# (*E*)-1,2-Bis(5-aryl-1,3,4-oxadiazol-2-yl)ethenes

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*Dedicated to Prof. H. Meier on the occasion of his 60th birthday*

**Abstract:** A series of (*E*)-1,2-bis(1,3,4-oxadiazol-2-yl)ethenes with a variety of aromatic substituents in the 5-positions of the heterocycles was prepared by acylation of the corresponding tetrazoles with fumaryl chloride and subsequent thermal ring transformation. The modified Huisgen reaction renders a new pathway to 3-(1,3,4-oxadiazol-2-yl)propenoic acids and subsequently to the title compounds with different substituents.

**Key words:** heterocycles, Huisgen reaction, stilbene, 1,3,4-oxadiazole

1,3,4-Oxadiazoles with aromatic substituents in the 2- and 5-position and bis(1,3,4-oxadiazolyl)arenes are classes of compounds with wide technical importance. Their fluorescence is used in plastic scintillators and optical whiteners,[1,2] their semiconducting properties and film forming capabilities were recently utilised for electron conducting layers in organic light emitting diodes.[3,4] Polymeric compounds, displaying tough mechanical properties and excellent heat resistance are advanced materials for high-performance applications.[4] In substituted 1,3,4-oxadiazoles the heterocycle is, from the spectral and electronic points of view, similar to a *p*-phenylene unit. The stability, the hypsochromic shifted absorption maximum, intense fluorescence, and the lowered HOMO and LUMO energy levels[5] are interesting features for the application in electrooptical devices. Sinigersky, Wegner, and Shopov investigated poly(arylenevinylene)s with alternating *p*-phenylene and 1,3,4-oxadiazole units.[6] The conductivity of these materials was close to that of poly(*p*-phenylenevinylene). Balanced charge transporting properties for both, electrons and holes and an efficient light emission has been reported for poly(phenylenevinylene)s containing 2,5-diaryl-1,3,4-oxadiazole segments in the main chain.[7]

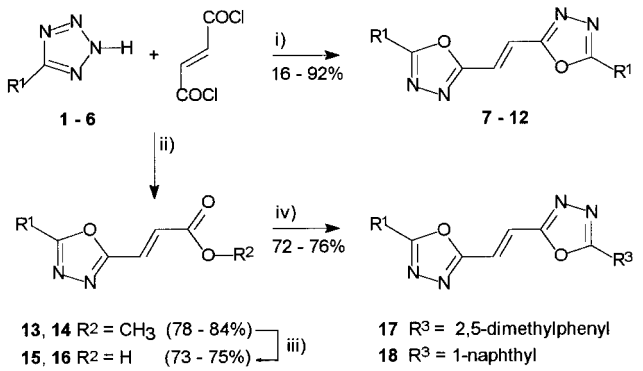
There are two widely used general principles[8] for the synthesis of 1,3,4-oxadiazoles, cyclocondensation of acyl hydrazides and the thermal ring transformation of acylated tetrazoles (Huisgen reaction). Recently, Kraft reported the synthesis of 1,3,4-oxadiazole containing dendrimers via palladium catalysed carbonylation of aromatic halides in the presence of hydrazides or tetrazoles. The acylated intermediates were transformed to the oxadiazoles by dehydration or thermally.[9]

The chemistry and physics of stilbene[10] and stilbenoid oligomers and polymers has been studied extensively. Their application profile ranges from anthelmintics and optical whiteners to hole conducting layers in light emitting diodes. Contrary to the vast knowledge about these classes of compounds, hitherto only two 1,2-bis(1,3,4-oxadiazolyl)ethenes have been described.[11,12] We are interested in molecules with extended conjugation and high electron affinity as model compounds for poly(hetarylenevinylene)s. Herein, the synthesis of aryl substituted (*E*)-1,2-bis(1,3,4-oxadiazol-2-yl)ethenes by direct reaction of tetrazoles with fumaryl chloride is reported. The Huisgen reaction provides an elegant way to compounds sensitive to drastic reaction conditions. The required tetrazoles are easily accessible from nitriles and inorganic azides,[13] or primary acid amides employing triazidochlorosilane.[14] Huisgen and co-workers prepared 2,5-bisaryl-1,3,4-oxadiazoles in excellent yields by heating solutions of tetrazoles and carboxylic acid chlorides in pyridine. This procedure was not transferable to the reaction of tetrazoles with fumaryl chloride. Using pyridine as base and solvent led to several side reactions.[15] In the absence of a base, using high-boiling ethers like diglyme as solvent, the acylation/ring transformation required elevated temperatures resulting in decomposition of the tetrazole and to side reactions due to acidic cleavage of the solvent. Adding only stoichiometric amounts of collidine or quinoline to a solution of fumaryl chloride and the tetrazole in aromatic ethers like anisole or diphenyl ether and subsequent heating proved to be successful for the conversion to the title compounds. A series of bis-oxadiazolylethenes with aromatic substituents and extended conjugation could be prepared in a one-pot procedure (Scheme). The transformation of the heterocycles (**1–6** to **7–12**) was monitored by the gas evolution, starting at bath temperatures between 85 °C (**7**) and 180 °C (**12**). Tetrazoles with electron-rich substituents (**1**, **2**) proved to be more reactive than those with arenes of higher electronegativity (**4**, **5**), the reaction with phenylethenyl tetrazole **6** competed with decomposition resulting in a low yield (16%) of **12**.

Using an excess of fumaryl chloride in the presence of collidine offered a straightforward access to the hitherto nearly unknown[16,17] β-(oxadiazolyl)acrylic esters (**13**, **14**) and, by hydrolysis of the ester, to the corresponding acids (**15**, **16**). Their transformation to the acid chlorides and subsequent Huisgen reactions opened the possibility to synthesise compounds with different substituents (**17**, **18**).

Attempts to prepare the corresponding (*Z*)-β-(oxadiazolyl)acrylic acids or (*Z*)-1,2-bisoxadiazolylethenes from

tetrazoles and maleic anhydride failed due to decomposition of the tetrazoles at the required reaction temperatures. Huisgen reported similar results for the reaction of tetrazoles with phthalic anhydride.[5]

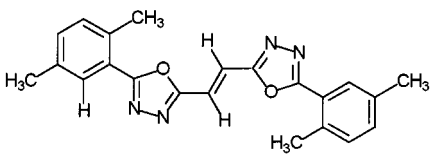



| Product | R1 | Product | R1 |
|---|---|---|---|
| 1, 7, 13, 15, 17 | | 4, 10 | |
| 2, 8, 14, 16, 18 | | 5, 11 | |
| 3, 9 | | 6, 12 | |

i) anisole or diphenyl ether, collidine or quinoline, 85–180 °C; ii) anisole, excess fumaryl chloride, collidine, 95 °C, then MeOH, r.t.; iii) propan-2-ol, NaOH, $H_2O$, 90 °C, then HCl; iv) $PCl_3$, benzene, r.t., 14 h, then tetrazole (**2**, **5**), anisole, collidine, 120 °C.

**Scheme**

The model compound **8** was studied by NMR spectroscopy. The *trans*-configuration of the vinylene protons was proved by the vicinal coupling constant of $J$ = 16.4 Hz (from $^{13}C$ satellites). Irradiation into their signal caused positive NOEs at the resonance frequencies of the aromatic protons *ortho* to the oxadiazole (1.7%) and of the *ortho* methyl groups (1.0%). The reverse experiments, irradiation into the signal of the *ortho*-methyl group or the *ortho*-hydrogen enhanced the intensity of the vinylene signal (0.8%, 1.7%).



**8**

**Figure 1**. Calculated Energy-Lowest Conformation of **8**

These unexpected nuclear Overhauser effects from protons on one side of the oxadiazole to hydrogen on the other side prompted us to calculate the spatial distances and the conformational distribution in this compound. Force field calculations[18] gave two groups of minima divided by about 2 kcal/mol in their heats of formation. All minima were essentially planar, the three predominant populated conformers with *s-trans* geometry of the ethylene unit and C=N bonds of the adjacent heterocycles were more stable than the second group of minima with one or two *s-cis* orientations. Rotation of the xylene moiety led to differences in the heats of formation of 0.31 kcal/mol or less. The absolute minimum was calculated to be planar and both *ortho*-methyl groups had *s-cis* orientation to the oxygen of the adjacent heterocycle, this conformation is depicted in Figure 1. For these three low-energy conformers, the intramolecular distances of protons responsible for the long range NOEs were calculated to be in the range of 3.28 to 3.41 Å (ethene–methyl, 1% NOE) and 3.73 to 3.89 Å (ethene-*ortho*-H, 1.7% NOE).

In accordance with the calculations, X-ray analysis revealed the *s-trans* orientation of ethene and adjacent C=N bonds (Figure 2). Contrary to the calculated gas phase structure, we found s-trans geometry of *ortho*-methyl groups and the heterocyclic oxygen in the solid state. The distance of vinylene proton and aromatic *ortho*-hydrogen was 3.62 Å, all dihedral angles of aromatic and alkenic units were less than 3.5°. These investigations proved a high degree of planarity in this molecule in the solid state as well as in solution or in the gas phase.

In conclusion, we have extended the Huisgen reaction to the synthesis of (*E*)-1,2-bis(1,3,4-oxadiazolyl)ethenes and oxadiazolyl propenoic acids with a variety of aromatic substituents on the heterocycle. Compounds with extended conjugation and high electron affinity are accessible. NMR and X-ray analysis revealed a high degree of planarity even by *ortho*-substitution at the heteroanalogous biphenylene unit.

IR-Spectra: in KBr, Beckman Acculab 4. NMR Spectra: in $CDCl_3$ or DMSO-$d_6$, Bruker AC 200 and AM 400. Mass spectra: 70 eV, Varian MAT 711. Mps: not corrected. Eluent mixtures are v/v. The nitriles, except 4-[(*E*)-2-(4-methylphenylethen-1-yl]benzonitrile[19] were commercially available. Chemicals were used as received, solvents dried according to standard procedures and distilled.

**Tetrazoles 1–6; General Procedure**

Magnetically stirred mixtures of the corresponding nitrile (0.1 mol), $NH_4Cl$ (6.9 g, 0.13 mol) and $NaN_3$ (8.45 g, 0.13 mol) in anhyd DMF (60 mL) were heated to 140 °C for 48 h. The cooled mixtures were poured into $H_2O$ (300 mL) and acidified to pH = 2 with concentrated hydrochloric acid. After 12 h at 4 °C, the suspension was filtrated using a Büchner funnel, the residue was washed with $H_2O$, $H_2O$/EtOH (1/1) and $H_2O$ and dried. Recrystallisation from EtOH or propan-2-ol gave analytically pure products.

**5-(4-Methoxyphenyl)tetrazole[20] (1)**

Yield: 17.1 g (97%),white crystals, mp 235 °C, (Lit.: 237 °C).

**5-(2,5-Dimethylphenyl)tetrazole (2)**

Yield: 15.4 g (94%), white crystals.

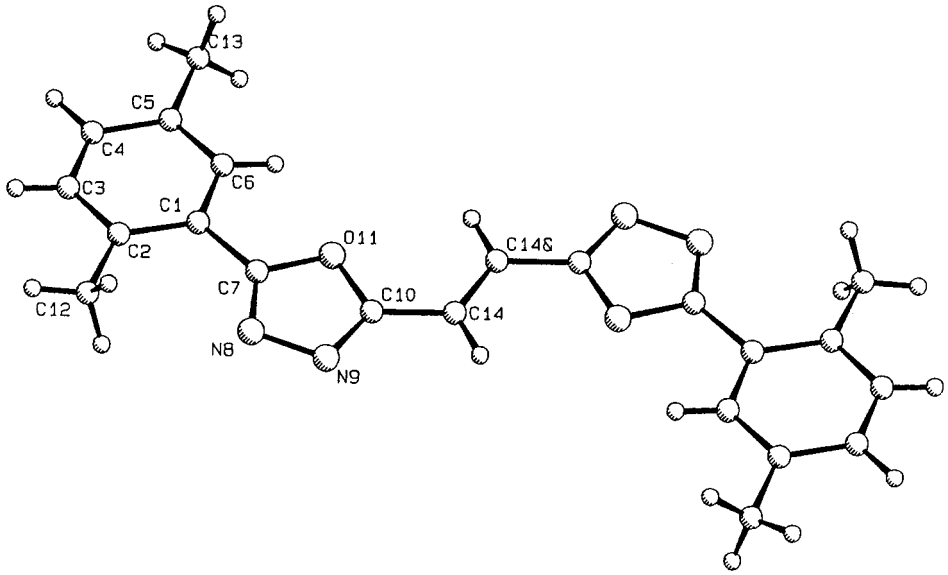



**Figure 2**. X-ray Structure of **8**

**5-{4-[(*E*)-2-(4-Methylphenyl)ethen-1-yl]phenyl}tetrazole (3)**
Prepared from 4-[(*E*)-2-(4-methylphenyl)ethen-1-yl]benzonitrile,[19] yield: 23.9 g (91%), white crystals, mp 248 °C (dec.).

**4-(2*H*-Tetrazol-5-yl)pyridine**[21] **(4)**
Yield: 12.3 g (84%), light brown crystals, mp 265 °C (dec.).

**5-(1-Naphthyl)tetrazole**[22] **(5)**
Yield: 18.0 g (92%), mp 192 °C (dec.) (Lit.: 217–218 °C).

**(*E*)-5-(2-Phenylethenyl)tetrazole (6)**
Yield: 13.4 g (78%), light brown crystals, mp 154 °C (175 °C dec.).

**Huisgen Reaction; General Procedure**
A round-bottom flask was equipped with a magnetic stirring bar, the tetrazole (**1–6**) (2 mmol), solvent (20 mL) and fumaryl chloride (153 mg, 1 mmol) were added. While stirring, collidine (242 mg, 2 mmol) diluted with solvent (2 mL) was added dropwise and the flask was connected to a gas burette. The flask was heated until gas evolution occurred and kept at this temperature. As the gas evolution ceased, the bath temperature was raised about 20 °C and kept for further 20 min. The mixture was cooled and poured on a chromatography column filled with silica gel and petroleum ether/toluene 1/1. After the solvent was eluted, toluene with gradually increased content of EtOAc was used as an eluent.

**(*E*)-1,2-Bis[5-(4-methoxyphenyl)-1,3,4-oxadiazol-2-yl]ethene (7)**
Anisole as solvent, gas evolution started at 85 °C. Yield: 318 mg (92%), colourless crystals.

**(*E*)-1,2-Bis[5-(2,5-dimethylphenyl)-1,3,4-oxadiazol-2-yl]ethene (8)**
Anisole was used as solvent, $N_2$ evolution occurred above 95 °C. Yield: 331 mg (89%), colourless crystals.

**(*E*)-1,2-Bis{5-[4-((*E*)-2-{4-methylphenyl}ethen-1-yl)phenyl]-1,3,4-oxadiazol-2-yl}ethene (9)**
Diphenyl ether was used as solvent, $N_2$ evolution started at 140 °C. Purification by pouring the mixture into petroleum ether (100 mL), filtration and subsequent washing with toluene, EtOAc and EtOH. Stirring the crude product first with aq MeOH (1/1, 50 mL) and than with hot $CHCl_3$ (100 mL). Yield: 537 mg (92%), mp 368°C (dec.).

IR (KBr): $\nu$ = 3012 $cm^{-1}$, 2895, 1588, 1530, 1496, 1408, 1084, 956, 828, 796, 740.

MS (*m*/*z*,%): 548 (13) [$M^+$], 221 (42) [$C_{16}H_{13}O^+$], 193 (5), 178 (29), 44 (100).

**(*E*)-1,2-Bis[5-(4-pyridyl)-1,3,4-oxadiazol-2-yl]ethene (10)**
Diphenyl ether was used as solvent, no base was added, nitrogen evolution occurred above 170 °C. Yield: 203 mg (64%), colourless crystals.

**(*E*)-1,2-Bis[5-(naphth-1-yl)-1,3,4-oxadiazol-2-yl]ethene (11)**
Anisole was used as solvent, $N_2$ evolution occurred above 140 °C, 3 h. Yield: 349 mg (84%), colourless crystals.

**Table 1** Selected Bond Lengths and Angles for **8** in the Solid State

| distance | Å | bond angles | deg | torsion angles | deg |
|---|---|---|---|---|---|
| C1 – C7 | 1.458 | C7 – C1 – C6 | 118.0 | C6 – C1 – C2 – C12 | –178.2 |
| C7 – N8 | 1.291 | C3 – C2 – C1 | 116.7 | C7 – C1 – C2 – C3 | –175.6 |
| C7 – O11 | 1.367 | C12 – C2 – C1 | 123.7 | C7 – C1 – C2 – C12 | 4.5 |
| N9 – C10 | 1.284 | C1 – C7 – N8 | 131.1 | C2 – C1 – C7 – N8 | 3.4 |
| C10 – C14 | 1.440 | N9 – C10 – C14 | 127.8 | C6 – C1 – C7 – O11 | 2.9 |
| C14 – C14´ | 1.323 | C10 – C14 – C14´ | 123.4 | N9 – C10 – C14 – C14´ | 177.7 |

**Table 2** Compounds **2, 3** and **6–18** Prepared

| Product (Yield) | mp (°C) | $^1$H NMR : δ, *J* (Hz) | $^{13}$C NMR : δ | MS *m/z* (rel. int., %) | IR (KBr) ν (cm$^{-1}$) |
|---|---|---|---|---|---|
| **2** (94%) | 174 | 2.32 (s, 3 H, $CH_3$), 2.48 (s, 3 H, $CH_3$), 7.18 (d, 2 H, 3-H, 4-H), 7.23 (d, 1 H, 6-H)[b] | 19.8, 20.2, ($CH_3$), 123.7 (C-1, Ph),155.3 (C-5), 129.7, 131.1, 131.2 (C-3, C-4, C-6, Ph), 133.9, 135.3 (C-2, C-5, Ph)[b] | 174 (71) [M$^+$], 145 (100), 131 (77) [M$^+$-$HN_3$] | 3005, 2900, 2730, 2620, 1582, 1503, 1250, 1166, 1092, 993, 899, 818 |
| **3** (91%) | 248 (dec.) | 2.31 (s, 3 H, $CH_3$), 7.21 (m, 3 H, 3-H 5-H, Tol, 1-H, Tet), 7.24 (d, *J* = 16.5, 1 H, Eth), 7.37 (d, *J* = 16.5, 1 H, Eth), 7.51 (d, *J* = 7.5, 2 H, 2-H, 6-H, Tol), 7.78 (d, J = 7.9, 2 H, 3-H, 5-H, Ph), 8.02 (d, *J* = 8.1, 2 H 2-H, 6-H, Ph)[b] | 20.9 ($CH_3$), 126.7, 127.1, 127.3, 129.4 (ar CH), 126.3, 130.4 (Eth), 122.8, 133.9, 137.6, 139.9 ($C_q$, ar), 155.2 (C-5, Tet)[b] | 262 (51) [M$^+$], 234 (100) [M$^+$-$N_2$], 219 (30) [M$^+$-$HN_3$] | 3010, 2915, 2850, 2730, 1604, 1560, 1508, 1488, 1433, 1156, 1056, 978, 840, 811, 752 |
| **6** (78%) | 154 (175° dec.) | 7.69 (d, *J* = 7.9 Hz, 2 H, 2-H, 6-H, Ph), 7.64 (d, *J* = 16.5 Hz, 1 H, 2-H), 7.41 (m, 3 H, 3-H, 4-H, 5-H, Ph), 7.32 (d, *J* = 16.5 Hz, 1 H, 1-H)[b] | 110.3, 127.4, 128.9, 129.5, , 137.8, 137.9, 154.6 (C-5)[b] | 172 (16) [M$^+$], 144 (35) [M$^+$-$N_2$], 115 (100) [$C_9H_7^+$] | 3005 , 2970, 2600, 1634, 1549, 1410, 1234, 1041, 968, 760 |
| **7** (92%) | 264 | 3.89 (s, 6 H, $OCH_3$), 7.05 (d, *J* = 9, 4 H, 3-H, 5-H, Ph), 7.58 (s, 2 H, Eth), 8.02 (d, *J* = 9, 4 H, 2-H, 6-H, Ph)[a] | 55.5 ($OCH_3$), 114.7 (C-2, C-5, Ph), 118.8 (Eth), 129.0 (C-3, C-5, Ph), 162.6, 164.0 (C-2, C-5, Od)[a] | 376 (42) [M$^+$], 135 (100) [$C_8H_7O_2^+$] | 3050, 2930, 1600, 1485, 1250, 1170, 1089, 1028, 832, |
| **8** (89%) | 195 | 2.41 (s, 6 H, 5-$CH_3$), 2.82 (s, 6 H, 2-$CH_3$), 7.25 (s, 4 H, 3-H, 4-H, Ph), 7.59 (s, 2 H, Eth), 7.84 (s, 2 H, 6-H, Ph)[a] | 20.7, 21.6 (2-$CH_3$, 5-$CH_3$, Xyl), 119.1 (Eth), 129.5, 131.9, 132.6, (C-3, C-4, C-6, Xyl), 122.0, 135.7, 136.0 (C-1, C-2, C-5, Xyl), 162.0, 165.5 (C-2, C-5, Od)[a] | 372 (100) [M$^+$], 226 (28), 133 (96) [$C_9H_9O^+$] | 3070, 3010, 2970, 1553, 1527, 1495, 1435, 1382, 1252, 1060, 996, 825, 816, 749, 740 |
| **10** (64%) | 345 (dec.) | 7.97 (s, 2 H, Eth), 8.13 (d, *J* = 5.5, 2 H, 3-H, 5-H, Py), 8.89 (d, *J* = 5.5 Hz, 2 H, 2-H, 6-H, Py)[b] | 120.5, 120.2 (C-3, C-5, Py, C-1, C-2, Eth), 150.9 (C-2, C-6, Py)[23b] | 318 (16) [M$^+$], 106 (100) [$C_6H_4NO^+$], 78 (97) [$C_5H_4N^+$] | 3040, 1600, 1546, 1528, 1413, 1269, 1107, 980, 838, 752, 706, 681 |
| **11** (84%) | 228 | 7.76 (s, 2 H, Eth), 7.57 - 7.77 (m, 3 H), 7.90 (d, *J* = 8.4, 2 H), 8.09 (d, *J* = 7.8, 2 H), 8.30 (d, *J* = 7.3, 2 H), 9.27 (d, *J* = 8.4, 2 H)[a] | 119.5, 125.0, 126.1, 127.0, 128.5, 128.9, 129.0, 133.4 [23] [a] | 416 (1) [M$^+$], 294 (29), 155 (100) [$C_{11}H_7O^+$], 127 (66) | 3015. ,1568, 1550, 1518, ,1395, 1238, 1130, 1032, 996, 965, 803, 771 |
| **12** (16%) | 320 | 7.07 (d, *J* = 16, 2 H, Eth), 7.28 - 7.38 (m, 8 H, 3-H, 4-H, 5-H, Ph, 1-H, 2-H, Eth), 7.50 (m, 4 H, 2-H, 6-H, Ph), 7.67 (d, *J* = 16.0, 2 H, Eth)[a] | | 368 (4) [M$^+$], 115 (100) | ($CDCl_3$): 3040, 1631, 1508, 1258, 1200, 1030, 965, 799, 760, 701 |
| **13** (78%) | 145 | 3.86 (s, 3 H, $OCH_3$), 3.88 (s, 3 H, $OCH_3$), 6.85 (d, *J* = 16.6, 1 H, 1-H, Eth), 7.01 (d, *J* = 8.8, 2 H, 3-H, 5-H, Ph), 7.59 (d, *J* = 16.6, 1 H, 2-H, Eth), 8.02 (d, *J* = 8.8, 2 H, 2-H, 6-H, Ph)[a] | 55.5, 52.4 ($OCH_3$), 114.7 (C-3, C-5, Ph), 115.6 (C-1, Ph), 126.9, 125.3 (C-1, C-2, Eth), 129.1 (C-2, C-6, Ph), 161.9, 162.9, 165.2, 165.4, (C-2, C-5, Od, C-4 Ph, C=O)[a] | 260 (73) [M$^+$], 135 (100) [$C_8H_7O_2^+$] | 3058, 2948, 1718, 1641, 1604, 1490, 1423, 1308, 1255, 1183, 1090, 1028, 930, 841, 753 |
| **14** (84%) | 72 | 2.49 (s, 3 H), 2.68 (s, 3 H, $CH_3$ Xyl), 3.85 (s, 3 H, $OCH_3$), 6.88 (d, *J* = 16.6, 1 H), 7.62 (d, *J* = 16.6, 1 H) (1-H, 2-H, Eth), 7.23 (m, 2 H, 3-H, 4-H, Ph), 7.80 (s, 1 H, 6-H, Ph)[a] | 20.8, 21.7 ($CH_3$), 52.4 ($OCH_3$), 122.0 (C-1, Ph), 125.4, 127.3, 129.6, 131.9, 132.7, (C-3, C-4, C-6, Ph, C-1, C-2, Eth), 135.8, 136.0 (C-2, C-5, Ph), 161.8, 165.4, 165.7 (C-2, C-5, Od, C=O)[a] | 258 (45) [M$^+$], 133 (100) [$C_9H_9O^+$] | 3060, 3042, 2990, 2948, 2920, 1710, 1642, 1528, 1440, 1358, 1305, 1222, 1181, 1170, 1000, 820, 748 |
| **15** (73%) | 164 (dec.) | 3.88 (s, 3 H, $OCH_3$), 6.91 (d, *J* = 16.0, 1 H, 1-H,Eth), 7.15 (d, *J* = 8.0, 2 H, 3-H, 5-H, Ph), 7.42 (d, *J* = 16.0, 1 H, 2-H, Eth), 8.05 (d, *J* = 8, 2 H, 2-H, 6-H, Ph), 13.2 (br s, 1 H, OH)[b] | 55.5 ($OCH_3$), 114.8, 128.8 (C-2, C-3, C-5, C-6, Ph), 115.0, 124.1, 124.7, (C-1, Ph, C-1, C-2, Eth), 161.7, 162.4, 164.3, 165.8 (C-2, C-5, Od, C-4, Ph, C=O)[b] | 246 (23) [M$^+$], 202 (19), 135 (100) [$C_8H_7O_2^+$] | 3050, 2900, 1710, 1609, 1492, 1305, 1255, 1188, 1172, 1089, 1018, 987, 834, 754, 669 |

**Table 2** (Continued)

| Product (Yield) | mp (°C) | $^1$H NMR : δ, *J* (Hz) | $^{13}$C NMR : δ | MS *m/z* (rel. int., %) | IR (KBr) ν ($cm^{-1}$) |
|---|---|---|---|---|---|
| **16** (75%) | 227 | 2.48 (s, 3 H), 2.68 (s, 3 H, $CH_3$), 6.83 (d, *J* = 16.0, 1 H, 1-H, Eth), 7.25 (s, 2 H, 3-H, 4-H, Ph), 7.51 (d, *J* = 16.0 Hz, 1 H, 3-H, Eth), 7.80 (s, 1 H, 6-H, Ph)[a] | 19.8, 20.6 ($CH_3$), 121.0 (C-1, Ph), 123.6, 128.2, 128.5, 130.9, 131.7, (C-3, C-4, C-6, Ph, C-1, C-2, Eth), 134.5, 134.9 (C-2, C-5, Ph), 161.0, 164.4, 165.4 (C-2, C-5, Od, C=O)[b] | 244 (100) [$M^+$], 199 (15), 133 (97) [$C_9H_9O^+$], 104 (98) | 3040, 2950, 1705, 1645, 1528, 1470, 1280, 1245, 1175, 963, 948, 828, 768, 689, 640 |
| **17** (76%) | 183 | 8.07 (d, J = 9.0, 2 H, 2-H, 6-H, Ph), 7.84 (s, 1 H, 6-H, Xyl), 7.56 (s, 2 H, 1-H, 2-H), 7.26 (s, 2 H, 3-H, 4-H, Xyl), 7.04 (d, *J* = 9 Hz, 2 H, 3-H, 4-H, Ph), 3.89 (s, 3 H, $OCH_3$), 2.70 (s, 3 H, 2-$CH_3$), 2.40 (s, 3 H, 5-$CH_3$)[a] | 162.9, 162.1 (C-2, C-5, Od, C-4 An), 136.1, 135.8, 132.7, 132.0, 129.6, 129.1, 122.0, 119.2 (2 C), 118.8, 115.6, 114.8 (2 C) (CH, $C_q$), 55.6 ($OCH_3$), 21.7, 20.9 ($CH_3$)[a] | 374 (55) [$M^+$], 227 (43) 135 (100) [$C_8H_7O^+$], 133 (41), 107 (6), 105 (19) | 3070, 2920, 2838, 1608, 1528, 1490, 1306, 1260, 1179, 1090, 1030, 960, 845, 750, 696 |
| **18** (76%) | 177 | 9.27 (d, *J* = 8.8 Hz, 1 H, Nap), 8.28 (dd, *J* = 7.6, *J* = 2.0, 1 H, Nap), 8.07 (d, *J* = 8.8, 1 H, Nap), 7.94 (d, *J* = 8.8, 1 H, Nap), 7.85 (s, 1 H, 6-H Xyl), 7.76–7.55 (m, 3 H, Nap), 7.67 (s, 2 H, Eth), 7.26 (m, 2 H, 3-H, 4-H, Xyl), 2.71 (s, 3 H, $CH_3$), 2.42 (s, 3 H, 2-$CH_3$)[a] | 162.2, (Od), 141.0 ($C_q$), 136.1($C_q$), 135.8 ($C_q$), 133.9 ($C_q$), 133.4, 132.8, 132.0, 129.7, 129.0, 128.9, 128.5, 126.9, 126.1, 125.0, 122.7 ($C_q$), 119.6, 119.1, 21.8 ($CH_3$), 20.9 ($CH_3$)[a] | 394 (100) [$M^+$], 155 (63) [$C_{11}H_7O^+$], 133 (27) [$C_9H_9O^+$], 127 (34) [$C_{10}H_7^+$] | 3040, 2910, 2840, 1570, 1540, 1517, 1470, 1393, 1130, 996, 954, 807, 770, 745 |

Abbreviations: An: 4-methoxyphenyl, Eth: ethylene, Nap : 1-naphthyl, Od: 1,3,4-oxadiazole, Py: pyridine, Tet: tetrazole, Tol: 4-methylphenyl, Xyl: 2,5-dimethylphenyl

[a] $CDCl_3$
[b] DMSO-$d_6$

**(*E*)-1,2-Bis{5-[(*E*)-2-phenylethenyl]-1,3,4-oxadiazol-2-yl}ethene (12)**
Diphenyl ether was used as solvent, $N_2$ evolution occurred above 180 °C. The mixture was diluted with petroleum ether (100 mL), filtered, and the residue washed with toluene, MeOH, MeOH/$H_2O$ (1/1), MeOH, and dried. Yield: 52 mg (16%), light brown crystals.

**(*E*)-3-(5-Aryl-1,3,4-oxadiazol-2-yl)propenoic Acid Methyl Esters (13, 14); General Procedure**
The tetrazole (**1**, **2**) (0.01 mol) and fumaryl chloride (4.53 g, 0.03 mol) were dissolved in diphenyl ether (10 mL), collidine (1.46 g, 0.011 mol) was added dropwise and the stirred mixture was slowly heated until gas evolution occurred (95 °C). As the gas evolution ceased, heating was continued for further 15 min, the mixture poured into abs. MeOH (60 mL) and stirred for 30 min. The MeOH was evaporated and the residue washed with $H_2O$ (3 x 50 mL) and brine (50 mL). Purification by chromatography. A second product was isolated in low yield and identified as bis-aryloxadiazolylethene (**7**, **8**) by IR and mp.

**(*E*)-3-[5-(4-Methoxyphenyl)-1,3,4-oxadiazol-2-yl]propenoic Acid Methyl Ester (13)**
Diphenyl ether as solvent, gas evolution starting at 95 °C. Yield: 2.03 g (78%), colourless crystals.

**(*E*)-3-[5-(2,5-Dimethylphenyl)-1,3,4-oxadiazol-2-yl]propenoic Acid Methyl Ester (14)**
Yield: 2.16 g (84%), pale yellow crystals.

**3-(1,3,4-Oxadiazolyl)propenoic Acids; General Procedure**
The ester (**13**, **14**) (0.005 mol) was dissolved in propan-2-ol (15 mL) and a solution of NaOH (0.8 g, 0.02 mol) in $H_2O$ (4 mL) was added. The mixture was stirred and heated to reflux until the ester had disappeared. The solution was neutralized with hydrochloric acid, the alcohol distilled off and the crude acid (**15**, **16**) isolated by filtration. Recrystallization was from EtOAc.

**(*E*)-3-[5-(4-Methoxyphenyl)-1,3,4-oxadiazol-2-yl]propenoic Acid (15)**
Yield: 900 mg (73%), colourless crystals.

**(*E*)-3-[5-(2,5-Dimethylphenyl)-1,3,4-oxadiazol-2-yl]propenoic Acid (16)**
Yield: 1.03 g (75%), pale yellow crystals.

**(*E*)-1,2-Bis(5-aryl-1,3,4-oxadiazol-2-yl)ethenes with Different Substituents (17, 18); General Procedure**
The acrylic acid (**15**, **16**) (1 mmol) was stirred in a mixture of $PCl_3$ (0.4 mmol, 0.54 g) and benzene (5 mL) overnight at ambient temp. The layers were separated, the solvent distilled off and the acid chloride dissolved in anisole (10 mL). The tetrazole (**2**, **5**) (1 mmol) and collidine (121 mg, 1 mmol) were added, the conversion followed the general procedure (vide supra).

**(*E*)-1-[5-(2,5-Dimethylphenyl)-1,3,4-oxadiazol-2-yl]-2-[5-(4-methoxyphenyl)-1,3,4-oxadiazol-2-yl]ethene (17)**
Yield: 284 mg (76%).

**(*E*)-1-[5-(2,5-Dimethylphenyl)-1,3,4-oxadiazol-2-yl]-2-[5-(1-naphthyl)-1,3,4-oxadiazol-2-yl]ethene (18)**
Yield: 299 mg (76%).

X-ray structure determination of **8** was performed with an Enraf-Nonius Turbo-CAD4 equipped with rotating anode using a transparent, colourless single crystal. Crystal data: $C_{22}H_{20}N_4O_2$, *M* = 372.4 g $mol^{-1}$, 0.12 x 0.16 x 1.28 mm, monoclinic, space group *P* $2_1/n$, Cu-$K_\alpha$, graphite monochromation: 1.54180 Å, *T* = *298 K*, unit cell dimensions: *a* = 888.07(2), *b* = 595.26(1), *c* = 1846.43(3) pm, β = 96.785(2)°, *V* = 0.96926(3) $nm^3$, *Z* = 2, $D_{calc}$ = 1.276 g $cm^{-3}$, absorption coefficient μ = 0.68 $mm^{-1}$, the Θ range for data collection

was 1.5°to 75° and the index ranges $0 \le h \le 11$, $0 \le k \le 7$, $-23 \le l \le 22$. Number of reflections collected: 2006; independent reflections: 2006 [$R_{sigma'} = 0.0157$]. The structure was solved by direct methods (program SHELXS 93).[24] Structure refinement by full-matrix least squares on $F^2$ on 102 parameters, weighted refinement: $w = 1/[\sigma^2(F_0^2) + (0.0597 \times P)^2 + 0.15 \times P]$ with $P = [\max(F_0^2,0) + 2 \times F_c^2]/3$, hydrogen atoms located from difference Fourier synthesis and refined isotropic assuming a riding motion model, all non-hydrogen atoms refined with anisotropic temperature factors. Goodness-of-fit on S = 1.078, maximum change of parameters 0.000 x e.s.d, final R indices: $R_1 = 0.0397$, $wR_2 = 0.0423$, the final difference Fourier map showed minimum and maximum values of –0.12 and 0.16 e $Å^{-3}$.

Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository number CSD-410648 (8).

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