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REACTION BETWEEN Δ^2-OXAZOLIN-5-ONES AND NITROSOBENZENE. FORMATION OF 1,2,4-OXADIAZOLINES

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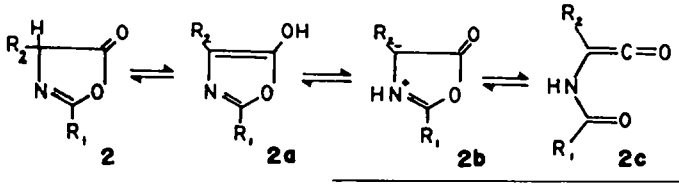
Abstract—2,4-diphenyl- and 2-p-methylphenyl-4-phenyl-Δ^2-oxazolin-5-ones react at 80–110°C with nitrosobenzene to give benzamidines. However, reactions conducted at room temperature afford in high yield, the heretofore undescribed Δ^4-1,2,4-oxadiazolin-3-carboxylic acids by regiospecific 1,3-dipolar cycloaddition. Thermal decomposition of the oxadiazolinecarboxylic acids gives the corresponding benzamidines.

Δ^2-Oxazolin-5-ones having at least one hydrogen at C-4 may add to multiple bonds either by 1,3-dipolar cycloadditions, giving rise to 5-membered heterocyclic compounds, or by [2 + 2] cycloaddition, resulting in a four-membered ring.

The first group includes reactions with alkenes that produce Δ^1-pyrrolines; or, with excess of very reactive dipolarophiles, forming derivatives of 7-azabicyclo[2.2.1]-heptane;[1,2] and with alkynes giving rise to pyrroles.[3,4]

The second group includes reactions between oxazolinones and imines to form azetidinones,[5] and reactions between oxazolinones produced *in situ* and alkenes, forming cyclobutanones and N-acylated-Δ^2-pyrrolines.[6]

This behaviour of oxazolinones can be reasonably explained by equilibria between the tautomers **2**, **2a**, and **2b**, and of the valence tautomer **2c**[7,8,9] is:



2 **2a** **2b** **2c**

1,3-Dipolar cycloaddition would take place between the mesoionic form **2b** and the unsaturated compound. On the other hand, [2 + 2] cycloaddition would occur between the ketene form **2c** and the unsaturated compound. The position of the tautomeric equilibrium depends on the solvent and the structure of the oxazolinone, while the course of the reaction is a function of the reactants.

The nitroso group could participate in cycloaddition reactions with oxazolinones, giving rise to derivatives of 1,2,4-oxadiazolines if the reaction follows a [3 + 2] course, or to oxazetidines if the course is [2 + 2].

Huisgen *et al.*[10] have described the reaction between nitrosobenzene **1** and the mesoionic oxazolinone 2,4-diphenyl-3-methyl-5-oxazolonium to give N-methyl-N-benzoyl-N'-phenylbenzamidine.

This paper reports on the reaction between **1** and 2-aryl-4-phenyl-2-oxazolin-5-one (aryl = phenyl or p-tolyl), in an attempt to determine (i) if cycloaddition occurs between simple oxazolinones and **1**, (ii) if the reaction is a [2 + 2] or a [3 + 2] cycloaddition, and (iii) the regiochemistry of the reaction.

RESULTS AND DISCUSSION

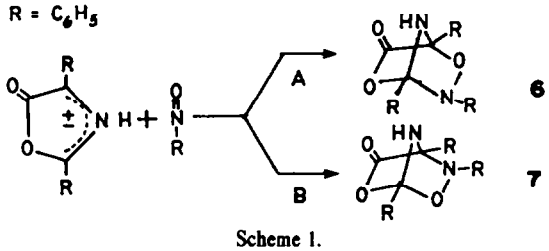
Reaction between 2,4-diphenyl-2-oxazolin-5-one **3** *and* **1**

When one equivalent of **3** was allowed to react with one or two equivalents of **1** in xylene at 80°, CO_2 was evolved and an oily residue was obtained, from which N-benzoyl-N'-phenylbenzamidine **4** crystallized. The identity of **4** was confirmed by comparing it with the product obtained from phenylbenzamidine and benzoyl chloride.[11]

When **3** was allowed to react with **1** at room temperature colorless crystals began separating after about four minutes without the evolution of CO_2. The crystalline product **5** melted at 101–102° with evolution of gas, changing into another solid that melted at 141°. The elemental analysis of **5** agreed with $C_{21}H_{16}N_2O_3$, pointing to an addition between **3** and **1**.

If 1,3-dipolar cycloaddition occurs between the mesoionic form of **3** as the 1,3-dipole, and the N=O group of **1** as the dipolarophile, the bicyclic compound **6** or **7** would be formed, depending on the geometry of the cycloaddition.

The IR spectrum of **5**, the product of the room temperature reaction, showed the wide band between 3100 and 2200 cm^{-1} and the strong absorption at 1740 cm^{-1} characteristic of carboxyl groups. When **5**, was treated with diazomethane in ether and the product crystallized from petroleum ether, a white solid **8** that melted at 106–107° was obtained. Elemental analysis agreed with $C_{22}H_{18}N_2O_3$. The NMR spectrum of **8** in CCl_4 showed a



6

7

Scheme 1.

singlet at 3.75 ppm and an absorption in the aromatic region with a ratio of 3:15 protons. The experiments carried out between **1** and **3** led to the conclusion that at room temperature the reaction gave an acid whose molecular formula agrees with the addition of the reactants. On the other hand, at 80° the reaction released CO_2 and N-benzoyl-N'-phenylbenzamidine was formed.

Huisgen has suggested[10] **10** as an intermediate in the reaction between **1** and 3-methyl-2,4-diphenyloxazolonium-5-olate **9**:

10 could not be isolated, since apparently it decomposes already at room temperature into N-methyl-N-benzoyl-N'-phenylbenzamidine **11**, as shown in step *a* of Scheme 2.

The decomposition of **10** can also take place assisted by the +M effect of nitrogen-7, forming an unstable zwitterion intermediate that, in turn, decomposes into CO_2 and **11** according to step *b* (Scheme 3).

The latter route agrees with our findings for the reaction between **3** and **1**. The intermediates **6** or **7** obtained from [3+2] cycloaddition would undergo spontaneous opening of the lactone ring, assisted by the +M effect of N-7, giving rise to zwitterions **6a** and/or **7a**, presumably in equilibrium with acids **6b** or **7b** respectively. These zwitterion structures are common in aminoacids, and they may become stabilized in the nonpolar xylene medium in which the reactions are taking place, by means of a prototropic migration yielding aminoacids **6b** and/or **7b** which, being insoluble in the medium, would precipitate (thereby assisting the reaction).

Acids **6b** and **7b** are quite different, and the determination of the structure of the acid obtained experimentally would clarify the steroechemistry of the addition. Neither of the acids seems to have been described, and an attempt to differentiate them would not be an easy task.

Acid **5** and its methyl ester were shown to be single compounds, and not mixtures, by TLC and by NMR spectroscopy, thereby proving that the reaction was regiospecific. Upon heating, **5** underwent quantitative decarboxlylation and formed **4**, thus explaining the behaviour of **5** when its melting point was determined: it melted with decomposition at 101°, evolving a gas and forming another compound that melted at 141°, which was the melting point of **4**. This thermal decarboxylation supports the participation of an aminoacid or its zwitterion as an intermediate in the reaction between **3** and **1** at 80°.

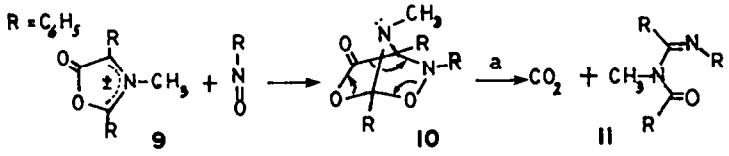
The structure of **5** cannot be established simply by a decarboxylation reaction, since both **6b** and **7b**, or their corresponding zwitterions, can yield **4** by thermal decomposition.

However, the introduction of a substituent on one of the phenyl groups of the oxazolinone would enable a distinction to be made between the two orientations of the cycloaddition, since each one would finally yield a different amidine.

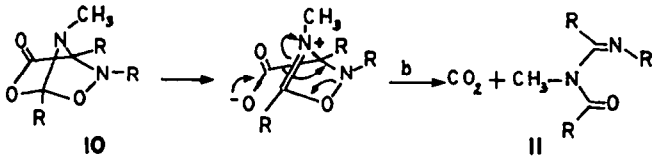
For synthetic reasons it was decided to introduce a methyl group in the C-2 of the oxazolinone.

Reaction between 2-p-methylphenyl-4-phenyl-2-oxazolin-5-one **12** *and* **1**

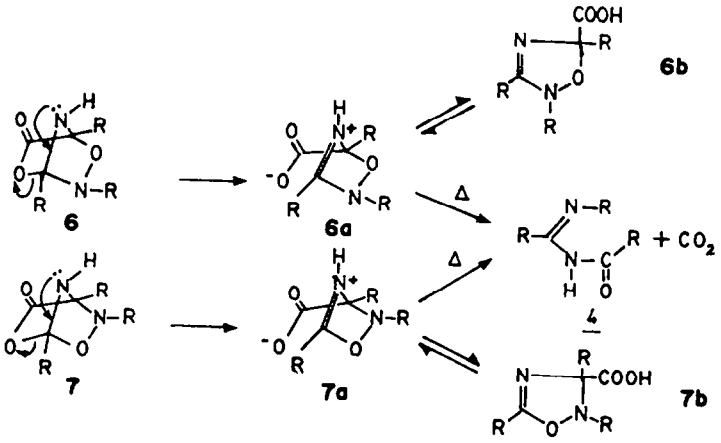
Using xylene as a solvent, **12** was made to react with **1**. At room temperature the reaction yielded 86.7% of acid



Scheme 2.



Scheme 3.



13b (m.p. 123–124°), whose methyl ester **14** melted at 99–100°.

Tlc of **13b** and **14** in different solvents showed that both were single component products. The NMR spectrum in CCl_4 showed a very sharp single peak for the methoxycarbonyl group.

When **12** was made to react with **1** at 100°, N-phenyl-N'-p-methylbenzoylbenzamidine, **15** was obtained as an oil. The m.p., after recrystallization from ethanol is 110–113°.

When **15** was subjected to controlled alkaline hydrolysis[10] which selectively hydrolyzes the amide function, the products were p-methylbenzoic acid and N-phenylbenzamidine. This result supports structures **13**, **13a** and **13b** for the respective adduct, zwitterion and aminoacid that are produced when **12** reacts with nitrosobenzene.

If the cycloaddition had taken place with the inverse orientation, decarboxylation would have yielded N - benzyl - N' - phenyl - p - methylbenzamidine, and benzoic acid and N - phenyl - p - methylbenzamidine would have resulted from the alkaline hydrolysis.

This result allowed route B (Scheme 1) to be postulated for the cycloaddition between **1** and **3**. Compound **5** would then be 2,3,5 - triphenyl - Δ^4 - 1,2,4 - oxadiazoline - 3 - carboxylic acid **7b**.

^{1}H-NMR with chemical shift reagents

Acid **5** was converted into its methyl ester, **8**, whose elemental analysis agreed with that of methyl 2,3,5 - triphenyl - Δ^4 - 1,2,4 - oxadiazolin - 3 - carboxylate. The IR spectrum of **8** showed a C=N absorption at 1623 cm^{-1}, the ester C=O at 1748 cm^{-1}, and the C–O peaks at 1255 and 1100 cm^{-1}. The greater stability of **8** as compared with **5** made it advisable to use the former for the NMR studies. Similarly, the acid **13b**, obtained from the reaction between **12** and **1**, was converted to its methyl ester **14** by reaction with diazomethane.

The NMR spectrum of **8** in CCl_4 showed a three-proton signal at 3.75 ppm that can be assigned to the methoxycarbonyl group. A complex signal that integrates for 15 protons appears in the region between 6.9 and 8.0 ppm. From the integral, this signal may be subdivided into two parts, a four proton section between 6.9 and 7.5 ppm. The four protons were tentatively assigned to the ortho hydrogens of the phenyl goups on C-3 and C-5.

Paramagnetic effects of several lanthanide complexes (shift reagents) have been widely used in structure determination and NMR signal assignation of organic molecules.[12–18]

Particularly, the linearity of a plot of the experimental chemical shift of each proton against the molar ratio, X, (moles of lanthanide complex/moles of substrate) confirm the consistency in the assignments of the signals of a spectrum.

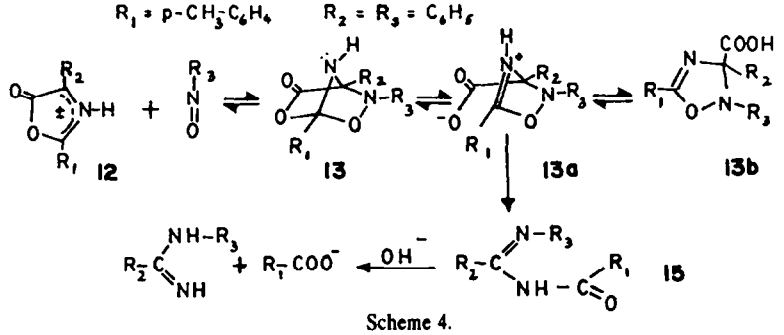
The NMR spectrum of **14** in CCl_4 (methyl ester of **13b** (Scheme 4), in which R_1 = p-tolyl = benzene ring A; R_2 = benzene ring B and R_3 = benzene ring C) shows a 3-proton siglet at 2.3 ppm that can be assigned to the CH_3 of the p-tolyl group; another 3-proton siglet due to the methoxycarbonyl group appears at 3.65 ppm; in the region between 6.9 and 7.7 ppm there is a 14-proton complex signal that may be described as composed of a 4-proton multiplet centered at 7.6 ppm, assigned tentatively to the ortho hydrogens of the A and B benzene rings ($2A_o + 2B_o$), and another multiplet at 7.2 ppm corresponding to the remaining ten protons. The progressive addition of $Eu(fod)_3$ to a solution of **14** in CCl_4 brought about an adequate resolution to allow the identification of well defined groups of aromatic protons. At values of X equal to or greater than 0.42 the signals due to the ortho-hydrogens of the A, B and C benzene rings ($2A_o + 2B_o + 2C_o$) were seen to separate in two groups, the one at the lower field corresponding to $2A_o + 2B_o$, and the other to $2C_o$.

The meta-hydrogens ($2B_m$) and the p-hydrogen (B_p) appear further upfield. Finally, the aromatic proton signal that appears at the highest field and integrates for 5 protons corresponds to three protons of ring C and two of ring A ($2C_m + C_p + 2A_m$). Figure 1 shows a plot of the LIS against the mole fraction, X, of $Eu(fod)_3$ for **14**. A linear relation is observed in all cases, pointing to the consistency of the assignments.

Sanders and Williams[12] determined the relative order in which various aliphatic functional groups tend to form complexes with $Eu(DPM)_3$ and found that this tendency decreases in the order amine > alcohol > ketone > aldehyde > ether > nitrile. Rodríguez and Joseph–Nathan[19] observed that the order is different in aromatic compounds, where phenols and ethers hardly associate at all, while primary amines associate better than secondary amines, and N,N-dimethylaniline is completely inert. This would suggest that, for the association of **14** with $Eu(fod)_3$, the most probable site for coordination would be N-4 of the oxadiazoline ring.

The ortho protons of rings A and B ($2A_o + 2B_o$) would be the ones most strongly affected because of their proximity to the coordination site, followed, in that order, by the methoxycarbonyl group and the C ring protons ($2C_o$). The assignments for the aromatic region were further confirmed by studying the $Eu(fod)_3$ complexes formed by **14a**, the perdeuterated C-ring analog of ester **14**.

In Fig. 1 it is observed that, for $Eu(fod)_3$ substrate ratios smaller than or equal to 0.3, three groups of signals



Scheme 4.

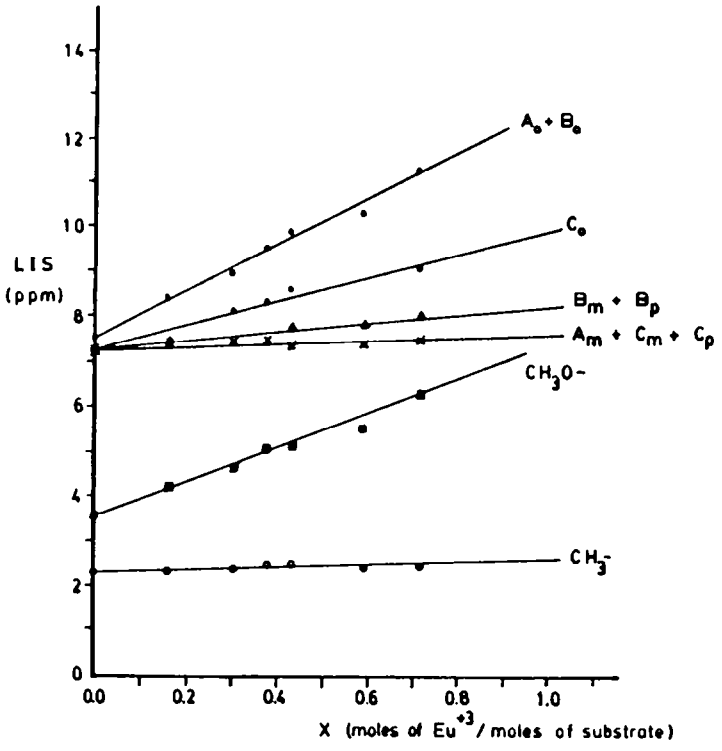


Fig. 1. Variation in chemical shift for carbon-bonded protons of **14** in CCl_4 with increasing concentration of $Eu(fod)_3$.

that integrates for 4, 2 and 8 protons, respectively, appear for the aromatic protons of **14**.

The progressive addition of $Eu(fod)_3$ ($X \leq 0.3$) to **14a** showed that the most highly affected signal had the same slope as that of **14**, and therefore corresponds to the 4 ortho protons, $2A_o + 2B_o$. Of course the signal that corresponds to the ortho protons of ring C, which had been displaced by deuterium, was missing. Finally, a 5-proton signal was observed that could be assigned to $2A_m + 2B_m + B_p$.

EXPERIMENTAL

Melting points were determined on a Leitz microscope hot stage and are uncorrected. IR spectra were obtained on a Leitz IIIG spectrophotometer, and NMR spectra on a Varian EM-360 spectrometer using TMS as an internal standard (60 MHz).

Materials. Nitrobenzene-d_5 (E. Merck, Darmstadt, Uvasol grade, 99% deuteration). Europium (III) tris-(1,1,1,2,2,3,3 - heptafluor - 7, 7 - dimethyl - 4, 6 - octadioate) ($Eu(fod)_3$) (Thompson–Packard).

2,4-Diphenyl-2-oxazolin-5-one **3** was prepared as described[7] from 3.00 g N-benzoyl-α-phenylglycine, yield: 2.39 g (87.5%), m.p. 102° (lit.[7] 103–105°); IR (KBr): 1825 (s), 1647 (s), 765 (s), 764 (s), 701(s) and 697 (s) cm^{-1}; NMR (CCl_4): 8.2 (m, 2H), 7.5 (m, 7H) and 5.45 (s, 1H) ppm.

2-p-Methylphenyl-4-phenyl-2-oxazolin-5-one **12**. p - Methylbenzoyl - α - phenylglycine (2.0 g; 7.43 mmol) was added with stirring under N_2 to 4.0 g (3.7 ml; 39 mmol) Ac_2O at 50–60°.

When the acid was dissolved (approx 15 min), heating was stopped. Upon cooling, **12** crystallized. The crystals were filtered off and washed with 5 ml of petroleum ether 50–70°, to yield 1.21 g (69.4%) of yellow crystals, m.p. 109°. Recrystallization from petroleum ether 50–70° yielded yellow crystals of **12**, m.p. 109–110°; IR (KBr): 1818 (s), 1639 (s) 833 (s), 729 (s) and 639 (s) cm^{-1}; NMR (CCl_4): 9.7 (d, 2H), 7.36 (m, 7H), 5.36 (s, 1H) and 2.47 (s, 3H) ppm. (Found: C, 76.76; H, 5.37; N, 5.37%; $C_{16}H_{13}NO_2$ requires: C, 76.47; H, 5.21; N, 5.58%).

Reaction between 2,4 - diphenyl - 2 - oxazolin - 5 - one **3** *and nitrosobenzene* **1** *at room temperature* (25°). A soln of 0.22 g (2 mmol) of **1** in 3 ml of xylene was added with stirring to 0.25 g (1 mmol) of **3** in 3 ml of xylene at room temperature. After 4 min a ppt started forming and increased rapidly. Stirring was continued for 15 min, the ppt filtered off and washed with petroleum ether 50–70° to dissolve the excess of **1**. The solid was air-dried, and the drying completed in a drying pistol over P_2O_5, to yield 0.22 g (59.5%) of 2,3,5 - triphenyl - Δ^4 - 1,2,4 - oxadiazolin - 3 - carboxylic acid **5**, m.p. 101–102° with evolution of gas and formation of another solid with m.p. 141°. IR (KBr): 3100–2200 (broad), 1740 (s) 1613 (s), 710 (s), 695 (s) and 690 (s) cm^{-1}; NMR (CD_3–CO–CD_3): 7.3–7.9 (m). (Found; C, 73.42; H, 4.77; N, 8.07%; $C_{21}H_{16}N_2O_3$ requires: C, 73.24; H, 4.68; N, 8.14%). The product was soluble in 10% aqueous NaOH, and reprecipitated upon addition of 1:1 HCl, yielding the original compound.

2,3,5 - Triphenyl - Δ^4 - 1,2,4 - oxadiazolin - 3 - carboxylic acid methyl ester **8**. A solution of diazomethane in ether was added dropwise, at room temperature, to a vigorously stirred solution of 0.2 g of **3** in 9 ml of ether until all the solid had dissolved and a yellowish color was observed. Evaporation of the solvent under reduced pressure yielded a pasty mass which, upon recrystallization from petroleum ether 80–100°, yielded 0.142 g (66.3%) of colorless crystals, m.p. 106–107°. IR (KBr): 1748 (s), 1623 (s), 1255 (s) and 1100 (s) cm^{-1}; NMR (CCl_4): 7.25–8.3 (m, 15H, arom), and 3.75 (s, 3H, CH_3O–) ppm.

Thermal decomposition of 2,3,5 - triphenyl - Δ^4 - 1,2,4, - oxadiazolin - 3 - carboxylic acid **5**. A mixture of acid **5** (132.4 mg; 0.384 mmol) and benzene was heated in a water bath with stirring. When the temperature reached 80° the acid dissolved with evolution of CO_2, forming a yellow solution. by evaporation of the solvent under reduced pressure and recrystallization of the residue from petroleum ether 50–75°, an almost quantitative yield of N - benzoyl - N' - phenylbenzamidine was obtained (IR, NMR and m.p. determinations).

N-Benzoyl-N'-phenylbenzamidine **4**. N-Phenylbenzamidine (0.49 g; 2.50 mmol) was treated as described[11] to yield 0.13 g (17.3%) of **4**, m.p. 142° (lit.[20] 143°). IR (KBr): 3226 (m, NH) and 1613 (s, C=N) cm^{-1}; NMR (CCl_4): 13 (broad, 1H), 8.4 (m, 2H) and 7.5 (M, 13H) ppm. (Found: C, 80.19; H, 5.37; N 9.17%; $C_{20}H_{16}N_2O$ requires: C, 79.97; H, 5.37; N, 9.33%).

Reaction between 2,4 - diphenyl - 2 - oxazolin - 5 - one **3** *with nitrosobenzene* **1**. In a flask carrying a condenser connected to a gas buret were placed 0.476 g (2 mmol) of **3**, 0.426 g (4 mmol) of **1**

and 3 ml of xylene. The flask was immersed in a liquid paraffin bath and its contents were stirred magnetically. Some crystals separated from the homogeneous solution. The mixture was heated, and at 80° the crystals dissolved with evolution of gas. The complete reaction lasted 20 min. Upon cooling, the volume of gas evolved was found to be the equivalent of 2 mmol of CO_2. The identity of the gas was confirmed by allowing it to react with barium hydroxide solution. The solution yielded crystals having m.p. 141.5–142°. The spectroscopic properties of the Product were the same as those of **4** obtained by Peak's method.[11] (Found: N, 9.28%; $C_{20}H_{16}N_2O$ requires: N, 9.33%).

Alkaline hydrolysis of N - benzoyl - N' - phenylbenzamidine **4**. A mixture of **4** (41.6 mg; 0.14 mmol), obtained by decarboxylation of **5**, and 1.5 ml of a 20% NaOH solution in methanol was boiled for 30 min, cooled, and diluted with 5 ml of water. A precipitate was formed which was filtered, washed with water and dried. The solid had m.p. 115°, and its properties were the same as those of N-phenylbenzamidine. The fraction that was soluble in the alkaline medium was acidified to pH 1 with 25% H_2SO_4, the methanol was distilled, and the residue left overnight. Colorless crystals with m.p. 122° and with spectral properties identical with those of benzoic acid were obtained.

Reaction between 2 - p - methylphenyl - 4 - phenyl - 2 - oxazolin - 5 - one **12** *and nitrosobenzene* **1**. *Preparation of 2,3 - diphenyl - 5 - p - tolyl - Δ^4 - 1,2,4 - oxadiazolin - 3 - carboxylic acid* **13b**. Solutions of 0.26 g (1.02 mmol) of **12** in 4 ml of xylene and 0.22 g (2.03 mmol) of **1** in 1 ml of xylene were stirred together at room temperature. A copius white ppt appeared within 2 min. Reaction was stopped after 18 min, the precipitate was filtered and washed with petroleum ether (50–70°), to yield 0.32 g (86.7%) of **13b** as a white solid m.p. 123–124°. IR (KBr): 3500–2200 (broad), 1244 (s) 826 (s), 781 (s), 735 (s) and 696 (s) cm^{-1}; NMR (DMSO-d_6): 7.0–7.7 (m, 14H) and 2.1 (s, 3H) ppm. (Found: N, 7.85%; $C_{22}H_{18}N_2O_3$ requires: N, 7.82%).

2,3 - Diphenyl - 5 - p - methylphenyl - Δ^4 - 1,2,4 - oxadiazolin - 3 - carboxylic acid methyl ester **14**. An ether solution of diazomethane was added dropwise to a suspension of **13b** (42 mg, 0.117 mmol) in 2 ml of ethyl ether until the acid dissolved and the solution had a light yellow color. The solvent was evaporated under reduced pressure, and the resulting oil recrystallized from petroleum ether 80–100° to yield 39.5 mg (90.7%) of a white solid, m.p. 99–100°. IR (KBr): 1745 (s), 1610 (s), 1240 (s), 1030 (s), 770 (s) and 690 (s) cm^{-1}; NMR (CCl_4): 6.9–7.7 (m, 14H), 3.7 (s, 3H) and 2.3 (s, 3H) ppm. (Found: C, 73.99; H, 5.38; N, 7.58%; $C_{23}H_{20}N_2O_3$ requires: C, 74.17; H, 5.41; N, 7.52%).

Reaction between 2 - p - methylphenyl - 4 - phenyl - 2 - oxazolin - 5 - one **12** *and nitrosobenzene* **1** *at* 100°. The procedure described for the preparation of **4** was applied to 0.25 g (1.01 mmol) of **12** and 0.21 g (2.02 mmol) of **1** at 100°, yielding 251 mg (80%) of an oil. The m.p. after recrystallization from ethanol is 110–113°. NMR (CCl_4): 11.4 (broad, 1H), 8.1 (m, 2H), 6.8–7.7 (m, 12H) and 2.3 (s, 3H) ppm. The reaction product, subjected to alkaline hydrolysis as described for **4**, yielded p-methylbenzoic acid, identified by its m.p. and IR spectrum, and N-phenylbenzamidine, identical with that obtained by Cooper and Partridge's method.[20]

Nitrosobenzene-d_5 **16**. Following the method described by Vogel,[21] a 36% yield was obtained from 1.0 g of nitrobenzene-d_5.

Reaction between nitrosobenzene-d_5 **16** *and 2 - p - methylphenyl - 4 - phenyl - 2 - oxazolin - 5 - one* **12**. A solution of 30 mg (0.27 mmol) of **16** in 1 ml of xylene was reacted with 67 mg (0.27 mmol) of **12** in 1 ml of xylene at 40° as described for the same reaction with **1**. The yield of acid was 70 mg (71.5%), m.p. 112–114°. The corresponding methyl ester had a m.p. of 96–97°.

Treatment of **16** *with europium(III) tris-1,1,1,2,2,3,3 - heptafluoro - 7,7 - dimethyl - 4,6 - octadioate (Eu(fod)$_3$)*. A solution of 65 mg of **13** in 0.5 ml of CCl_4 was mixed gradually with successive small portions of the Eu compound, and the NMR spectrum recorded after each addition. The [Eu(fod)$_3$]/[ester] ratio was determined from the integrals of the signals at 0.7 ppm due to the t-butyl group at the end of the Eu(fod)$_3$ chains as compared with those at 2.3 ppm due to the methyl protons of the p-tolyl group. The treatment of the deuterated ester with Eu compound was done similarly.

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