48. The 1,3-Dipolar Cycloadditions of Nitrile Oxides and Nitrile Imines to Alkyl Dicyanoacetates

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The readily available alkyl dicyanoacetates **1** reacted with the 1,3-dipolar reagents arenecarbonitrile oxides **2'** and arenecarbonitrile imines **5'** to afford 1,2,4-oxadiazol and 1,2,4-triazol derivatives. The arenecarbonitrile oxides **2'** with electron-donating groups on the arene ring gave products **3a–d** resulting from addition on both CN groups of **1**, and those with electron-withdrawing groups provided mono-adducts **4a–e** (*Scheme 1*). Arylnitrile imines **5'** reacted with **1** to offer both bis- and mono-addition products (*Scheme 2*): the bis-adducts **8a,b** possess an ester structure, whereas the mono-adducts **6a–d** present a ketene-hemiacetal structure.

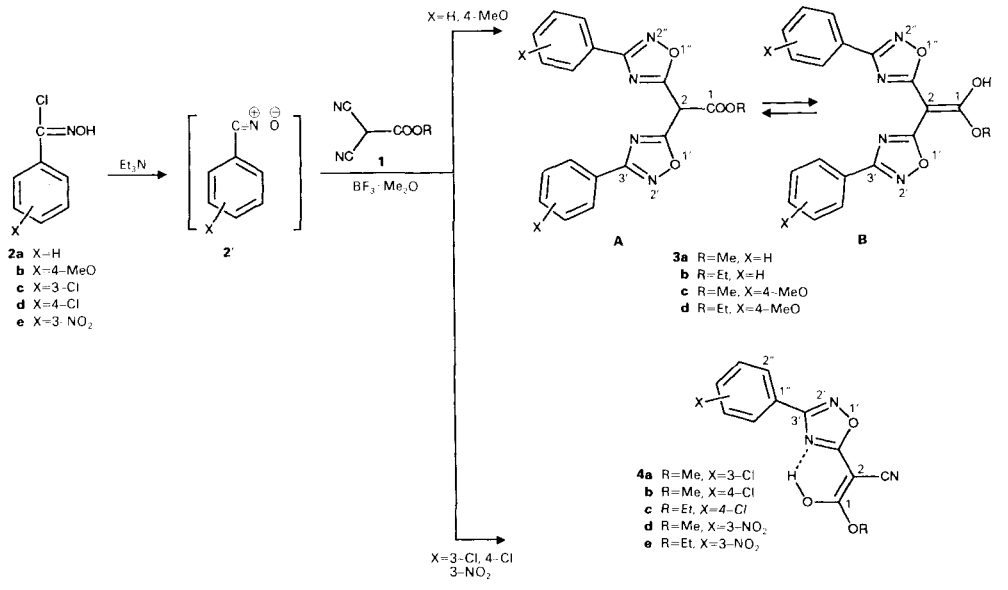
Introduction. – We shall describe herein 1,3-dipolar cycloadditions of arenecarbonitrile oxides **2'** and arenecarbonitrile imines **5'** to the CN groups of alkyl dicyanoacetates **1** [1–9] which have been shown to be useful synthons in the synthesis of heterocyclic compounds [10–14].

Since the pioneering work of *Huisgen* [15], 1,3-dipolar cycloadditions have developed into a generally useful method of five-membered-heterocyclic-ring synthesis. However, nitriles undergo 1,3-dipolar cycloadditions only under certain conditions. The CN group must be activated, and *Lewis*-acid catalysis must often be used [16–18]. Since the CN groups in alkyl dicyanoacetates **1** are activated by the ester group, we investigated their reactivities in cycloadditions with some 1,3-dipoles.

Results. – *Starting Materials.* The carbonitril oxides **2'** used for the cycloadditions were prepared from aldehyde oximes and *tert*-butyl hypochlorite; from the intermediate arenecarbohydroximoyl chlorides **2a–e**, HCl was eliminated *in situ* at −10 to 0° in the presence of Et_3N according to [19] [20]. Carbonitrile imines **5'** were synthesized from arenecarbohydrazonoyl chlorides **5a, b** by elimination of HCl during the cycloaddition using $AlCl_3$ as catalyst [21], and alkyl dicyanoacetates **1** were obtained from malonodinitrile and alkyl chloroformates as described in [1].

Cycloadditions of Arenecarbonitrile Oxides **2'** *with* **1**. The reactions were carried out at −10° under catalysis with BF_3. If the arene ring of **2'** was substituted by an electron-donating group or not substituted, both CN groups of **1** were attacked, yielding the bis-adducts **3a–d** (*Scheme 1*). In $CDCl_3$ solution, an equilibrium between two tautomers **A** and **B** was observed (^{1}H-NMR: **A**/**B** *ca.* 3:1; ^{13}C-NMR: *d* for C(2) of tautomer **A**) which was shifted to the ketene hemiacetal from **B** in more polar solvents (DMSO). If the arene moiety of **2'** was substituted by an electron-withdrawing group such as a Cl-atom or a NO_2 group, the mono-adducts **4a–e** were obtained which adopt the ketene-hemiacetal structure both in $CDCl_3$ and in DMSO (*Scheme 1*).

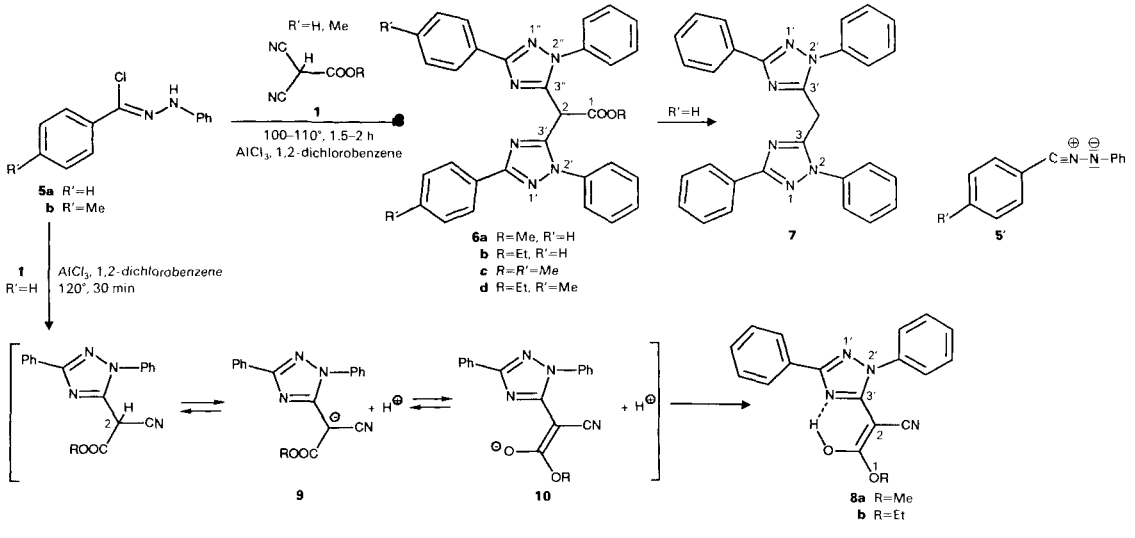
Scheme 1



The formation of a mono-adduct from **2'** without substituent or with an electron-donating group appears to favor the further 1,3-dipolar cycloaddition on the other CN group of **1**, even if the ratio **2**/**1** is **1**. On the other hand, the 1,3-dipoles **2'** with electron-withdrawing groups do not undergo bis-additions, even not when **2'** is in excess. It seems that the electron-withdrawing group in **2'** enhances the energy difference of the frontier orbitals of the 1,3-dipole and the dipolarophile.

Cycloadditions of Arenecarbonitrile Imines **5'** *with* **1**. Treatment of arenecarbohydrazonoyl chlorides **5a** and **5b** with **1** in the presence of $AlCl_3$ at 100–110° for 1.5–2 h afforded the bis-adducts **6a–d** (*Scheme 2*). In the case of R' = H, compound **7** was isolated as side

Scheme 2



product, which seemed to be formed from **6a** and **6b** by elimination of the ester group. This was confirmed by the fact that **5a** did not afford any **7** when submitted to cycloaddition with malonodinitrile ($CH_2(CN)_2$) under the same conditions. The mono-adducts **8a** and **8b** were obtained as main products if the suspension of $AlCl_3$ and **1** was heated quickly to 120°, before **5a** was added, and if the reaction time was 30 min (*Scheme 2*).

Because of the stronger electron-withdrawing effect of the CN group in comparison with the triazoyl group, the acidity of the proton at C(2) of the mono-adducts is higher than that of the corresponding proton of the bis-adducts **6a,b** so that the ketene hemiacetal structure **8a,b** can be easily formed through intermediates **9** and **10**. In the bis-adducts, the steric hindrance of the two triazoyl groups favors the ester structure as shown by the molecular-modelling structures **C** (ester) and **D** (ketene hemiacetal) of **6a** (*Fig.*). In **C**, C(2) exhibits a tetrahedral configuration, and the large diphenyltriazoyl groups are far away from each other, in contrast to the situation in **D** with planar configuration at C(2).

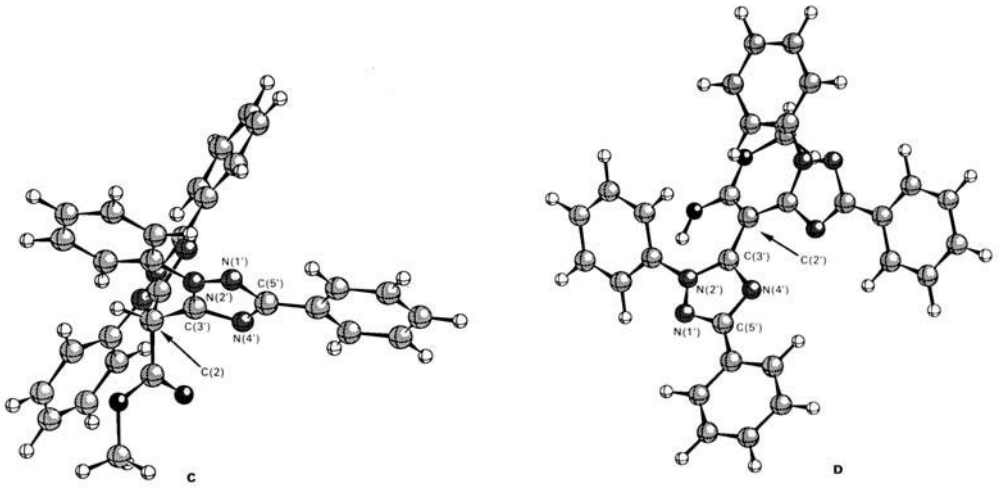
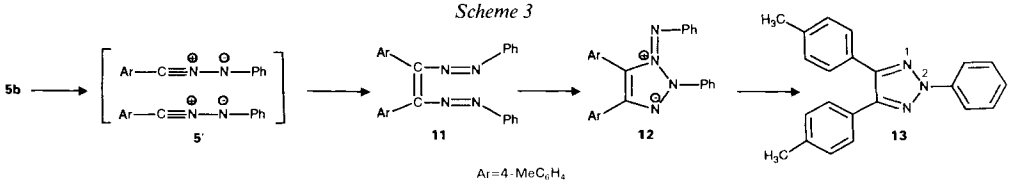


Figure. *Plots of molecular-modelling structures* **C** (ester) *and* **D** (ketene hemiacetal) *of* **6a**

At higher temperature (> 130°), 1,2,3-triazol **13** was isolated from the attempted cycloaddition of **5b** and **1** (*Scheme 3*). The formation of **13** can be explained by a head-head dimerization [21] of the corresponding nitrile imine **5'** through intermediates **11** and **12** [22].

Scheme 3



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Experimental Part

General. M.p.: *Reichert* hot-stage microscope; uncorrected. UV spectra (λ_{max} (log ε) in nm): *Carl-Zeiss-DMR-10* spectrophotometer. IR spectra (in cm^{-1}): *Perkin-Elmer-325* spectrophotometer. NMR spectra: *Bruker-WM-250* spectrometer (^{1}H-NMR at 250.13 MHz, ^{13}C-NMR at 62.89 MHz); δ values rel. to TMS; primary, secondary, tertiary, and quaternary C-atoms were differentiated either by off-resonance decoupling or *J*-modulated spin echo experiments (signal phase: '+' = C, CH_2; '−' = CH, CH_3). MS (*m/z* (%)): *Varian-MAT-311-A* instrument (ionization energy 80 eV). Microanalyses were performed on a *Heraeus* automatical analyzer.

Methyl 2,2-Bis(3-phenyl-1,2,4-oxadiazol-5-yl)acetate (**3a**), *Typical Procedure for* **3a–d**. A soln. of Et_3N (1.01 g, 10 mmol) and Et_2O (5 ml) was dropped slowly with stirring at −10° into a soln. of benzenecarbohydroximoyl chloride (**2a**; 1.57 g, 10 mmol) in abs. Et_2O (40 ml) and then stirred at −10° for further 10 min. The precipitate was filtered off and the filtrate immediately added at −10 to 0° to a soln. of methyl dicyanoacetate **1**, R = Me; 0.62 g, 5 mmol) and $BF_3 \cdot Me_2O$ (1.14 g, 10 mmol) in abs. Et_2O (50 ml). The mixture was stirred at r.t. for 4 h, then refluxed for 1 h, and evaporated. H_2O was added to the residue, which was then filtered and recrystallized from MeOH: **3a** (1.05 g, 58%). White crystals. M.p. 129° (MeOH). UV/VIS (MeCN): 233 (4.360), 263 (4.427), 322 (4.087). IR (KBr): 3030*w* (arom. CH), 1665*s*. ^{1}H-NMR (250.13 MHz, $CDCl_3$): 3.93 (*s*, 2.25 H, MeO, **A**); 3.96 (*s*, 0.75 H, MeO, **B**); 5.92 (*s*, 0.75 H, H–C(2), **A**); 7.45–7.59, 7.85–8.15 (2*m*, 10 arom. H). ^{13}C-NMR (62.89 MHz, $CDCl_3$): 43.7 (*d*, C(2), **A**); 51.7 (*s*, C(2), **B**); 52.5, 54.5 (2 *q*, MeO, **A** and **B**); 126.0 (*s*, C_{ipso}, **A**); 127.7, 128.9, 131.7 (3 *d*, arom. CH, **A**); 163.1 (*s*, C(5′,5″), **A**); 166.1 (*s*, C(3′,3″), **A**); 170.4 (*s*, C(1), **A**). MS: 362 (100, M^+), 318 (4), 119 (95, $C_7H_5NO^+$), 103 (67, $C_7H_5N^+$). Anal. calc. for $C_{19}H_{14}N_4O_4$ (362.36): C 62.98, H 3.89, N 15.47; found: C 62.96, H 4.04, N 15.21.

Ethyl 2,2-Bis(3-phenyl-1,2,4-oxadiazol-5-yl)acetate (**3b**). From **2a** (1.57 g, 10 mmol), ethyl dicyanoacetate (**1**, R = Et; 0.69 g, 5 mmol), and $BF_3 \cdot Me_2O$ (1.14 g, 10 mmol). Column chromatography (silica gel, $CHCl_3$/AcOEt 1:1) gave **3b** (0.745 g, 32%). White crystals. M.p. 128–130° (AcOEt). UV/VIS (MeCN): 231 (4.391), 262 (4.442), 322 (4.126). IR (KBr): 3005*w* (arom. CH), 1655*s*. ^{1}H-NMR (250.13 MHz, $CDCl_3$): 1.34 (*t*, 2.25 H, CH_3CH_2, **A**); 1.44 (*t*, 0.75 H, CH_3CH_2, **B**); 4.40 (*q*, 2H, CH_3CH_2); 5.89 (*s*, 0.75 H, H–C(2), **A**); 7.45–7.62, 7.97–8.13 (2*m*, 10 arom. H). ^{13}C-NMR (62.89 MHz, $CDCl_3$): 13.9 (*q*, CH_3CH_2, **A**); 14.4 (*q*, CH_3CH_2, **B**); 43.9 (*d*, C(2), **A**); 60.6 (*s*, C(2), **B**); 61.6, 64.1 (2*t*, CH_3CH_2, **A** and **B**); 126.0 (*s*, C_{ipso}, **A**); 127.7, 128.9, 131.7 (3 *d*, arom. CH, **A**); 162.6 (*s*, C(5′,5″), **A**); 169.1 (*s*, C(3′,3″), **A**); 170.3 (*s*, C(1), **A**). MS: 376 (54, M^+), 318 (4), 119 (100, $C_7H_5NO^+$), 103 (72, $C_7H_5N^+$). Anal. calc. for $C_{20}H_{16}N_4O_4$ (376.39): C 63.82, H 4.28, N 14.89; found C 63.86, H 4.31, N 14.85.

Methyl 2,2-Bis[3-(4-methoxyphenyl)-1,2,4-oxadiazol-5-yl]acetate (**3c**). From **2b** (1.86 g, 10 mmol), **1** (R = Me; 0.62 g, 5 mmol), and $BF_3 \cdot Me_2O$ (1.14 g, 10 mmol), **3c** (0.53 g, 25%) was obtained as white crystals. M.p. 155–157° (MeOH). UV/VIS (MeCN): 260 (4.407), 315 (3.741). IR (KBr): 1715*m*, 1615*s*. ^{1}H-NMR (250.13 MHz, $CDCl_3$): 3.87 (*s*, 4.5 H, *Me*O-Ar, **A**); 3.90 (*s*, 1.5 H, *Me*O-Ar, **B**); 3.92 (*s*, 2.25 H, MeOOC, **A**); 3.96 (*s*, 0.75 H, *Me*OC(OH), **B**); 5.81 (*s*, 0.75 H, H–C(2), **A**); 6.98 (*d*, ^3J = 9, 3 H, H_o, **A**); 7.06 (*d*, 1 H, H_o, **B**); 7.93 (*d*, 1 H, H_n, **B**); 8.03 (*d*, ^3J = 9, 3 H, H_m, **A**). ^{13}C-NMR (62.89 MHz, $CDCl_3$): 43.7 (−, C(2), **A**); 54.4 (−, COO*Me*, **A**); 55.4, 55.6 (−, *Me*O-Ar, **A** and **B**); 114.3, 114.7 (−, C_o, **A** and **B**); 118.4 (+, C_p, **A**); 128.9, 129.3 (−, C_m, **A** and **B**); 162.3 (+, C_{ipso}, **A**); 163.2 (+, C(5′,5″), **A**); 168.7 (+, C(3′,3″), **A**); 169.9 (+, C(1), **A**). MS: 422 (72, M^+), 148 (100). HR-MS: 422.1228 (M^+, calc. 422.1227). Anal. calc. for $C_{21}H_{18}N_4O_6$ (422.42): C 59.71, H 4.30, N 13.27; found: C 59.07, H 4.37, N 13.27.

Ethyl 2,2-Bis[3-(4-methoxyphenyl)-1,2,4-oxadiazol-5-yl]acetate (**3d**). From **2a** (1.86 g, 10 mol), **1** (R = Et; 0.69 g, 5 mmol), and $BF_3 \cdot Me_2O$ (1.14 g, 10 mmol) **3d** (0.34 g, 16%) was obtained as white crystals. M.p. 133–134° (EtOH). UV/VIS (MeCN): 258 (4.594), 320 (3.986). IR (KBr): 1710*s*, 1615*s*. ^{1}H-NMR (250.13 MHz, $CDCl_3$): 1.33, 1.43 (2*t*, 3 H, CH_3CH_2); 3.86, 3.89 (2*s*, 6 H, *Me*O-Ar); 4.39 (*q*, 2 H, CH_3CH_2); 5.85 (*s*, 0.75 H, H–C(2), **A**); 6.98 (*d*, ^3J = 9, 3 H, H_o, **A**); 7.03 (*d*, 1 H, H_o, **B**); 7.91 (*d*, 1 H, H_n, **B**); 8.03 (*d*, ^3J = 9, 3 H, H_m, **A**). ^{13}C-NMR (62.89 MHz, $CDCl_3$): 13.9 (−, CH_3CH_2, **A** and **B**); 43.8 (−, C(2), **A**); 55.4 (−, *Me*O-Ar, **A** and **B**); 64.0 (+, CH_3CH_2, **A** and **B**); 114.3 (−, C_o, **A** and **B**); 118.4 (+, C_p, **A**); 122.3 (−, C_m, **A** and **B**); 162.3 (+, C_{ipso}, **A**); 162.7 (+, C(5′,5″), **A**); 168.9 (+, C(3′,3″), **A**); 170.0 (+, C(1), **A**). MS: 436 (100, M^+). Anal. calc. for $C_{22}H_{20}N_4O_6$ (436.44): C 60.54, H 4.62, N 12.84; found: C 60.53, H 4.64, N 12.88.

Methyl 2-[3-(3-Chlorophenyl)-1,2,4-oxadiazol-5-yl]-2-cyanoacetate (ketene-hemiacetal form; **4a**), *Typical Procedure for* **4a–e**. A soln. of Et_3N (1.01 g, 10 mmol) in Et_2O (5 ml) was dropped slowly with stirring at −10 to 0° into a soln. of *3-chlorobenzenecarbohydroximoyl chloride* (**2c**; 1.90 g, 10 mmol) in abs. Et_2O (20 ml). After stirring at the same temp. for further 10 min, the precipitate was filtered off and washed with CH_2Cl_2. The filtrate was immediately added at −10 to 0° into a soln. of **1** (R = Me; 1.24 g, 10 mmol) and $BF_3 \cdot Me_2O$ (1.14 g, 10 mmol) in abs. Et_2O (20 ml). The mixture was stirred at r.t. for 30 h and filtered and the precipitate washed with Et_2O and H_2O. Recrystallization from MeOH gave **4a** (0.45 g, 16%). With crystals. M.p. 164–165° (MeOH). UV/VIS (MeCN): 205 (4.528), 265 (4.280). IR (KBr): 33300–2900 (br., OH), 2230*s* (CN), 1705*s*, 1645*s*. ^{1}H-NMR (250.13 MHz, (D_6)acetone): 3–4 (br., OH); 3.77 (*s*, MeO); 7.67 (*dd*, ^3J(4″,5″) = ^3J(5″,6″) = 8, H–C(5″)); 7.76 (*ddd*,

$^3J(5'',6'') = 8$, $^4J = 1.3$, 1.3, H–C(6'')); 8.01 (*td*, $^3J(4'',5'') = 8$, $^4J = 1.5$, H–C(4'')); 8.12 (*t*, $^4J = 1.6$, H–C(2'')). ^{13}C-NMR (62.89 MHz, (D_6)acetone): 52.1 (–, MeO); 56.9 (+, C(2)); 114.9 (+, CN); 123.8 (+, C(3'')); 127.5, 128.8, 131.8, 133.6 (–, arom. CH); 135.4 (+, C(1'')); 157.4 (+, C(5')); 166.4 (+, C(3')); 173.0 (+, C(1)). MS: 279 (11, $[M + 2]^+$), 278 (5, $[M + 1]^+$), 277 (32, M^+), 245 (1, $[M - MeOH]^+$), 218 (2, $[M - COOMe]^+$), 153 (11, $C_7H_4ClNO^+$), 137 (15, $C_7H_4ClN^+$), 59 (100, $COOMe^+$). HR-MS: 277.0246 (M^+, calc. 277.0250). Anal. calc. for $C_{12}H_8ClN_3O_3$ (277.68): C 51.91, H 2.90, Cl 12.77, N 15.14; found: C 51.53, H 2.93, Cl 12.14, N 15.15.

Methyl 2-[3-(4-Chlorophenyl)-1,2,4-oxadiazol-5-yl]-2-cyanoacetate (ketene-hemiacetal form; **4b**). From *4-chlorobenzenecarbohydroximoyl chloride* (**2d**; 1.90 g, 10 mmol), **1** (R = Me; 0.62 g, 5 mmol), and $BF_3 \cdot Me_2O$ (1.14 g, 10 mmol), **4b** (1.05 g, 76% based on was obtained as white crystals. M.p. 162–163° (MeOH). UV/VIS (MeCN): 202 (4.258), 265 (4.292). IR (KBr): 3300–2900 (br., OH), 2210*s* (CN), 1720*s*, 1640*s*. ^{1}H-NMR (250.13 MHz, (D_6)DMSO): 3.64 (*s*, MeO); 7.58 (*d*, $^3J(2'',3'') = J(5'',6'') = 9$, H–C(2''), H–C(6'')); 7.93 (*d*, $^3J(2'',3'') = J(5'',6'') = 9$, H–C(3''), H–C(5'')); 11.47 (br. *s*, OH). ^{13}C-NMR (62.89 MHz, (D_6)DMSO): 50.9 (–, MeO); 54.1 (+, C(2)); 118.2 (+, CN); 122.5 (+, C(4'')); 129.1, 129.7 (–, arom. CH); 135.9 (+, C(1'')); 160.3 (+, C(5)); 165.3 (+, C(3')); 174.3 (+, C(1)). MS: 279 (11, $[M + 2]^+$), 278 (5, $[M + 1]^+$), 277 (32, M^+), 145 (1, $[M - MeOH]^+$), 218 (2, $[M - COOMe]^+$), 153 (11, $C_7H_4ClNO^+$), 137 (15, $C_7H_4ClN^+$), 59 (100, $COOMe^+$). Anal. calc. for $C_{12}H_8ClN_3O_3$ (277.68): C 51.91, H 2.90, Cl 12.77, N 15.14; found: C 51.85, H 2.97, Cl 12.94, N 15.18.

Ethyl 2-[3-(4-Chlorophenyl)-1,2,4-oxadiazol-5-yl]-2-cyanoacetate (ketene-hemiacetal form; **4c**). From **2d** (1.90 g, 10 mmol), **1** (R = Et; 1.38 g, 10 mmol), and $BF_3 \cdot Me_2O$ (1.14 g, 10 mmol), **4c** (0.63 g, 22%) was obtained as white crystals. M.p. 156–158° (EtOH). UV/VIS (MeCN): 202 (4.448), 265 (4.499). IR (KBr): 3300–2900 (br., OH), 2230*s* (CN), 1715*s*, 1645*s*. ^{1}H-NMR (250.13 MHz, (D_6)DMSO): 1.20 (*t*, CH_3CH_2); 4.10 (*q*, CH_3CH_2); 7.59 (*d*, $^3J(2'',3'') = J(5'',6'') = 9$, H–C(2''), H–C(6'')); 7.94 (*d*, $^3J(2'',3'') = J(5'',6'') = 9$, H–C(3''), H–C(5'')); 8.78 (br. *s*, OH). ^{13}C-NMR (62.89 MHz, (D_6)DMSO): 14.7 (–, CH_3CH_2); 53.8 (+, C(2)); 58.9 (+, CH_3CH_2); 118.8 (+, CN); 123.2 (+, C(4'')); 129.0/129.3 (–, arom. CH); 136.4 (+, C(1'')); 161.0 (+, C(5')); 164.9 (+, C(3')); 175.0 (+, C(1)). MS: 293 (16, $[M + 2]^+$), 292 (7, $[M + 1]^+$), 291 (46, M^+), 153 (25, $C_7H_4ClNO^+$), 152 (100). Anal. calc. for $C_{13}H_{10}ClN_3O_3$ (291.70): C 53.53, H 3,46, Cl 12.15, N 14.41; found C 53.50, H 3.47, Cl 12.09, N 14.38.

Methyl 2-[3-(3-Nitrophenyl)-1,2,4-oxadiazol-5-yl]-2-cyanoacetate (ketene-hemiacetal form; **4d**). From *3-nitrobenzenecarbohydroximoyl chloride* (**2e**; 1.05 g, 5 mmol), **1** (R = Me; 0.31 g, 2.5 mmol) and $BF_3 \cdot Me_2O$ (0.57 g, 5 mmol), **4d** (0.31 g, 48%) was obtained as white crystals. M.p. 175–177° (MeOH). UV/VIS (MeCN): 215 (4.288), 265 (4.480). IR (KBr): 3200–2700 (br., OH), 2220*s* (CN), 1720*s*, 1635*s*, 1540*s* (NO_2), 1350*s* (NO_2). ^{1}H-NMR (250.13 MHz, (D_6)DMSO): 3.66 (*s*, MeO); 7.86 (*dd*, $^3J(4'',5'') = {}^3J(5'',6'') = 8$, H–C(5'')); 8.37 (*d*, $^3J(5'',6'') = 8$, H–C(6'')); 8.43 (*d*, $^3J(4'',5'') = 8$, H–C(4'')); 8.78 (*t*, $^4J = 1.6$, H–C(2'')). ^{13}C-NMR (62.89 MHz, (D_6)DMSO): 50.6 (–, MeO); 53.4 (+, C(2)); 119.6 (+, CN); 122.3, 126.0, 130.8, 133.6 (–, arom. CH); 127.0, 148.0 (+, arom. C); 161.6 (+, C(5)); 165.6 (+, C(3)); 176.2 (+, C(1)). MS: 288 (2, M^+), 99 (100). Anal. calc. for $C_{12}H_8N_4O_5$ (288.24): C 50.00, H 2.80, N 19.44; found: C 49.86, H 2.79, N 19.47.

Ethyl 2-[3-(3-Nitrophenyl)-1,2,4-oxadiazol-5-yl]-2-cyanoacetate (ketene-hemiacetal form; **4e**). From **2e** (1.05 g, 5 mmol), **1** (R = Et; 0.345 g, 2.5 mmol), and $BF_3 \cdot Me_2O$ (0.57 g, 5 mmol), **4e** (0.35 g, 46%) was obtained as white crystals. M.p. 168–169° (EtOH). UV/VIS (MeCN): 215 (4.387), 265 (4.561). IR (KBr): 3250–2900 (br., OH), 2220*s* (CN), 1700*s*, 1650*s*, 1535*s* (NO_2), 1360*s* (NO_2). ^{1}H-NMR (250.13 MHz, (D_6)acetone): 1.29 (*t*, CH_3CH_2); 4.25 (*q*, CH_3CH_2); 5.3–6.0 (br., OH); 7.98 (*dd*, $^3J(4'',5'') = {}^3J(5'',6'') = 8$, H–C(5'')); 8.49 (*d*, $^3J(5'',6'') = 8$, H–C(6'')); 8.57 (*d*, $^3J(4'',5'') = 8$, H–C(4'')); 8.93 (*t*, $^4J = 1.9$, H–C(2'')). ^{13}C-NMR (62.89 MHz, (D_6)acetone): 14.7 (–, CH_3CH_2); 57.3 (+, C(2)); 61.4 (+, CH_3CH_2); 114.9 (+, CN); 123.9 (+, C(3'')); 124.2, 128.2, 131.8, 135.1 (–, arom. CH); 148.0 (+, C(1'')); 157.3 (+, C(5)); 166.1 (+, C(3)); 173.2 (+, C(1)). MS: 302 (22, M^+), 230 (100), 164 (9, $C_7H_4N_2O_3^+$). Anal. calc. for $C_{13}H_{10}N_4O_5$ (302.26): C 51.66, H 3.33, N 18.54; found C 51.66, H 3.37, N 18.60.

Methyl 2,2-Bis(2,5-diphenyl-1,2,4-triazol-3-yl)acetate (**6a**) *and 3,3'-Methylene-2,2',5,5'-tetraphenylbis[2H-1,2,4-tetrazole]* (7). *N'-Phenylbenzenecarbohydrazonoyl chloride* (**5a**; 0.991 g, 4.3 mmol) was added to a suspension of **1** (R = Me; 0.62 g, 5 mmol) and $AlCl_3$ (0.688 g, 5 mmol) in abs. 1,2-dichlorobenzene (20 ml). The suspension was stirred at 100–110° (oil-bath: 120–130°) for 2 h, cooled in an ice-bath, and neutralized with dil. NaOH soln. The org. layer was separated, the solvent removed by H_2O-vapour destillation, and the residue of the org. phase separated by column chromatography (silica gel, pentane/AcOEt 2:1), yielding 0.35 g (42%) of *1,4-dihydro-1,3,4,6-tetraphenyl-1,2,4,5-tetrazine* (R_f 0.72; m.p. 202–204° ([23]: 200–203°)), 0.25 g (23%) of **6a**, and 50 mg (5%) of **7**.

Data of **6a**: R_f 0.37. M.p. 84–85° (MeOH). UV/VIS (CH_2Cl_2): 248 (4.574). IR (KBr): 3010 (arom. CH), 2970*w* (CH), 1755*s* (C=O). ^{1}H-NMR (250.13 MHz, $CDCl_3$): 3.56 (*s*, MeO); 5.58 (*s*, H–C(2)); 7.26–7.46 (*m*, 16 arom. H); 8.13–8.17 (*m*, 4H, H_o of Ph–C(5',5'')). ^{13}C-NMR (62.89 MHz, $CDCl_3$): 43.2 (*d*, C(2)); 53.4 (*q*, MeO); 125.6 (*d*, C_o of Ph–C(5',5'')); 126.7 (*d*, C_p of Ph–C(5',5'')); 128.5 (*d*, C_m of Ph–C(5',5'')); 129.5, 129.6, 129.7 (3*d*, C_o, C_m, C_p of Ph–N(2',2'')); 130.4 (*s*, C_{ipso} of Ph–C(5',5'')); 136.9 (*s*, C_{ipso} of Ph–N(2',2'')); 149.7 (*s*, C(3',3'')); 162.1 (*s*, C(5',5'')); 166.1 (*s*, C(1)). MS: 512 (41, M^+), 481 (3, $[M, MeO]^+$), 480 (9, $[M - MeOH]^+$), 453 (4, $[481 - CO]^+$), 91 (100,

$C_6H_5N^+$). HR-MS: 512.1959 (M^+, calc. 512.1960). Anal. calc. for $C_{31}H_{24}N_6O_2$ (512.59): C 72.64, H 4.72, N 16.40; found: C 72.73, H 4.70, N 16.25.

Data of **7**: R_f 0.28. M.p. 258–260° (MeOH). UV/VIS (CH_2Cl_2): 249 (4.558). IR (KBr): 3050 (arom. CH), 1500*s* (arom.). ^{1}H-NMR (250.13 MHz, $CDCl_3$): 5.58 (*s*, CH_2); 7.40–7.75 (*m*, 16 arom. H); 8.05–8.15 (*dd*, 4H, H_o of Ph–C(5,5′)). ^{13}C-NMR (62.89 MHz, $CDCl_3$): 25.2 (+, CH_2); 125.4 (–, C_o of Ph–C(5,5′)); 126.6 (*d*, C_p of Ph–C(5,5′)); 128.6 (–, C_m of Ph–C(5,5′)); 129.5, 129.6, 129.7 (–, C_o, C_m, C_p of Ph–N(2,2′)); 130.6 (+, C_{ipso} of Ph–C(5,5′)); 137.2 (+, C_{ipso} of Ph–N(2,2′)); 151.1 (+, C(3,3′)); 161.9 (+, C(5,5′)). MS: 454 (49, M^+), 91 (100, $C_6H_5N^+$). HR-MS: 454.1908 (M^+, calc. 454.1907). Anal. calc. for $C_{29}H_{22}N_6$ (454.56): C 76.63, H 4.88, N 18.49; found: C 76.36, H 4.97, N 18.36.

Ethyl 2,2-Bis(2,5-diphenyl-1,2,4-triazol-3-yl)acetate (**6b**) *and* **7**. From **5a** (0.75 g, 3.84 mmol), **1** (R = Et; 0.53 g, 3.84 mmol), and $AlCl_3$ (0.51 g, 3.84 mmol) in abs. 1,2-dichlorobenzene (25 ml). Column chromatography (silica gel, $CHCl_3$/AcOEt 20:1) gave 0.105 g (14%) of *1,4-dihydro-1,3,4,6-tetraphenyl-1,2,4,5-tetrazine* (R_f 0.55), 0.42 g (49%) of **6b**, and **7** (R_f 0.14).

Data of **6b**: R_f 0.38. M.p. 144–145° (MeOH). UV/VIS (CH_2Cl_2): 268 (4.687). IR (KBr): 3070 (arom. CH), 1750*s* (C=O). ^{1}H-NMR (250.13 MHz, $CDCl_3$): 1.12 (*t*, CH_3CH_2); 4.01 (*q*, CH_3CH_2); 5.57 (*s*, H–C(2)); 7.38, 7.51 (*m*, 16 arom. H); 8.13–8.17 (*m*, 4H, H_o of Ph–C(5′,5″)). ^{13}C-NMR (62.89 MHz, $CDCl_3$): 13.8 (*q*, CH_3CH_2); 43.5 (*d*, C(2)); 62.9 (*t*, CH_3CH_2); 125.6 (*d*, C_o of Ph–C(5′,5″)); 126.7 (*d*, C_p of Ph–C(5′,5″)); 128.5 (*d*, C_m of Ph–C(5′,5″)); 129.5, 129.5, 129.6 (3 *d*, C_o, C_m, C_p of Ph–N(2′,2″)); 130.5 (*s*, C_{ipso} of Ph–C(5′,5″)); 137.0 (*s*, C_{ipso} of Ph–N(2′,2″)); 149.9 (*s*, C(3′,3″)); 162.1 (*s*, C(5′,5″)); 165.6 (*s*, C(1)). MS: 526 (50, M^+), 480 (2, $[M - EtOH]^+$), 91 (100, $C_6H_5N^+$). Anal. calc. for $C_{32}H_{26}N_6O_2$ (526.62): C 72.98, H 4.98, N 15.96; found: C 73.22, H 5.07, N 15.86.

Methyl 2,2-Bis[5-(4-methylphenyl)-2-phenyl-1,2,4-triazol-3-yl]acetate (**6c**). From *4-Methyl-N-phenylbenzenecarbohydrazonoyl chloride* (**5b**; 0.55 g, 2.45 mmol), **1** (R = Me; 0.31 g, 2.5 mmol), and $AlCl_3$ (0.33 g, 2.45 mmol). After column chromatography (silica gel, $CHCl_3$/AcOEt 10:1), **6c** (0.32 g, 48%) was obtained. M.p. 85° (pentane/CH_2Cl_2). UV/VIS (CH_2Cl_2): 265 (4.563). IR (KBr): 3040 (arom. CH), 2960*w* (CH), 1755*s* (C=O). ^{1}H-NMR (250.13 MHz, $CDCl_3$): 2.39 (*s*, 2 arom. Me); 3.56 (*s*, MeO); 5.56 (*s*, H–C(2)); 7.22 (*d*, $^3J(o,m) = 8$, 4H, H_m of Ar–C(5′,5″)); 7.28–7.29 (*m*, H_o, H_m, H_p of Ph–N(2′,2″)); 8.03 (*d*, $^3J(o,m) = 8$, 4H, H_o of Ar–C(5′,5″)). ^{13}C-NMR (62.89 MHz, $CDCl_3$): 21.5 (*q*, arom. Me); 43.2 (*d*, C(2)); 53.4 (*q*, MeO); 125.7 (*d*, C_o of Ar–C(5′,5″)); 126.7 (*d*, C_m of Ar–C(5′,5″)); 127.7 (*s*, C_p of Ar–C(5′,5″)); 129.2, 129.5, 129.6 (3 *d*, C_o, C_m, C_p of Ph–N(2′,2″)); 137.01 (*s*, C_{ipso} of Ar–C(5′,5″)); 136.5 (*s*, C_{ipso} of Ph–N(2′,2″)); 149.6 (*s*, C(3′,3″)); 162.2 (*s*, C(5′,5″)); 166.2 (*s*, C(1)). MS: 540 (48, M^+), 508 (8, $[M - MeOH]^+$), 91 (100, $C_6H_5N^+$). Anal. calc. for $C_{33}H_{28}N_6O_2$ (540.65): C 73.31, H 5.22, N 15.55; found: C 73.26, H 5.22, N 15.59.

Ethyl 2,2-Bis[5-(4-methylphenyl)-2-phenyl-1,2,4-triazol-3-yl]acetate (**6d**). From **5b** (R = Me; 0.55 g, 2.45 mmol), **1** (R = Et; 0.345 g, 2.5 mmol), and $AlCl_3$ (0.33 g, 2.45 mmol). After column chromatography (silica gel, $CHCl_3$/AcOEt 10:1, **6d** (0.295 g, 44%) was obtained. M.p. 92° (MeOH). UV/VIS (CH_2Cl_2): 250 (4.703). IR (KBr): 3070 (arom. CH), 2995*w* (CH), 1755*s* (C=O). ^{1}H-NMR (250.13 MHz, $CDCl_3$): 1.12 (*t*, CH_3CH_2); 2.39 (*s*, 2 arom. Me); 4.01 (*q*, CH_3CH_2); 5.55 (*s*, H–C(2)); 7.22 (*d*, $^3J(o,m) = 8$, 4H, H_m of Ar–C(5′,5″)); 7.43–7.46 (*m*, 10H, H_o, H_m, H_p of Ph–N(2′,2″)); 8.03 (*d*, $^3J(o,m) = 8$. 4H, H_o of Ar–C(5′,5″)). ^{13}C-NMR (62.89 MHz, $CDCl_3$): 13.8 (*q*, CH_3CH_2); 21.4 (*q*, arom. Me); 43.4 (*d*, C(2)); 62.8 (*t*, CH_3CH_2); 125.6 (*d*, C_o of Ar–C(5′,5″)); 126.6 (*d*, C_m of Ar–C(5′,5″)); 127.7 (*s*, C_p of Ar–C(5′,5″)); 129.2, 129.5 (*d*, C_o, C_m, C_p of Ph–N(2′,2″)); 137.1 (*s*, C_{ipso} of Ar–C(5′,5″)); 139.44 (*s*, C_{ipso} of Ph–N(2′,2″)); 149.7 (*s*, C(3′,3″)); 162.1 (*s*, C(5′,5″)); 165.7 (*s*, C(1)) ppm. MS: 554 (64, M^+), 509 (10, $[M - EtO]^+$), 508 (19, $[M - EtOH]^+$), 481 (15, $[M - COOEt]^+$), 91 (100, $C_6H_5N)^+$. Anal. calc. for $C_{34}H_{30}N_6O_2$ (554.67): C 73.63, H 5.45, N 15.15; found: C 73.72, H 5.42, N 15.29.

Methyl 2-Cyano-2-(2,5-diphenyl-1,2,4-triazol-3-yl)acetate (ketene-hemiacetal form; **8a**). A suspension of **1** (R = Me; 0.31 g, 2.5 mmol) and $AlCl_3$ (0.33 g, 2.45 mmol) in abs. 1,2-dichlorobenzene (20 ml) was at first heated to 120°. Then, **5a** (0.496 g, 2.45 mmol) was added, the suspension stirred at 120° for 30 min and cooled to r.t., the mixture neutralized with dil. NaOH soln. (pH *ca.* 7) and extracted with CH_2Cl_2, the combined org. phase removed by H_2O-vapour destillation, and the residue of the org. phase purified by column chromatography (silica gel, $CHCl_3$/AcOEt 5:1). **8a** (0.18 g, 26%). White crystals. R_f 0.43. M.p. 181–183° ($CHCl_3$/AcOEt). UV/VIS (CH_2Cl_2): 230 (4.492), 290 (4.364). IR (KBr): 3070*w*, 2960*w* (CH), 2210*m* (CN). ^{1}H-NMR (250.13 MHz, $CDCl_3$): 3.81 (*s*, MeO); 7.49–7.56 (*m*, 8H, H_o, H_m, H_p of Ph–N(2′), H_m, H_p of Ph–C(5′)); 7.84–7.88 (*m*, H_o of Ph–C(5′)); 12.80 (br. *s*, OH). ^{13}C-NMR (62.89 MHz, $CDCl_3$): 51.4 (*s*, C(2)); 51.8 (*q*, MeO); 116.2 (*s*, CN); 124.0 (*s*, C_{ipso} of Ph–C(5′)); 126.0, 127.1 (2 *d*, arom. CH); 129.3, 129.4, 130.7, 131.9 (4 *d*, arom. CH); 135.46 (*s*, C_{ipso} of Ph–N(2′)); 147.99 (*s*, C(3′)); 152.61 (*s*, C(5′)); 170.78 (*s*, C(1)). MS: 318 (68, M^+), 287 (7, $[M - MeO]^+$), 286 (19, $[M - MeOH]^+$), 259 (7, $[M - COOMe]^+$), 91 (100, $C_6H_5N^+$). HR-MS: 318.1114 (M^+, calc. 318.1115). Anal. calc. for $C_{18}H_{14}N_4O_2$ (318.35): C 67.91, H 4.43, N 17.60; found: C 67.62, H 4.45, N 17.45.

Ethyl 2-Cyano-2-(2,5-diphenyl-1,2,4-triazol-3-yl)acetate (ketene-hemiacetal form; **8b**). From **1** (R = Et; 0.69 g, 5 mmol), $AlCl_3$ (0.67 g, 5 mmol), and **5a** (0.99 g, 4.3 mmol), similarly to **8a**, **8b** (0.33 g, 26%) was obtained as white crystals. M.p. 195–196° (CCl_4). UV/VIS (MeCN): 230 (4.366), 290 (4.299). IR (KBr): 3070*w*, 2985*w* (CH), 2210*m* (CN). ^{1}H-NMR (250.13 MHz, $CDCl_3$): 1.33 (*t*, CH_3CH_2); 4.28 (*q*, CH_3CH_2); 7.49–7.56 (*m*, 8H, H_o, H_m, H_p of Ph–N(2′), H_m, H_p of Ph–C(5′)); 7.84–7.88 (*m*, 2H, H_o of Ph–C(5′)); 12.86 (br. *s*, OH). ^{13}C-NMR (62.89 MHz, $CDCl_3$): 14.6 (*q*, CH_3CH_2); 51.6 (*s*, C(2)); 60.7 (*t*, CH_3CH_2); 116.2 (*s*, CN); 124.0 (*s*, C_{ipso} of Ph–C(5′)); 126.0 (*d*, arom. CH); 127.1, 129.2, 129.4, 130.7, 131.8 (6*d*, arom. CH); 135.5 (*s*, C_{ipso} of Ph–N(2′)); 148.0 (*s*, C(3′)); 152.7 (*s*, C(5′)); 170.4 (*s*, C(1)). MS: 332 (51, M^+), 287 (6, $[M - EtO]^+$), 286 (9, $[M - EtOH]^+$), 259 (25, $[M - COOEt]^+$), 91 (100, $C_6H_5N^+$). Anal. calc. for $C_{19}H_{16}N_4O_2$ (332.36): C 68.66, H 4.85, N 16.86; found: C 68.73, H 4.85, N 16.87.

4,5-Bis(4-methylphenyl)-2-phenyl-1,2,3-triazol (**13**). Chloride **5b** (0.55 g, 2.45 mmol) was added to a suspension of **1** (R = Me; 0.31 g, 2.5 mmol) and $AlCl_3$ (0.33 g, 2.45 mmol) in abs. 1,2-dichlorobenzene (20 ml). The suspension was stirred at 130–140° for 0.5 h, cooled in an ice-bath, and neutralized with dil. NaOH soln. The org. layer was separated, the solvent removed by H_2O-vapeur destillation, and the residue of the org. phase purified by column chromatography (silica gel, $CHCl_3$): **13** (0.21 g, 58%). Yellow needles. M.p. 140–142° ([22]: 142°). UV/VIS (CH_2Cl_2): 215 (sh, 4.437), 298 (4.388). IR (KBr): 1600*m*, 1500*s* (arom.). ^{1}H-NMR (250.13 MHz, $CDCl_3$): 2.39 (*s*, 2 Me); 7.20 (*d*, $^3J = 8$, 4H, H_m of Ar–C(4,5)); 7.29–7.51 (*m*, 3H, H_m, H_p of Ph–N(2)); 7.54 (*d*, 4H, H_o of Ar–C(4,5)); 8.15–8.19 (*m*, 2H, H_o of Ph–N(2)). ^{13}C-NMR (62.89 MHz, $CDCl_3$): 21.4 (–, Me); 118.7, 127.2 (–, arom. CH); 128.0 (+, C_{ipso} of Ar–C(4,5)); 128.3, 129.2, 129.3 (–, arom. CH); 138.5, 139.9 (+, C_{ipso} of Ph–N(2)); 145.9 (+, C(5)). MS: 325 (97, M^+), 310 (6, $[M - Me]^+$), 91 (100, $C_7H_7^+$).

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