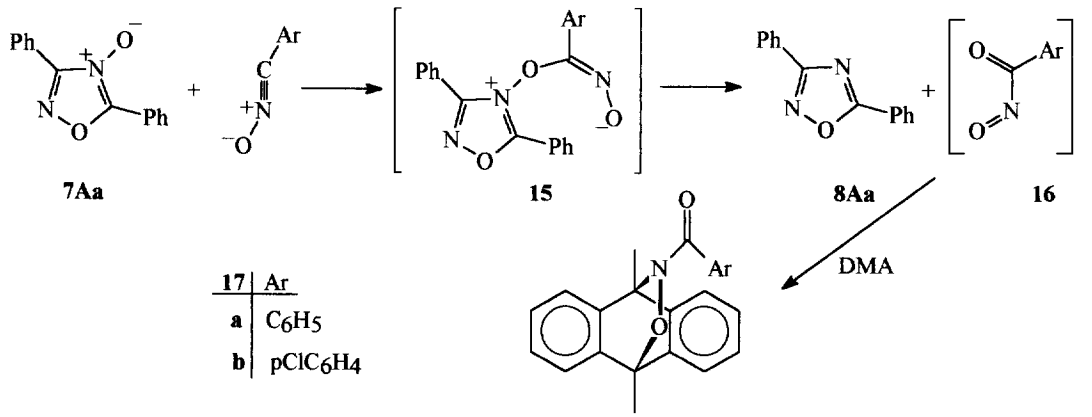
stay well below the theoretical yields for a fully efficient cyclic mechanism (dashed lines). On the other hand the amount of furoxan **15** (triangles) remains modest while the yields of the unexpected oxadiazole **8Aa** (circles) increase steadily and even surpass those of **7Aa** at high BNO excess, thus becoming the main detectable product of the reactions.

Similar plots have been obtained for the cycloadditions of excess BNO to the morpholino and pyrrolidino derivatives **11y,z**. Figure 2 shows the results obtained with the morpholino derivative **11y**. The turn-over is slightly more efficient and the yields of **7Aa** reach a limiting value of 1.9. The dotted line gives the amount of amidoxime **11y** present in the reaction mixtures and shows only a slow decrease with excess nitrile oxide. The pyrrolidino derivative **11z** gives a plot intermediate between Figure 1 and 2. Since the pK_a of pyrrolidine (11.27) and morpholine (8.70) differ by more than 2 units,[10] the results show that the basicity of the amines has only a secondary role on the outcome of these reactions.

Origin of the oxadiazole.

The formation of the oxadiazole **8Aa** in the cycloadditions with excess BNO looked at first puzzling. However, since the oxadiazole is formed under conditions in which both the oxide **7Aa** and BNO are present in significant amounts, a conceivable route to **8Aa** could be the oxygen transfer from the oxide **7Aa** to the nitrile oxide, through the adduct **15**, to yield the oxadiazole **8Aa** and a nitroso carbonyl intermediate **16** (Scheme 4). The latters are well-known intermediates.[11] They are usually generated by oxidation of hydroxamic acids and are trapped with dienes, e.g. 9,10-dimethylantracene (DMA).

To test this hypothesis, to a stirred methanol solution of BNO (generated *in situ*) or the stable *p*.chloroBNO and excess DMA (1.5 equivs.) the oxide **7Aa** (1 equiv.) was added. After 2 days at room temperature the oxadiazole **8Aa** and the nitroso carbonyl adducts **17a,b** could be isolated in moderate yields (50-60%).



Scheme 4

Under comparable conditions the furoxans **1** are not deoxygenated by nitrile oxides and are recovered unchanged. The furoxans are more resistent than the 1,2,4-oxadiazole-4-oxides to the deoxygenation with trialkylphosphites and their deoxygenations require more drastic conditions (triethylphosphite, 160 °C, 5h).[12]

The oxygen transfer takes place readily with non-aromatic amine oxides and we have recently reported a convenient procedure for the generation of nitroso carbonyl intermediates by the mild oxidation of nitrile oxides with N-methyl-morpholine N-oxide.[13]

FINAL REMARKS

The cycloadditions of nitrile oxides to amidoximes is a general method for the synthesis of 1,2,4-oxadiazole-4-oxides. The yields are only moderate because of interfering side reactions. The main side-product is the amidoxime itself. The fragmentation of the primary cycloadducts affords the 1,2,4-oxadiazole-4-oxides and releases the amine, which efficiently adds to the nitrile oxide and reforms the amidoxime. On the other hand, in the presence of excess nitrile oxides the 1,2,4-oxadiazole-4-oxides undergo in part a slower disproportionation reaction with the nitrile oxides affording the deoxygenated heterocycles and nitroso carbonyl intermediates, which can be trapped with DMA.

The observed disproportionation nicely accounts for the puzzling formation of small amounts of 1,2,4-oxadiazoles in the dimerization of nitrile oxides[14] and shed some light on the deceptively regiospecific formation of furoxans. Conceivably the dimerizations afford mainly the furoxans **1** along with minor amounts of 1,2,4-oxadiazoles-4-oxides **3**, which undergo ready deoxygenation in the presence of excess nitrile oxide.

EXPERIMENTAL

All melting points are uncorrected. Elemental analyses were done on a C. Erba 1106 elemental analyzer. ^{1}H-nmr spectra were recordered on a Bruker AC 300 spectrometer in $CDCl_3$ solutions. Chemical shifts are expressed in ppm from internal tetramethylsilane (δ). Ir spectra (nujol mulls) were recorded on a Perkin Elmer 881 spectrophotometer. Hplc analyses were carried out by means of a Waters 510 instrument equipped with a RP C-18 Intersil ODS-2 column and a Waters 490E UV detector; a mixture of H_2O/CH_3CN (from 50 to 70 % in CH_3CN) was used as eluent, using 5,5-dimethyl-3-phenyl-4,5-diidroisoxazole as internal standard in quantitative analyses (samples in CH_3CN 25 mL). Column chromatography and tlc:silica gel H60 and GF_{254} (Merck) respectively, eluant cyclohexane/ethyl acetate 9:1 to 5:5. The identification of samples from different experiments was secured by mixed mps and superimposable ir spectra.

Starting and reference materials. The hydroximoyl chlorides **4** were prepared according to the literature.[1] Amidoximes **5** were prepared following well-known procedures[1,15] by adding the hydroximoyl chloride to a stirred ice-cooled diethyl ether solution of an excess (10 equivs.) of the suitable amine. After keeping two days at r.t., the amine hydrochloride was filtered off. Evaporation of the filtrate gave the crude amidoxime, which were crystallized from a suitable solvent. The physical data for the amidoximes **5a-e**, **10h,m** and **11x-z** are gathered in Table 2.

Preparation of 3,5-diaryl-1,2,4-oxadiazole-4-oxides 7. Method A. To a stirred solution of amidoxime **5** (5 mmol) and triethylamine (5 mmol) in benzene (50 mL), a solution of the hydroximoyl chloride (5 mmol) in the same solvent (30 mL) was added dropwise. After keeping the reaction mixture two days at r.t., triethylamine hydrochloride was filtered off and the filtrate was evaporated. The residue was dissolved in dichloromethane (50 mL) and washed with 5% HCl for the separation of the amidoxime, which was recovered

Table 2: Yields and physical data for amidoximes.

	mp °C	Solvent	Yield %	Formula	Elemental Analyses[a]		
					C	H	N
5a	80-1 (81)[b]	Ligroin	73				
5b	110-2	EtOH	99	$C_{12}H_{18}N_2O$	70.2 (69.9)	8.9 (8.7)	13.5 (13.6)
5c	108-9	C_6H_6/Ligroin	62	$C_{12}H_{18}N_2O_2$	65.3 (64.9)	8.3 (8.1)	12.6 (12.6)
5d	109-110	EtOH	70	$C_{11}H_{15}N_2OCl$	58.5 (58.3)	6.7 (6.6)	12.3 (12.4)
5e	105-7[c]	EtOH/H_2O	99				
10h	78-9 (79)[d]	Ligroin	82				
10m	163-4 (163-4)[e]	MeOH	76				
11x	120-1 (120)[f]	EtOH	80				
11y	122-3	C_6H_6/ Ligroin	86	$C_{11}H_{14}N_2O_2$	64.4 (64.1)	6.8 (6.8)	13.7 (13.6)
11z	151-3	C_6H_6/ Ligroin	75	$C_{11}H_{14}N_2O$	69.7 (69.5)	7.6 (7.4)	14.8 (14.7)

(a). Calculated values in parentheses; (b). ref. 15b; (c). ref. 15c; (d). ref. 15d; (e). ref. 15e; (f). ref. 15f

from the acid aqueous phase in fair yields (80-90%) by neutralization with sodium bicarbonate and filtration. The dried ($MgSO_4$) dichloromethane solution was evaporated and the residue submitted to chromatographic separation affording the 1,2,4-oxadiazole-4-oxides **7**.

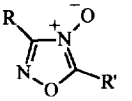
Method B. To a stirred solution of amidoxime **5** (5mmol) and triethylamine (5 mmol) in methanol (50 mL), a solution of hydroximoyl chloride (5 mmol) in the same solvent (30 mL) was added dropwise. After keeping the reaction mixture two days at r.t., the solution was evaporated. The residue was then taken up with dichloromethane and 5% HCl and processed as described for Method A.

The yields and the physical constants of 1,2,4-oxadiazole 4-oxides **7** are gathered in Table 1 and the spectroscopic and analytical data of the new oxides **7** are reported in Table 3.

Deoxygenation with trimethyl phosphite. A solution of the 1,2,4-oxadiazole-4-oxide **7** and trimethyl phosphite (2 equivs.) in benzene (30 mL) was refluxed 2 hrs. Evaporation of the solvent afforded the crude 1,2,4-oxadiazoles **8**, which were crystallized from a suitable solvent. All the oxadiazoles **8** are known compounds[16] and are identical with samples obtained by thermal cyclization of the O-acyl amidoximes **9** (toluene, reflux overnight) following well-established procedures.[8]

Product distribution on hplc. To solutions of amidoximes **5a** and **11y,z** (0.05 mmoles) in 25 mL of methanol at 25 °C, increasing amounts (from 1 to 9 equivs.) of benzhydroximoyl chloride were added. Then stoicheiometric amounts of triethylamine (1-9 equiv.) were added with a syringe. After stirring two days at 25 °C the solutions were evaporated and the residues were taken up with acetonitrile (25 mL) and analysed. The reactions were run in duplicate and the yields refer to an average of three independent hplc determinations (deviations ± 3%).

Table 3: Spectroscopic data and elemental analyses for the new 1,2,4-oxadiazole -4-oxides **7**.



7	ir $\nu_{C=N}$	^{1}H-nmr δ (ppm)	Formula	Elemental Analyses[a] C	H	N
Ab	1598	2.5 (s, 3H, *CH_3*) 7.6 and 8.5 (m, 5H, *arom. -3*) 7.4 and 8.6 (*AA'BB' arom.-5*)	$C_{15}H_{12}N_2O_2$	71.2 (71.4)	4.5 (4.8)	11.0 (11.1)
Ac	1607	3.9 (s, 3H, *OCH_3*) 7.6 and 8.5 (m, 5H, *arom. -3*) 7.1 and 8.7 (*AA'BB' arom. -5*)	$C_{15}H_{12}N_2O_3$	67.0 (67.2)	4.2 (4.5)	10.3 (10.5)
Ad	1595	7.6 (m, 5H, *arom. -3*) 8.5 and 8.6 (*AA'BB' arom. -5*)	$C_{14}H_9N_2O_2Cl$	62.2 (61.7)	3.0 (3.3)	9.9 (10.3)
Ae	1559	7.6 (m, 5H, *arom. -3*) 8.5 and 8.7 (*AA'BB' arom. -5*)	$C_{14}H_9N_2O_4$	58.5 (59.4)	2.8 (3.2)	13.6 (14.8)
Ba	1610	2.5 (s, 3H, *CH_3*) 7.4 and 8.4 (*AA'BB' arom. -3*) 7.6 and 8.7 (m, 5H, *arom. -5*)	$C_{15}H_{12}N_2O_2$	71.2 (71.4)	4.7 (4.8)	11.0 (11.1)
Ca	1609	3.9 (s, 3H, *OCH_3*) 7.1 and 8.5 (*AA'BB' arom. -3*) 7.6 and 8.7 (m, 5H, *arom. -5*)	$C_{15}H_{12}N_2O_3$	66.9 (67.2)	4.1 (4.5)	10.0 (10.5)
Da	1605	7.7 and 8.7 (m, 5H, *arom. -3*) 7.6 and 8.5 (*AA'BB' arom. -5*)	$C_{14}H_9N_2O_2Cl$	61.1 (61.7)	3.0 (3.3)	9.8 (10.3)
Ea	1576	7.7 (*AA'BB' arom. -3*) 8.4(m, 5H, *arom. -5*)	$C_{14}H_9N_3O_4$	59.3 (59.4)	3.1 (3.2)	14.8 (14.8)
Fd	1607	2.6 (s, 3H, *CH_3*) 7.6 and 8.6 (*AA'BB' arom. -5*)	$C_9H_7N_2O_2Cl$	51.2 (51.3)	3.3 (3.3)	13.2 (13.3)
Fe	1600	2.6 (s, 3H, *CH_3*) 8.4 and 8.8 (*AA'BB' arom. -5*)	$C_9H_7N_3O_4$	49.1 (48.9)	3.1 (3.2)	19.0 (19.0)

(a). Calculated values in parentheses.

Deoxygenation of 1,2,4-oxadiazole 4-oxides 7Aa with nitrile oxides. To a stirred solution of 3,5-diphenyl-1,2,4-oxadiazole-4-oxide **7Aa** (1 mmol), DMA (1.5 mmol) and benzhydroximoyl chloride (1 mmol) in methanol (50 mL), triethylamine (1 mmol) was added with a syringe. After keeping the reaction mixture two days at r.t., the solution evaporated and the residue was separated by column chromatography affording the oxadiazole **8Aa** (62%) and the DMA adduct **17a** (47%), colorless crystals, mp 125-6 °C from diisopropyl ether, and identical with an authentic sample.[17]

Analogous work-up procedure was followed with *p*.chlorobenzonitrile oxide (1 mmol), which was added to a solution of **7Aa** (1 mmol) and DMA (1.5 mmol) in methanol (50 mL). The chromatographic separation of the residue afforded the oxadiazole **8Aa** (60%) and the DMA adduct **17b** (58%), colorless crystals, mp 128-9 °C from ligroin, and identical with an authentic sample.[13]

Acknowledgements: Financial support by CNR and MURST is gratefully acknowledged.

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