

## 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.

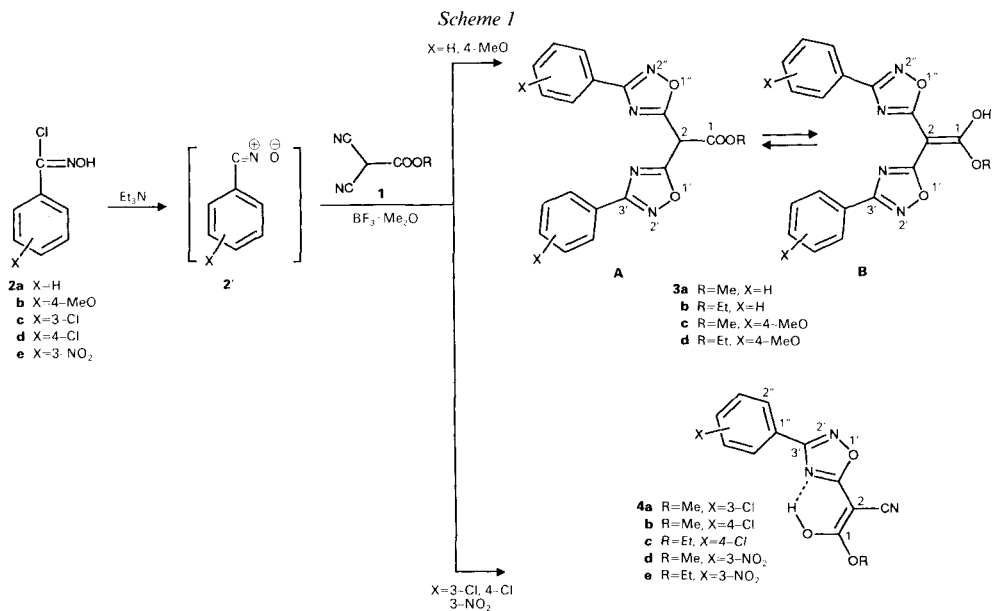
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**Introduction.** – We shall describe herein 1,3-dipolar cycloadditions of arenecarbonitrile oxides **2'** and arenecarbonitrile imines **5'** to the CN groups of alkyl dicyanoacetates **1** [1–9] which have been shown to be useful synthons in the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

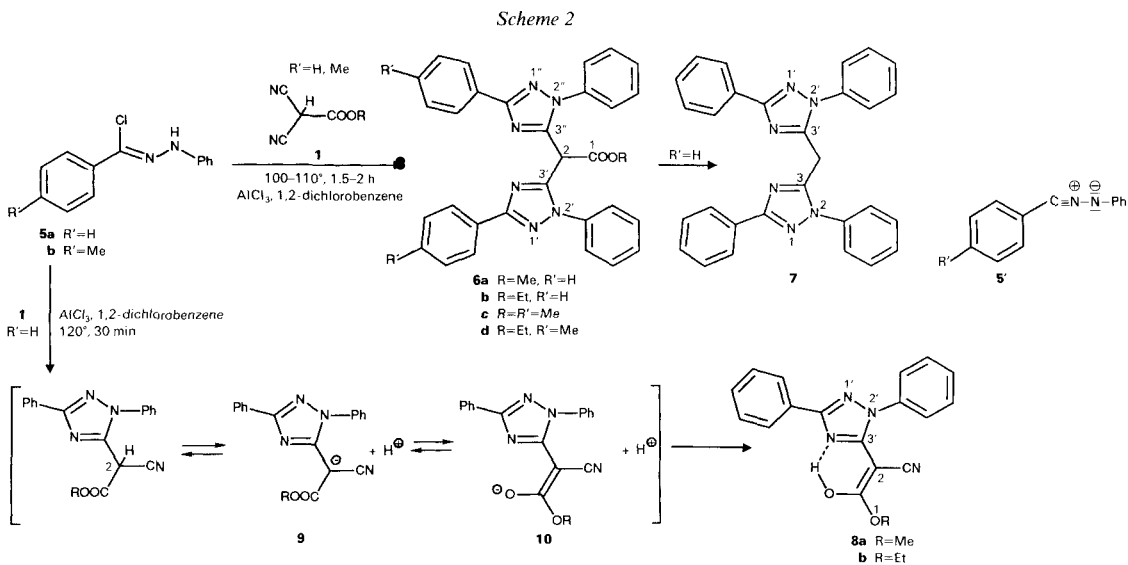
**Results.** – *Starting Materials.* The carbonitril oxides **2'** used for the cycloadditions were prepared from aldehyde oximes and *tert*-butyl hypochlorite; from the intermediate arenecarbohydroximoyl chlorides **2a–e**, HCl was eliminated *in situ* at –10 to 0° in the presence of Et<sub>3</sub>N according to [19] [20]. Carbonitrile imines **5'** were synthesized from arenecarbohydrazonoyl chlorides **5a,b** by elimination of HCl during the cycloaddition using AlCl<sub>3</sub> 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<sub>3</sub>. 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<sub>3</sub> solution, an equilibrium between two tautomers **A** and **B** was observed (<sup>1</sup>H-NMR: **A/B** ca. 3:1; <sup>13</sup>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<sub>2</sub> group, the mono-adducts **4a–e** were obtained which adopt the ketene-hemiacetal structure both in CDCl<sub>3</sub> and in DMSO (*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 Arenecarbohydrazonyl Imines 5' with 1.* Treatment of arenecarbohydrazonyl chlorides **5a** and **5b** with **1** in the presence of AlCl<sub>3</sub> 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



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 ( $\text{CH}_2(\text{CN})_2$ ) under the same conditions. The mono-adducts **8a** and **8b** were obtained as main products if the suspension of  $\text{AlCl}_3$  and **1** was heated quickly to  $120^\circ$ , 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 triazolyl 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 triazolyl 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 diphenyltriazolyl groups are far away from each other, in contrast to the situation in **D** with planar configuration at C(2).

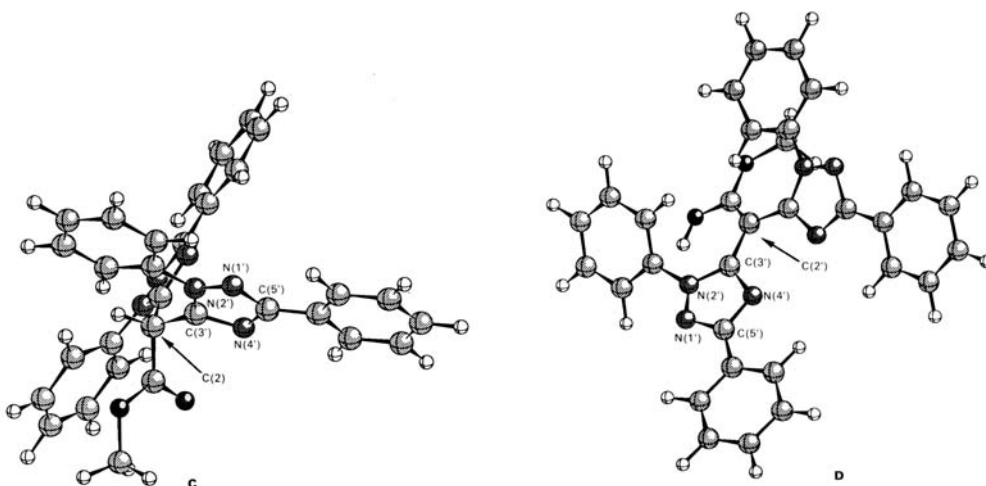
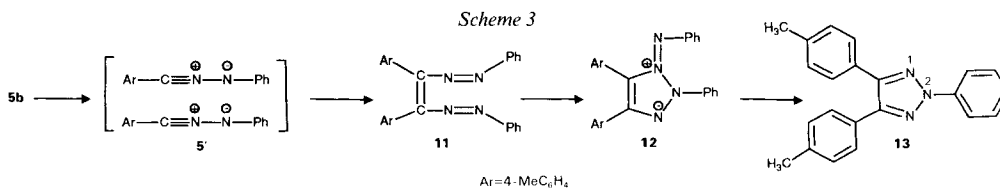


Figure. Plots of molecular-modelling structures **C** (ester) and **D** (ketene hemiacetal) of **6a**

At higher temperature ( $> 130^\circ$ ), 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].



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## Experimental Part

*General.* M.p.: Reichert hot-stage microscope; uncorrected. UV spectra ( $\lambda_{\max}$  (log  $\epsilon$ ) in nm): Carl-Zeiss-DMR-10 spectrophotometer. IR spectra (in  $\text{cm}^{-1}$ ): Perkin-Elmer-325 spectrophotometer. NMR spectra: Bruker-WM-250 spectrometer ( $^1\text{H-NMR}$  at 250.13 MHz,  $^{13}\text{C-NMR}$  at 62.89 MHz);  $\delta$  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,  $\text{CH}_2$ ; ' - ' = CH,  $\text{CH}_3$ ). MS (*m/z* (%)): Varian-MAT-311-A instrument (ionization energy 80 eV). Microanalyses were performed on a Heraeus automatic analyzer.

*Methyl 2,2-Bis[3-phenyl-1,2,4-oxadiazol-5-yl]acetate (3a), Typical Procedure for 3a-d.* A soln. of  $\text{Et}_3\text{N}$  (1.01 g, 10 mmol) and  $\text{Et}_2\text{O}$  (5 ml) was dropped slowly with stirring at  $-10^\circ$  into a soln. of benzenecarbohydroximoyl chloride (**2a**; 1.57 g, 10 mmol) in abs.  $\text{Et}_2\text{O}$  (40 ml) and then stirred at  $-10^\circ$  for further 10 min. The precipitate was filtered off and the filtrate immediately added at  $-10$  to  $0^\circ$  to a soln. of methyl dicyanoacetate **1**, R = Me; 0.62 g, 5 mmol) and  $\text{BF}_3 \cdot \text{Me}_2\text{O}$  (1.14 g, 10 mmol) in abs.  $\text{Et}_2\text{O}$  (50 ml). The mixture was stirred at r.t. for 4 h, then refluxed for 1 h, and evaporated.  $\text{H}_2\text{O}$  was added to the residue, which was then filtered and recrystallized from MeOH: **3a** (1.05 g, 58%). White crystals. M.p.  $129^\circ$  (MeOH). UV/VIS (MeCN): 233 (4.360), 263 (4.427), 322 (4.087). IR (KBr): 3030w (arom. CH), 1665s.  $^1\text{H-NMR}$  (250.13 MHz,  $\text{CDCl}_3$ ): 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 (2m, 10 arom. H).  $^{13}\text{C-NMR}$  (62.89 MHz,  $\text{CDCl}_3$ ): 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,  $\text{C}_{\text{ipso}}$ , 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,  $\text{C}_7\text{H}_5\text{NO}^+$ ), 103 (67,  $\text{C}_7\text{H}_5\text{N}^+$ ). Anal. calc. for  $\text{C}_{19}\text{H}_{14}\text{N}_4\text{O}_4$  (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  $\text{BF}_3 \cdot \text{Me}_2\text{O}$  (1.14 g, 10 mmol), column chromatography (silica gel,  $\text{CHCl}_3/\text{AcOEt}$  1:1) gave **3b** (0.745 g, 32%). White crystals. M.p.  $128$ – $130^\circ$  (AcOEt). UV/VIS (MeCN): 231 (4.391), 262 (4.442), 322 (4.126). IR (KBr): 3005w (arom. CH), 1655s.  $^1\text{H-NMR}$  (250.13 MHz,  $\text{CDCl}_3$ ): 1.34 (t, 2.25 H,  $\text{CH}_3\text{CH}_2$ , A); 1.44 (t, 0.75 H,  $\text{CH}_3\text{CH}_2$ , B); 4.40 (q, 2 H,  $\text{CH}_2\text{CH}_2$ ); 5.89 (s, 0.75 H, H-C(2), A); 7.45–7.62, 7.97–8.13 (2m, 10 arom. H).  $^{13}\text{C-NMR}$  (62.89 MHz,  $\text{CDCl}_3$ ): 13.9 (q,  $\text{CH}_3\text{CH}_2$ , A); 14.4 (q,  $\text{CH}_3\text{CH}_2$ , B); 43.9 (d, C(2), A); 60.6 (s, C(2), B); 61.6, 64.1 (2 t,  $\text{CH}_2\text{CH}_2$ , A and B); 126.0 (s,  $\text{C}_{\text{ipso}}$ , 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,  $\text{C}_7\text{H}_5\text{NO}^+$ ), 103 (72,  $\text{C}_7\text{H}_5\text{N}^+$ ). Anal. calc. for  $\text{C}_{20}\text{H}_{16}\text{N}_4\text{O}_4$  (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  $\text{BF}_3 \cdot \text{Me}_2\text{O}$  (1.14 g, 10 mmol), **3c** (0.53 g, 25%) was obtained as white crystals. M.p.  $155$ – $157^\circ$  (MeOH). UV/VIS (MeCN): 260 (4.407), 315 (3.741). IR (KBr): 1715m, 1615s.  $^1\text{H-NMR}$  (250.13 MHz,  $\text{CDCl}_3$ ): 3.87 (s, 4.5 H, MeO-Ar, A); 3.90 (s, 1.5 H, MeO-Ar, B); 3.92 (s, 2.25 H, MeOOC, A); 3.96 (s, 0.75 H, MeOOC(OH), B); 5.81 (s, 0.75 H, H-C(2), A); 6.98 (d,  $^3J = 9$ , 3 H,  $\text{H}_m$ , A); 7.06 (d, 1 H,  $\text{H}_o$ , B); 7.93 (d, 1 H,  $\text{H}_m$ , B); 8.03 (d,  $^3J = 9$ , 3 H,  $\text{H}_m$ , A).  $^{13}\text{C-NMR}$  (62.89 MHz,  $\text{CDCl}_3$ ): 43.7 (–, C(2), A); 54.4 (–, COOMe, A); 55.4, 55.6 (–, MeO-Ar, A and B); 114.3, 114.7 (–,  $\text{C}_o$ , A and B); 118.4 (+,  $\text{C}_p$ , A); 128.9, 129.3 (–,  $\text{C}_m$ , A and B); 162.3 (+,  $\text{C}_{\text{ipso}}$ , 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  $\text{C}_{21}\text{H}_{18}\text{N}_4\text{O}_6$  (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  $\text{BF}_3 \cdot \text{Me}_2\text{O}$  (1.14 g, 10 mmol) **3d** (0.34 g, 16%) was obtained as white crystals. M.p.  $133$ – $134^\circ$  (EtOH). UV/VIS (MeCN): 258 (4.594), 320 (3.986). IR (KBr): 1710s, 1615s.  $^1\text{H-NMR}$  (250.13 MHz,  $\text{CDCl}_3$ ): 1.33, 1.43 (2 t, 3 H,  $\text{CH}_3\text{CH}_2$ ); 3.86, 3.89 (2 s, 6 H, MeO-Ar); 4.39 (q, 2 H,  $\text{CH}_2\text{CH}_2$ ); 5.85 (s, 0.75 H, H-C(2), A); 6.98 (d,  $^3J = 9$ , 3 H,  $\text{H}_m$ , A); 7.03 (d, 1 H,  $\text{H}_o$ , B); 7.91 (d, 1 H,  $\text{H}_m$ , B); 8.03 (d,  $^3J = 9$ , 3 H,  $\text{H}_m$ , A).  $^{13}\text{C-NMR}$  (62.89 MHz,  $\text{CDCl}_3$ ): 13.9 (–,  $\text{CH}_3\text{CH}_2$ , A and B); 43.8 (–, C(2), A); 55.4 (–, MeO-Ar, A and B); 64.0 (+,  $\text{CH}_2\text{CH}_2$ , A and B); 114.3 (–,  $\text{C}_o$ , A and B); 118.4 (+,  $\text{C}_p$ , A); 122.3 (–,  $\text{C}_m$ , A and B); 162.3 (+,  $\text{C}_{\text{ipso}}$ , 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  $\text{C}_{22}\text{H}_{20}\text{N}_4\text{O}_6$  (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  $\text{Et}_3\text{N}$  (1.01 g, 10 mmol) in  $\text{Et}_2\text{O}$  (5 ml) was dropped slowly with stirring at  $-10$  to  $0^\circ$  into a soln. of 3-chlorobenzenecarbohydroximoyl chloride (**2c**; 1.90 g, 10 mmol) in abs.  $\text{Et}_2\text{O}$  (20 ml). After stirring at the same temp. for further 10 min, the precipitate was filtered off and washed with  $\text{CH}_2\text{Cl}_2$ . The filtrate was immediately added at  $-10$  to  $0^\circ$  into a soln. of **1** (R = Me; 1.24 g, 10 mmol) and  $\text{BF}_3 \cdot \text{Me}_2\text{O}$  (1.14 g, 10 mmol) in abs.  $\text{Et}_2\text{O}$  (20 ml). The mixture was stirred at r.t. for 30 h and filtered and the precipitate washed with  $\text{Et}_2\text{O}$  and  $\text{H}_2\text{O}$ . Recrystallization from MeOH gave **4a** (0.45 g, 16%). With crystals. M.p.  $164$ – $165^\circ$  (MeOH). UV/VIS (MeCN): 205 (4.528), 265 (4.280). IR (KBr): 33300–2900 (br., OH), 2230s (CN), 1705s, 1645s.  $^1\text{H-NMR}$  (250.13 MHz,  $\text{D}_6\text{O}$ 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'')).  $^{13}\text{C-NMR}$  (62.89 MHz,  $(\text{D}_6)$ 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,  $[M - \text{MeOH}]^+$ ), 218 (2,  $[M - \text{COOMe}]^+$ ), 153 (11,  $\text{C}_7\text{H}_4\text{ClNO}^+$ ), 137 (15,  $\text{C}_7\text{H}_4\text{ClN}^+$ ), 59 (100,  $\text{COOMe}^+$ ). HR-MS: 277.0246 ( $M^+$ , calc. 277.0250). Anal. calc. for  $\text{C}_{12}\text{H}_8\text{ClN}_3\text{O}_3$  (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  $\text{BF}_3 \cdot \text{Me}_2\text{O}$  (1.14 g, 10 mmol), **4b** (1.05 g, 76% based on white crystals. M.p. 162–163° (MeOH). UV/VIS (MeCN): 202 (4.258), 265 (4.292). IR (KBr): 3300–2900 (br., OH), 2210s (CN), 1720s, 1640s.  $^1\text{H-NMR}$  (250.13 MHz,  $(\text{D}_6)$ 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).  $^{13}\text{C-NMR}$  (62.89 MHz,  $(\text{D}_6)$ 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,  $[M - \text{MeOH}]^+$ ), 218 (2,  $[M - \text{COOMe}]^+$ ), 153 (11,  $\text{C}_7\text{H}_4\text{ClNO}^+$ ), 137 (15,  $\text{C}_7\text{H}_4\text{ClN}^+$ ), 59 (100,  $\text{COOMe}^+$ ). Anal. calc. for  $\text{C}_{12}\text{H}_8\text{ClN}_3\text{O}_3$  (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  $\text{BF}_3 \cdot \text{Me}_2\text{O}$  (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), 2230s (CN), 1715s, 1645s.  $^1\text{H-NMR}$  (250.13 MHz,  $(\text{D}_6)$ DMSO): 1.20 (*t*,  $\text{CH}_3\text{CH}_2$ ); 4.10 (*q*,  $\text{CH}_3\text{CH}_2$ ); 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).  $^{13}\text{C-NMR}$  (62.89 MHz,  $(\text{D}_6)$ DMSO): 14.7 (–,  $\text{CH}_3\text{CH}_2$ ); 53.8 (+, C(2)); 58.9 (+,  $\text{CH}_3\text{CH}_2$ ); 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,  $\text{C}_7\text{H}_4\text{ClNO}^+$ ), 152 (100). Anal. calc. for  $\text{C}_{13}\text{H}_{10}\text{ClN}_3\text{O}_3$  (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  $\text{BF}_3 \cdot \text{Me}_2\text{O}$  (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), 2220s (CN), 1720s, 1635s, 1540s ( $\text{NO}_2$ ), 1350s ( $\text{NO}_2$ ).  $^1\text{H-NMR}$  (250.13 MHz,  $(\text{D}_6)$ 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'')).  $^{13}\text{C-NMR}$  (62.89 MHz,  $(\text{D}_6)$ 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  $\text{C}_{12}\text{H}_8\text{N}_4\text{O}_5$  (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  $\text{BF}_3 \cdot \text{Me}_2\text{O}$  (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), 2220s (CN), 1700s, 1650s, 1535s ( $\text{NO}_2$ ), 1360s ( $\text{NO}_2$ ).  $^1\text{H-NMR}$  (250.13 MHz,  $(\text{D}_6)$ acetone): 1.29 (*t*,  $\text{CH}_3\text{CH}_2$ ); 4.25 (*q*,  $\text{CH}_3\text{CH}_2$ ); 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'')).  $^{13}\text{C-NMR}$  (62.89 MHz,  $(\text{D}_6)$ acetone): 14.7 (–,  $\text{CH}_3\text{CH}_2$ ); 57.3 (+, C(2)); 61.4 (+,  $\text{CH}_3\text{CH}_2$ ); 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,  $\text{C}_7\text{H}_4\text{N}_2\text{O}_3^+$ ). Anal. calc. for  $\text{C}_{13}\text{H}_{10}\text{N}_4\text{O}_5$  (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  $\text{AlCl}_3$  (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  $\text{H}_2\text{O}$ -vapour distillation, 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° [ $\eta_{\text{D}}^{20}$ : 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 ( $\text{CH}_2\text{Cl}_2$ ): 248 (4.574). IR (KBr): 3010 (arom. CH), 2970w (CH), 1755s (C=O).  $^1\text{H-NMR}$  (250.13 MHz,  $\text{CDCl}_3$ ): 3.56 (s, MeO); 5.58 (s, H–C(2)); 7.26–7.46 (*m*, 16 arom. H); 8.13–8.17 (*m*, 4H,  $\text{H}_o$  of Ph–C(5',5'')).  $^{13}\text{C-NMR}$  (62.89 MHz,  $\text{CDCl}_3$ ): 43.2 (*d*, C(2)); 53.4 (*q*, MeO); 125.6 (*d*,  $\text{C}_o$  of Ph–C(5',5'')); 126.7 (*d*,  $\text{C}_p$  of Ph–C(5',5'')); 128.5 (*d*,  $\text{C}_m$  of Ph–C(5',5'')); 129.5, 129.6, 129.7 (3*d*,  $\text{C}_o$ ,  $\text{C}_m$ ,  $\text{C}_p$  of Ph–N(2',2'')); 130.4 (*s*,  $\text{C}_{\text{ipso}}$  of Ph–C(5',5'')); 136.9 (*s*,  $\text{C}_{\text{ipso}}$  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,  $[M, \text{MeO}]^+$ ), 480 (9,  $[M - \text{MeOH}]^+$ ), 453 (4,  $[481 - \text{CO}]^+$ ), 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), 1500s (arom.).  $^1H$ -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), 1750s (C=O).  $^1H$ -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-phenylbenzene-carbohydrazonoyl 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), 2960w (CH), 1755s (C=O).  $^1H$ -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), 2995w (CH), 1755s (C=O).  $^1H$ -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 distillation, 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): 3070w, 2960w (CH), 2210m (CN).  $^1H$ -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<sub>3</sub> (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<sub>4</sub>). UV/VIS (MeCN): 230 (4.366), 290 (4.299). IR (KBr): 3070<sub>w</sub>, 2985<sub>w</sub> (CH), 2210<sub>m</sub> (CN). <sup>1</sup>H-NMR (250.13 MHz, CDCl<sub>3</sub>): 1.33 (*t*, CH<sub>3</sub>CH<sub>2</sub>); 4.28 (*q*, CH<sub>3</sub>CH<sub>2</sub>); 7.49–7.56 (*m*, 8H, H<sub>o</sub>, H<sub>m</sub>, H<sub>p</sub> of Ph–N(2')), H<sub>m</sub>, H<sub>p</sub> of Ph–C(5'')); 7.84–7.88 (*m*, 2H, H<sub>o</sub> of Ph–C(5'')); 12.86 (*br. s*, OH). <sup>13</sup>C-NMR (62.89 MHz, CDCl<sub>3</sub>): 14.6 (*q*, CH<sub>3</sub>CH<sub>2</sub>); 51.6 (*s*, C(2)); 60.7 (*t*, CH<sub>3</sub>CH<sub>2</sub>); 116.2 (*s*, CN); 124.0 (*s*, C<sub>ipso</sub> 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<sub>ipso</sub> of Ph–N(2')); 148.0 (*s*, C(3'')); 152.7 (*s*, C(5'')); 170.4 (*s*, C(1)). MS: 332 (51, M<sup>+</sup>), 287 (6, [M – EtO]<sup>+</sup>), 286 (9, [M – EtOH]<sup>+</sup>), 259 (25, [M – COEt]<sup>+</sup>), 91 (100, C<sub>6</sub>H<sub>5</sub>N<sup>+</sup>). Anal. calc. for C<sub>19</sub>H<sub>16</sub>N<sub>4</sub>O<sub>2</sub> (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<sub>3</sub> (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<sub>2</sub>O-vapour distillation, and the residue of the org. phase purified by column chromatography (silica gel, CHCl<sub>3</sub>): **13** (0.21 g, 58%). Yellow needles. M.p. 140–142° ([22]: 142°). UV/VIS (CH<sub>2</sub>Cl<sub>2</sub>): 215 (*sh*, 4.437), 298 (4.388). IR (KBr): 1600<sub>m</sub>, 1500<sub>s</sub> (arom.). <sup>1</sup>H-NMR (250.13 MHz, CDCl<sub>3</sub>): 2.39 (*s*, 2 Me); 7.20 (*d*, <sup>3</sup>*J* = 8, 4H, H<sub>m</sub> of Ar–C(4,5)); 7.29–7.51 (*m*, 3H, H<sub>m</sub>, H<sub>p</sub> of Ph–N(2)); 7.54 (*d*, 4H, H<sub>o</sub> of Ar–C(4,5)); 8.15–8.19 (*m*, 2H, H<sub>o</sub> of Ph–N(2)). <sup>13</sup>C-NMR (62.89 MHz, CDCl<sub>3</sub>): 21.4 (–, Me); 118.7, 127.2 (–, arom. CH); 128.0 (+, C<sub>ipso</sub> of Ar–C(4,5)); 128.3, 129.2, 129.3 (–, arom. CH); 138.5, 139.9 (+, C<sub>ipso</sub> of Ph–N(2)); 145.9 (+, C(5)). MS: 325 (97, M<sup>+</sup>), 310 (6, [M – Me]<sup>+</sup>), 91 (100, C<sub>7</sub>H<sub>7</sub><sup>+</sup>).

## REFERENCES

- [1] R. Neidlein, D. Kikelj, W. Kramer, Z. Sui, R. Boese, D. Bläser, D. Kocjan, *Chem. Ber.* **1989**, *122*, 1341.
- [2] B. C. Hesse, *J. Am. Chem. Soc.* **1896**, *18*, 723.
- [3] F. Arndt, H. Scholz, E. Frobel, *Liebigs Ann. Chem.* **1936**, *521*, 95.
- [4] J. A. Elvidge, P. N. Judson, A. Percival, R. Shah, *J. Chem. Soc., Perkin Trans. I* **1983**, 1741.
- [5] A. Dornow, H. Grabhoffer, *Chem. Ber.* **1958**, *91*, 1824.
- [6] W. J. Middleton, E. L. Little, D. Coffman, V. A. Engelhardt, *J. Am. Chem. Soc.* **1958**, *80*, 2795.
- [7] R. Schenk, H. Finken, *Liebigs Ann. Chem.* **1928**, *462*, 158.
- [8] D. Martin, S. Rackow, *Chem. Ber.* **1965**, *98*, 3662.
- [9] E. Grigat, R. Putter, E. Mühlbauer, *Chem. Ber.* **1965**, *98*, 3777.
- [10] R. Neidlein, Z. Sui, *Synthesis* **1990**, 959.
- [11] R. Neidlein, Z. Sui, *Chem. Ber.* **1990**, *123*, 2203.
- [12] R. Neidlein, Z. Sui, *Synthesis* **1991**, in press.
- [13] R. Neidlein, Z. Sui, *Chem. Ber.* **1991**, *124*, in press.
- [14] R. Neidlein, Z. Sui, *Rev. Roum. Chim.* **1991**, in press.
- [15] R. Huisgen, *Proc. Chem. Soc.* **1961**, 357.
- [16] G. Leandri, M. Palotti, *Ann. Chim. (Rome)* **1957**, *47*, 376.
- [17] R. Huisgen, W. Mack, E. Anneser, *Tetrahedron Lett.* **1961**, 587.
- [18] S. Conde, C. Corral, R. Madronero, *Synthesis* **1973**, 28.
- [19] C. Grundmann, R. Richter, *J. Org. Chem.* **1968**, *33*, 476.
- [20] S. Morrochi, A. Ricca, L. Velo, *Tetrahedron Lett.* **1967**, 331.
- [21] R. Huisgen, W. Fliege, W. Kolbeck, *Chem. Ber.* **1983**, *116*, 3027.
- [22] I. Bhatnagar, M. V. George, *J. Org. Chem.* **1967**, *32*, 2252.
- [23] R. Huisgen, M. Seidel, G. Wallbillich, H. Knupfer, *Tetrahedron* **1962**, *17*, 3.