Thermal Transformation of Arylamidoximes in the Presence of Phosphorus Ylides. Unexpected Formation of 3-Aryl-5-arylamino-1,2,4-oxadiazoles

Demetrios N. Nicolaides[a*], Konstantinos E. Litinas[a], Ioannis Vrasidas[a] and Konstantina C. Fylaktakidou[b]

[a]Laboratory of Organic Chemistry, Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki 54124, Greece
[b]Molecular Biology and Genetics Department, Democritus University of Thrace, Alexandroupolis 68100, Greece

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The unexpected formation of 3-aryl-5-arylamino-1,2,4-oxadiazoles took place, when arylamidoximes reacted thermally with ethoxycarbonylmethylene(triphenyl)phosphorane. Furoxans, nitriles, ureas were also isolated suggesting aryl cyanide oxides as intermediates. 3-Aryl-5-arylamino-1,2,4-oxadiazoles were formed *via* an aryl migration from the carbon atom to the nitrogen atom of the amidoxime, and the structure was further proved from the X-ray crystal structure of the *N*-(4-bromobenzoyl) derivative.

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Introduction.

Thermal transformations of arylamidoximes was the subject of interest in a number of scientific papers. For example, when arylamidoximes were heated with carboxylic acids [1-3], 3,5-bis-aryl-1,2,4-oxadiazoles **9** and arylamides **8** were produced, while 3-aryl-5-methyl-1,2,4-oxadiazoles [4] **4** were additionally isolated, when glacial acetic acid was used. Leandri and Rebora [5] reported the thermal transformation of neat benzamidoxime **2b** at 170 °C to benzonitrile **6b**, benzamide **8b**, 3,5-diphenyl-1,2,4-triazole, 2,4,6-triphenyl-1,3,5-triazine, 3,5-diphenyl-1,2,4-oxadiazole and gaseous products (N_2, N_2O, NH_3, H_2O). Srivastava *et al.* [6] later reported that compounds of the type **9** and **4** were isolated in moderate yields from thermal reactions of arylamidoximes **2** in acetic acid solutions. Interestingly, diaryloxadiazoles **9** were also formed upon heating at controlled temperatures in the absence of acetic acid showing that the presence of a carboxylic acid was not critical for the above transformation. Concerning the latest steps of the mechanism for the formation of bis-aryloxadiazoles three possibilities were suggested: i) reaction [7] between arylnitrile and arylnitrile oxide originally formed from **2**, ii) reaction [8] of nitrile oxide formed with starting amidoxime, iii) reaction [9] between the nitrile formed and the starting amidoxime. The last mechanism is supported by the fact that diarylfuroxans, always formed by further dimerization of nitrile oxides [10], has not been isolated in the reactions studied. In contrast arylnitriles were either isolated or identified in the reaction mixture.

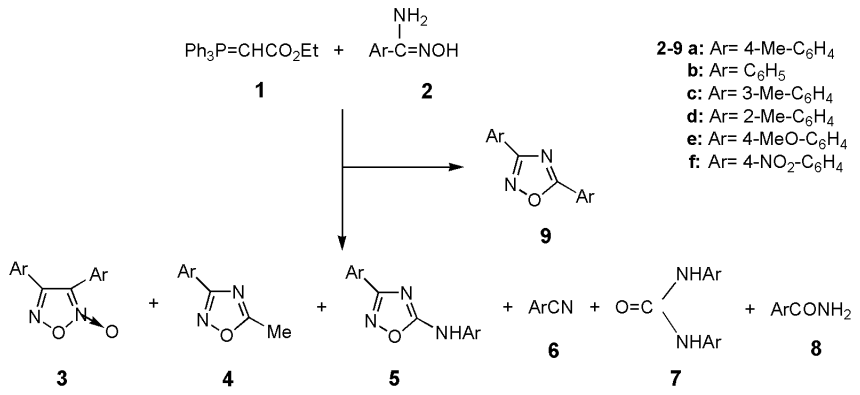
Our major scientific interests in the chemistry of amidoximes [11,12] and phosphorus ylides [13,14] prompted us to investigate the reactivity of phosphorus ylides towards amidoximes, taking into account our finding [15], where an O-alcylation or "Wittig type" olefination proceeded on some oximes C=NOH upon heating with phosphorus ylides.

The reactions studied and the products obtained, as well as the proposed mechanism (Schemes 1-4) are expected to enlighten further the thermal transformation of amidoximes.

Results and Discussion.

A solution of *p*-tolylamidoxime **2a** and an equimolar amount of ethoxycarbonylmethylene(triphenyl)-

Scheme 1



phosphorane **1** in toluene was heated under reflux for two days (Method A) and the complicated reaction mixture was then subjected to column chromatography to give *N*,*N*-bis(4-methylphenyl)urea **7a** (5.5%), 4-methylbenzamide **8a** (5%) and a product **5a** (19%, 28% on the basis of **2a** consumed) constructed from two molecules of amidoxime **2a** less an ammonia and a water molecule, as it is indicated by its analytical and spectral data (MS, ^{1}H-NMR, ^{13}C-NMR). The recorded ^{1}H-NMR spectrum of the product showed two absorptions for its methyl substituents at δ 2.33 and 2.40 ppm, while the ^{13}C-NMR spectrum also revealed a non-symmetric structure of the product in question. The recorded mass spectrum showed a molecular ion (M^+) m/z = 265. On the basis of these data we suggested for the product **5a** the structure of *N*,3-bis(4-methylphenyl)-1,2,4-oxadiazol-5-amine (Scheme 1).

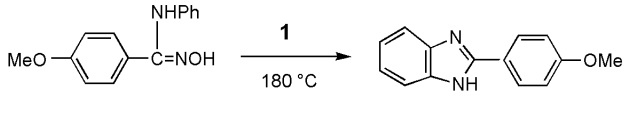
When a melted mixture of equimolar amounts of **1** and **2a** was heated at 135-140°C for 4,5 h (Method B) and the mixture separated as above compounds **5a** (29%), **7a** (10%) and **8a** (9%) were obtained again, along with 3,4-bis(4-methyphenyl)-furoxan **3a**[16] (2%) and 5-methyl-3-(4-methylphenyl)-1,2,4-oxadiazole **4a** [6] (2.5%). 3.5-Bis(4-methylphenyl)-1,2,4-oxadiazole **9a** [6], expected from the thermal transformation of **2a,** was separated in traces (0.4%) from the reaction mixture.

Similar products **5b** (15%, Method A), **5c** (17%, Method A), **5d** (9%, Method B) and **5e** (13%, Method B) were also obtained when amidoximes **2b, 2c**, **2d**, **2e** were treated with ylide **1**. In contrast to the above reactions, from the treatment of amidoxime **2f** with ylide **1** at ~150° for 4 h and separation of the complicated reaction mixture by column chromatography only 4-nitrobenzonitrile **6f** [6] (6%) and compounds **4f** (11%) were isolated. Efforts for separation or detection of oxadiazole **5f** among the reaction products were unsuccessful.

Finally, treatment of N-phenyl-4-methoxybenzamidoxime **10** with ylide **1** at ~180° for 3 h afforded the known [17] 2-(4-methoxyphenyl)-1*H*-benzimidazole **11** (17%) (Scheme 2).

Treatment of compound **5a** with methyl iodide/potassium carbonate afforded *N*-methyl-*N*,3-bis(4-methylphenyl)-1,2,4-oxadiazol-5-amine **21** (63%), while by treating of **5a** with acetic anhydride **22a** or with 4-bromobenzoic anhydride **22b** *N*-(4-methylphenyl)-*N*[3-(4-methylphenyl)-1,2,4-oxadiazol-5-yl]acetamide **23a** (78%) and 4-bromo*N*(4-methylphenyl-*N*[3-(4-methylphenyl)-1,2,4-oxadiazol-5-yl]benzamide **23b** (60%) respectively were obtained. The suggested structures of compounds **5a**, **21**, **23a** and **23b** were unequivocally established by X-ray crystallography of compound **23b** (see Figure 1 for ORTEP structure) [18].

Scheme 2



10 **11**

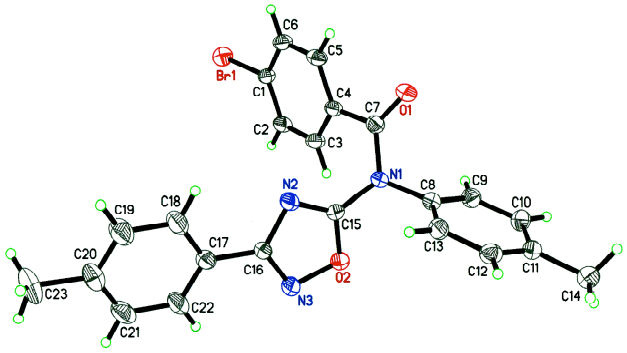
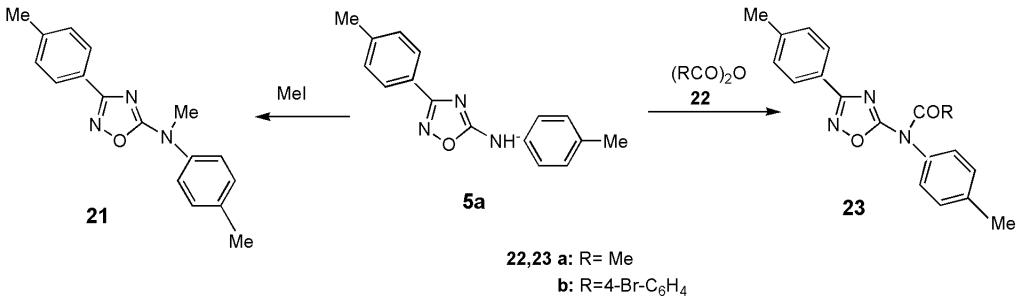


Figure 1. ORTEP presentation of benzamide **23b**.

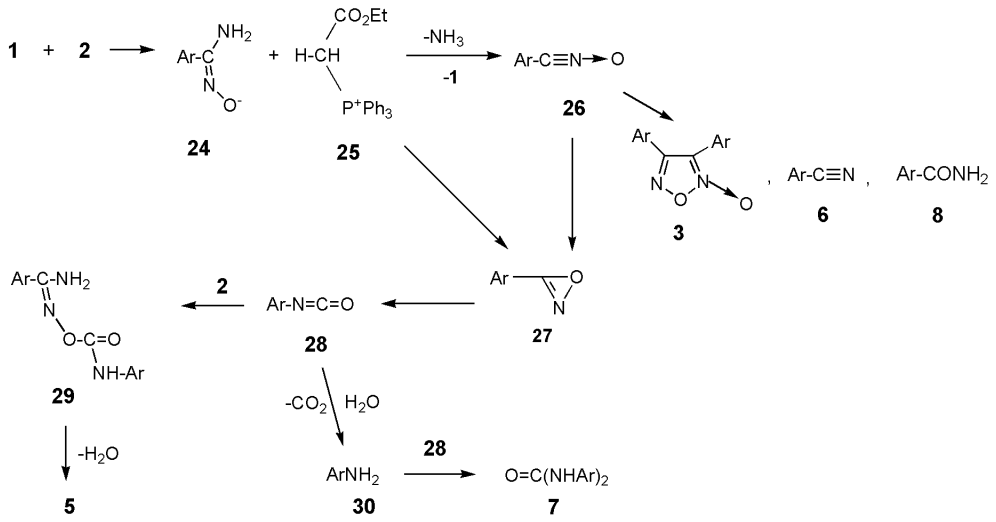
The observed aryl migration from the carbon to the nitrogen atom during the formation of **5** from **2** can be explained by supposing the intermediate formation of the corresponding aryl-isocyanate **28** *via* the oxazirene intermediate **27** as it is depicted in Scheme 4. An oxazirene intermediate of type **27** has also been suggested [19] to be formed during the known transformation of nitrile oxides to isocyanates, in addition to or instead of their dimerization [10] to the corresponding furoxans **3**. Although the direct formation of **27** from the intermediate **24** seems also possible, the isolation of the furoxan **3a** is strong evidence for the prior formation of the corresponding nitrile oxide **26**. Further attack [20] of amidoxime **2** to isocyanate **28**, followed by elimination of water from the intermediate **29** such formed can account for the formation of the unexpected 1,2,4-oxadiazoles **5** obtained. The suggested mechanism in Scheme 4 also explains the formation of the other products (**6-8**) obtained.

Deoxygenation of nitrile oxide **26** by triphenylphosphine produced can afford [19] nitrile **6** and further amide **8** from the later, while hydrolysis of the isocyanate **28** and further reaction of the amine such formed with **28** can lead to the formation of the corresponding urea **7**. It is obvious that the formation of nitrile oxide **26** is the key intermediate in the reactions studied and that it does not lead to the formation of 3,5-bisaryl-1,2,4-oxadiazoles **9**. Compounds **5** were formed thermally only in the presence of the ylide **1**, since when amidoxime **2a** was heated at 130-140° for 5 h only the formation of compound **9a** was observed. It must be noticed that compound **5a** was also formed, when amidoxime **2a** was

Scheme 3



Scheme 4



heated under reflux with ylide $Ph_3P=C(CH_2Ph)CO_2Et$ in toluene, as well as when only 1/10 equivalent of the ylide **1** was used for the reaction at ~180°, as it was indicated by tlc examinations of the above reaction mixtures. In an effort to exclude the participation of **1** in the reaction as a simple base, amidoxime **2a** was treated with *n*-butyl lithium in dry ether under an argon atmosphere for 16 h at r.t. and with 4-dimethylaminopyridine under reflux in toluene for 48 h. In both cases compound **5** was not detected by tlc examination, while starting material was found.

The formation of compound **4a** can be explained by the assumption that ylide **1** is partly thermally hydrolysed [21] to ethyl acetate, which reacts further [22] with the amidoxime **2a** used.

The analytical and spectral data of all new compounds are given in the experimental part and correspond well the structures suggested for them, while the known compounds gave data identical to those reported in the literature for them.

From the experimental data presented we can conclude that the transformation of amidoximes **2** to 1,2,4-oxadiazoles **5** proceeds thermally but only in the presence of an ylide, likely acting initially as a base for the abstraction of the hydrogen atom from the =NOH group. The phosphonium salt **25** so formed can act further as an acid for the abstraction of ammonia from the intermediate anion **24** to give nitrile oxide **26**. It is of interest to note that treatment of benzamide oximes with arylcyclohexylcarbodiimide also affords, as main products, 3-aryl-5-arylamino-1,2,4-oxadiazoles, but with participation of the aryl-substituent of the diimide as the arylamino-substituent in the oxadiazole product formed [23,24].

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. IR spectra were obtained with a Perkin-Elmer 1310 spectrophotometer as Nujol mulls except otherwise stated. Nmr spectra were recorded on a Bruker AM 300 (300 MHz, and 75 MHz for ^1H and ^{13}C respectively) using deuteriochloroform as solvent and TMS as an internal standard. Coupling constants (*J*) are reported in Hz. Mass spectra were determined on a VG-250 spectrometer at 70 eV under Electron

Impact (EI) conditions, or on a Perkin Elmer API 100 Sciex Simple quadrupole under Electrospray Ionization (ESI) conditions. High resolution mass spectra (hrms) were recorded on an Ionspec mass spectrometer under Matrix-Assisted Laser Desorption-Ionization Fourier Transform Mass Spectrometer (MALDI-FTMS) conditions with 2,5-dihydroxybenzoic acid (DHB) as the matrix. Microanalyses were performed on a Perkin-Elmer 2400-II Element analyzer. Silica gel N° 60, Merck A.G. has been used for column chromatographies. Earlier reported procedures were used for the preparation of amidoximes [1,25].

Reactions of Ylide **1** with Arylamidoximes **2a-f**, **10**.

General Procedure.

A mixture of ylide **1** (0.696 g, 2 mmoles) and the appropriate arylamidoxime **2a-f, 10** (2 mmoles) in toluene (10 ml) was heated under reflux for 4.5 h - 3 days (Method A) or was melted and heated at 135-180° for 1.5-4.5 h (Method B). The reaction mixture was then separated by column chromatography (silica gel, hexane/ethyl acetate 8:1 or dichloromethane/ethyl acetate 6:1 only in the case of the reaction of **10**).

3,4-Bis(4-methylphenyl)-1,2,5-oxadiazole-*N*-oxide (**3a**).

This compound was obtained as white crystals from the reaction between **1** and **2a** after heating the melted mixture at 135-145° for 4 h (Method B), (6 mg, 2 %) m.p. 112-114°C (lit [16] m.p. 113-114°C).

5-Methyl-3-(4-methylphenyl)-1,2,4-oxadiazole (**4a**).

This compound was obtained as white crystals by method B from the reaction between **1** and **2a**, eluted after **3a** (6 mg, 2.5 %), m.p. 73-74° C (lit [6] m.p. 74°C).

N,3-Bis(4-methylphenyl)-1,2,4-oxadiazol-5-amine (**5a**).

This compound was obtained from the reaction between **1** and **2a**, eluted after compounds **3a, 4a** (50 mg, 28 % by the method A, or 75 mg, 29 % by the method B), m.p. 189-191° C (light yellow crystals from chloroform/hexane); ir: 3283, 3025, 1631, 1578, 1513 cm^{-1}; ^{1}H-nmr: δ 2.34 (s, 3H), 2.41 (s, 3H), 7.17 (d, 2H, *J*=8.0 Hz), 7.26 (d, 2H, *J*=8.3 Hz), 7.39 (d, 2H, *J*=8.3 Hz), 7.94 (d, 2H, *J*=8.0 Hz), 7.82 (brs, 1H, exchanged by D_2O); ^{13}C-nmr: δ 20.8, 21.6, 118.6, 124.4, 127.3, 129.4, 129.9, 133.7, 134.5, 141.3, 168.2, 168.4; ms (EI): m/z 265 (55, M^+), 159 (12), 132 (100), 118 (8), 106 (16), 91 (55); For $C_{16}H_{16}N_3O$ hrms Calcd. 266.1288; Found 266.1290.

3,5-Bis(4-methylphenyl)-1,2,4-oxadiazole (**9a**).

This compound was obtained as light yellow crystals by Method B from the reaction between **1** and **2a** eluted after **3a** and before **4a** (1 mg, 0.4 %) ; m.p. 133-134 °C (lit [6] mp. 134 °C).

N,3-Diphenyl-1,2,4-ozadiazol-5-amine (**5b**).

This compound was obtained as white crystals from the reaction between **1** and **2b** according to method A (benzene, reflux 3 days) (36 mg, 15 %); m.p. 165-167 °C (lit [26] m.p. 168 °C).

N,3-Bis(3-methylphenyl)-1,2,4-oxadiazol-5-amine (**5c**).

This compound was obtained from the reaction between **1** and **2c** according to Method A (toluene, reflux 3 days) (44 mg, 17%), m.p. 115-116 °C (yellow crystals from ethyl acetate/hexane); ir: 3280, 3040, 1640, 1595 cm^{-1}; ^{1}H nmr: δ 2.33 (s, 3H), 2.38 (s, 3H), 6.95 (d, 1H, *J*=7.2 Hz), 7.22-7.42 (m, 5H), 7.83-7.92 (m, 2H), 8.10 (brs, 1H, exchanged by D_2O); ^{13}C nmr: δ 21.3, 21.4, 115.5, 119.1, 124.5, 124.9, 126.9, 127.9, 128.6, 129.2, 131.8, 136.8, 138.5, 139.4, 168.2, 168.4; ms (EI): m/z 265 (46, M^+), 158 (11), 132 (98), 131 (100), 117 (18), 91 (44).

Anal. Calcd. for $C_{16}H_{15}N_3O$: C: 72.42, H: 5.70, N: 15.85. Found C: 72.17, H: 5.68, N: 15.93.

N,3-Bis(2-methylphenyl)-1,2,4-oxadiazol-5-amine (**5d**).

This compound was obtained from the reaction between **1** and **2d** by the Method B (heating at 135-140 °C, 4 h) (23 mg, 9%); m.p. 130-132 °C (light yellow crystals from ethyl acetate/hexane); ir: 3260, 3030, 1630, 1590 cm^{-1}; ^{1}H nmr: δ 2.34 (s, 3H), 2.63 (s, 3H), 7.10 (d, 1H, *J*=7.4 Hz), 7.20-7.41 (m, 6H), 7.93 (d, 1H, *J*=7.0 Hz), 7.97 (d, 1H, *J*=8.4 Hz); ^{13}C nmr: δ 17.8, 22.0, 120.1, 124.7, 125.8, 127.2, 127.3, 129.9, 130.3, 130.4, 130.8, 131.2, 135.3, 138.1, 167.9, 169.2; ms (EI): m/z 265 (45, M^+), 159 (85), 131 (87), 118 (62), 106 (88), 105 (92), 91 (82), 90 (100).

Anal. Calcd. for $C_{16}H_{15}N_3O$: C: 72.42, H: 5.70, N: 15.85. Found C: 72.20, H: 5.95, N: 15.55.

N,3-Bis(4-methoxyphenyl)-1,2,4-oxadiazole-5-amine (**5e**).

This compound was obtained from the reaction between **1** and **2e** according to Method B (heating at 170 °C, 4 h) (38 mg, 13 %) m.p. 198-200 °C (yellow crystals from ethyl acetate/hexane); ir: 3280, 3040, 1640, 1590 cm^{-1}; ^{1}H nmr: δ 3.82 (s, 3H), 3.86 (s, 3H), 6.93 (d, 2H, *J*=9.0 Hz), 6.96 (d, 2H, *J*=8.9 Hz), 7.26 (brs, 1H), 7.44 (d, 2H, *J*=9.0 Hz), 7.98 (d, 2H, *J*=8.9 Hz); ^{13}C nmr: δ 55.4, 55.6, 114.1, 114.7, 120.6, 121.5, 128.9, 130.2, 160.0, 161.8, 168.4, 171.4,; ms (EI): m/z 297 (M^+, 57%), 148 (100), 133 (87), 122 (50), 106 (62).

Anal. Calcd. for $C_{16}H_{15}N_3O_3$: C; 64.62, H; 5.09, N: 14.14. Found C: 64.35, H: 5.39, N: 13.95.

2-(4-Methoxyphenyl)-1*H*-benzimidazole (**11**).

This compound was obtained as white crystals from the reaction between **1** and **10** according to Method B (heating at 180 °C, 3h) (78 mg, 17 %), m.p. 226-227 °C (lit [17] m.p. 227 °C).

5-Methyl-3-(4-nitrophenyl)-1,2,4-oxadiazole (**4f**).

This compound was obtained as light yellow crystals from the reaction between **1** and **2f** according to method B (heating at 150 °C, 4 h) (44 mg,11 %), m.p. 136-138 °C (lit [6] m.p. 138 °C).

N-Methyl-*N*,3-bis(4-methylphenyl)-1,2,4-oxadiazol-5-amine (**21**).

A mixture of compound **5a** (41 mg, 0.15 mmole), methyl iodide (8 drops, excess) and potassium carbonate (54 mg, 0.39 mmole) in DMF (4 ml) was stirred at room temperature for 24 h and then extracted first with water and then with ether. The organic layers dried over sodium sulphate and concentrated to give product **21** (27 mg, 63 %), m.p. 87-88 °C (yellow crystals from ethyl acetate/hexane); ir: 3020, 1580, 1500; ^{1}H nmr: δ 2.38 (s, 3H), 2.39 (s, 3H), 3.61 (s, 3H), 7.23 (d, 2H, *J*=8.3 Hz), 7.24 (d, 2H, *J*=8.1 Hz), 7.33 (d, 2H, *J*=8.3 Hz), 7.90 (d, 2H, *J*=8.1 Hz); ^{13}C nmr: δ 21.0, 21.5, 39.5, 123.8, 124.9, 127.2, 127.3, 129.9, 136.3, 139.8, 140.9, 168.6, 171.1; ms (EI): m/z 279 (M^+, 92%), 159 (16), 148 (100), 120 (53), 91 (34).

Anal. Calcd. For $C_{17}H_{17}N_3O$: C: 73.08, H: 6.1 4, N: 15.05. Found C: 72.85, H: 6.20, N: 14.79.

N-(4-Methylphenyl)-*N*-[3-(4-methylphenyl)-1,2,4-oxadiazol-5-yl]acetamide (**23a**).

A mixture of compound **5a** (100 mg, 0.377 mmole), acetic anhydride (0.1 ml, 0.108 g, 1.06 mmoles) and pyridine (3 drops) in dry benzene (3 ml) was heated under reflux for 22 h and the solution was concentrated in a rotary evaporator to give compound **23a** (90 mg, 78 %), m.p. 113-115 °C (yellow crystals from chloroform); ir: 3020, 1700, 1580, 1560 cm^{-1}; ^1H nmr: δ 2.41 (s, 3H), 2.43 (s, 3H), 2.57 (s, 3H), 7.19 (d, 2H, *J*=8.2 Hz), 7.26 (d, 2H, *J*=8.0 Hz), 7.31 (d, 2H, *J*=8.0 Hz), 7.91 (d, 2H, *J*=8.2 Hz); ^{13}C nmr: δ 21.3, 21.6, 25.0, 123.8, 127.3, 128.0, 129.5, 130.5, 135.1, 139.5, 141.7, 167.5, 168.9, 170.1; ms (EI): m/z 307 (M^+, 63%), 265 (69), 222 (53), 159 (58), 133 (100), 131 (88), 117 (83), 91 (86).

Anal. Calcd. For $C_{18}H_{17}N_3O_2$: C: 70.33, H: 5.58, N: 13.68. Found C: 70.25, H: 5.40, N: 13.6

4-Bromo-*N*-(4-methylphenyl)-*N*-[3-(4-methylphenyl)-1,2,4-oxadiazol-5-yl]benzamide (**23b**).

A mixture of compound **5a** (2 mg, 0.0075 mmole), triethylamine (0.75 mg, 0.0075 mmole), 4-dimethylaminopyridine (0.05 mg, 0.0004 mmole) and 4-bromobenzoylchloride (1.6 mg, 0.0075 mmole) in dichloromethane (2 ml) was heated under reflux for 20 h. The mixture was concentrated in a rotary evaporator and the residue was separated by column chromatography (silica gel, hexane/ethyl acetate to give compound **23b** (2 mg 60%), m.p. 151-152 °C (yellow crystals from ethyl acetate/hexane); ir: 3025, 1702, 1584, 1561, 1508 cm^{-1}; ^1H nmr: δ 2.36 (s, 6H), 7.15-7.23 (m, 6H), 7.46 (s, 4H), 7.79 (d, 2H, *J*=7.9 Hz); ^{13}C nmr: δ 21.2, 21.6, 123.6, 127.0, 127.2, 127.3, 129.4, 130.4, 130.5, 131.7, 132.6, 136.1, 139.0, 141.8, 168.6, 168.9, 169.8; ms (ESI): m/z 450/448 $(M+H)^+$, 472/470 $(M+Na)^+$.

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[18] Crystallographic data (excluding structure factors) for compound **23b** have been deposited with the Cambridge Crystallographic Data as Supplementary publication number CCDC 207973. Copies of the data can be obtained free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

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