40. Diazoaldehyde Chemistry

Part 3[1])

Synthesis of 4-Acyl-1*H*-1,2,3-triazole Derivatives

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Ten new α-diazo-β-oxoaldehydes were condensed with aniline, ammonia, hydroxylamine, and semicarbazide to yield new 4-acyl-(1-substituted)-1*H*-1,2,3-triazoles in moderate-to-good yields. The method is simple and regiospecific. The latter feature makes this method superior to the widely used acylacetylene + azide approach.

Introduction. – Triazoles constitute a large class of heterocycles, many of which are also biologically active. Numerous examples for their synthesis and their use as starting materials have been already reported [2] [3]. The vast majority of the synthetic methods leading to 1*H*-1,2,3-triazoles are based on dipolar cycloadditions of azides to multiple bonds [2–4]. Another method uses the condensation of amine derivatives with α-diazo-1,3-dicarbonyl compounds [4a] [5]. With this procedure, several triazole-containing antibiotics were prepared [6].

α-Diazo-β-oxoaldehydes **3** remained having only three examples until 1994 [5b,c], when *Sezer* and *Anaç* found that 2-azido-1-ethylpyridinium fluoroborate **2** diazotizes β-oxoaldehydes **1** partially without deformylation in the presence of AcONa [1a]. This reaction can be used as an alternative synthetic method for these diazoaldehydes. In this paper, we report the utilization of these diazooxoaldehydes in the synthesis of 4-acyl-(1-substituted)-1*H*-triazoles **5–20** as a continuation of our interest in heterocycle synthesis [7].

Results and Discussion. – Ten different α-diazo-β-oxoaldehydes **3** were condensed with amine derivatives, namely with $PhNH_2$, NH_3, NH_2OH, and semicarbazide (*Scheme*). The results are summarized in *Tables 1* and *2*.

Most of the reactions were straightforward, and no difficulty was encountered in the purification steps. The condensations with NH_2OH and $NH_2CONHNH_2$ went further, and the keto functions were converted to oximes and semicarbazones, respectively. ^1H- and ^{13}C-NMR spectra showed that **23** was contaminated with a small amount of the oxo compound (**23**/**20** 9:1 by moles). The ester groups of **18** and **19** remained intact as expected.

[1]) Part 1: [1a]; Part 2: [1b].

Scheme

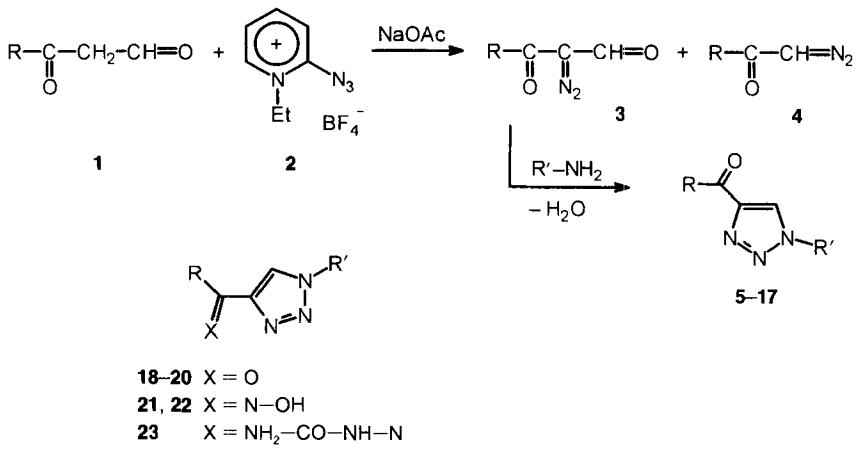

Table 1. *Reactions of* **3/4** *with Aniline* (R′ = Ph)

	R	Yield [%][a][b]	M.p. [°C]		R	Yield [%][a][b]	M.p. [°C]
5	Me	73	107–8[c]	**10**	3,4-Cl_2–C_6H_3	58 (78)	205–6
6	i-Pr	19 (52)	100–100.5	**11**	2,4-Cl_2–C_6H_3	75 (87)	135–136.5
7	i-Bu	17 (65)	107–8[d]	**12**	2,4-Br_2–C_6H_3	75 (80)	151–2
8	Naphth-1-yl	10 (26)	118–9	**13**	2,4,6-Me_3–C_6H_2	27 (29)	102–102.5
9	4-Cl–C_6H_4	28 (53)	183–4				

[a]) All diazooxoaldehydes were employed without separation from their by-standing diazomethyl ketones **4**, except for 2-diazo-3-oxobutanal (R = Me).

[b]) Yields after isolation, based on the starting β-oxoaldehyde **1**. The values in parentheses are the yields based on the α-diazo-β-oxoaldehydes **3**, calculated by the content of **3** in the mixture **3/4** (see [1a]).

[c]) 108–9° [8a], 113° [8b].

[d]) 90.5–91° [8a].

Table 2. *Reactions of* **3/4** *with* NH_3, NH_2OH, *and* $NH_2CONHNH_2$

R	R′ = H			R′ = OH			R′ = NH–CO–NH_2		
		Yield [%][a]	M.p. [°C]		Yield [%][a]	M.p. [°C]		Yield [%][a]	M.p. [°C]
EtO	**14**	50	111–2[b]	**18**	7	161–2	**19**	35	191[d]
Me	**15**	24	131[c]	**21**	12	168–70	**23** (+**20**)	64	239.5[d]
2,4-Cl_2–C_6H_3	**16**	20	153						
2,4-Br_2–C_6H_3	**17**	26	162.5–166	**22**	15	186[d][e]			

[a]) Yields after isolation. [b]) [9a]: 113–4°, [9b]: 112–3°. [c]) [10]: 129–132°. [d]) Decomposition. [e]) Softens around 150°.

The diazomethyl ketones **4**, which are formed besides **3** in the diazotization reaction, do not interfere this condensation. Therefore, the diazooxoaldehydes **3** may be safely employed as mixtures **3/4**. The highly crystalline nature of the triazole products simplify

the purification. In the worst cases, products were purified by preparative TLC very easily. Of the triazoles prepared in this work are 14 new compounds. We believe that our method may be even more convenient: comparably yielding and simpler for the already known **5** [8], **7** [8a], **14** [9], and **15** [10].

The advantage of this method is that it yields only one of the two possible regioisomers of the products. The condensation takes place with the highly electrophilic formyl group, and not with the acyl group. The probable presence of the other regioisomer was not detectable in our hands. The widely used azide + acylacetylene method is regioselective but not regiospecific; it usually gives the normal addition product with respect to the polarization of the acetylene, but the inverse adducts sometimes appear in varying amounts [4e–g]. The new method overcomes this problem.

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Experimental Part

General. All diazo compounds were prepared as described in [1a] and used without purification (see the main text and the *Footnotes a* and *b* to *Table 1*). Ethyl 2-diazo-3-oxopropanoate and 2-diazo-3-oxobutanal were used in pure form. M.p.: uncorrected, on an *Electrothermal* glass-bath apparatus in capillary tubes. IR (KBr, cm^{-1}): *Jasco FT-IR*, model *5300*. NMR (δ [ppm], (D_6)acetone): 200-MHz *Bruker* apparatus, TMS as internal standard; the coupling constants J are given in Hz. ^{13}C-NMR: at 50 MHz. MS: on a *VG-Zabspec* double-focusing spectrometer. EI-MS at 70 eV, CI-MS in isobutane.

Synthesis of Compounds **5**–**13** (R′ = Ph). A mixture **3**/**4** containing 10 mmol of **3** was dissolved in 5.5–7 ml of EtOH, and a mixture of 10.7 mmol of $PhNH_2$ and 1.25 ml of AcOH were added. The mixture was stirred at r.t. for 30 min. During this time, the triazoles **5**, **6**, **7**, and **10**–**12** precipitated and obtained pure after recrystallization from EtOH. The mixture from the reaction of 3-oxo-3-(2,4,6-trimethylphenyl)propanal (R = 2,4,6-Me_3-C_6H_2) was taken with CH_2Cl_2 and washed successively with H_2O. After drying and evaporating, a little EtOH was added, and **13** was obtained in crystalline form upon cooling. Isolations of **8** and **9** required thick-layer chromatography over silica gel *60* (light petroleum/AcOEt 20:1). The yields and m.p. are given in *Table 1*.

Synthesis of Compounds **14**–**17** (R′ = H). A soln. of 3 mmol of an α-diazo-β-oxoaldehyde in 1–2 ml of AcOH was added to a soln. of 3.3 mmol of $AcONH_4$ in 5–6 ml of AcOH, and the resulting mixture was stirred with heating at 80–90° for 2–3 h. Synthesis of **14** required heating at 100° for 3–4 h. The mixtures were evaporated to dryness on a rotary evaporator. The org. products were extracted with acetone. Compounds **14**, **16**, and **17** were purified by thick-layer chromatography on silica gel *60*: **16** almost remained at the start with hexane/AcOEt 5:1, whereas **14** and **17** both had R_f values of *ca.* 0.4 with hexane/acetone 2:1. Compound **15** was obtained almost in pure form by extraction with hot Et_2O and cooling. Further purification was affected by prep. TLC. The yields and m.p. are given in *Table 2*.

Synthesis of Compounds **18**, **21**, *and* **22** (R′ = OH). $NH_2OH \cdot HCl$ (6.6 mmol) was dissolved in H_2O, and pH was adjusted to 5 with AcONa. To this soln., a soln. of the α-diazo-β-oxoaldehyde (1.7 mmol) in EtOH was added, and the resulting mixture was stirred at r.t. for 2 d. The inorg. products were precipitated by addition of Et_2O. After filtration, the mixture was evaporated, and the products were purified by repeated recrystallization from H_2O. The yields and m.p. are given in *Table 2*.

Synthesis of Compounds **19** *and* **23** (R′ = NH–CO–NH_2). Semicarbazide · HCl (6 mmol) was dissolved in H_2O and the pH adjusted to 5 with AcONa. A α-diazo-β-oxoaldehyde (3 mmol) was dissolved also in H_2O, a few drops of EtOH were added if necessary, and the two solns. were combined. Compound **23** started to precipitate in a few minutes, whereas **19** required 2 d to precipitate at r.t. The products were collected, washed with H_2O, and analyzed without further purification. The yields and m.p. are given in *Table 2*.

*4-Acetyl-1-phenyl-1*H*-1,2,3-triazole* (**5**): IR: 3133, 1689, 1530, 1506, 1470. ^{1}H-NMR: 9.08 (*s*, H–C(5)); 8.03–7.95, 7.72–7.52 (*m*, 2 + 3 arom. H); 2.65 (*s*, Me). ^{13}C-NMR: 27.25; 121.64; 125.16; 130.17; 130.77; peaks for 2 arom. C and the CO peaks not observed. EI-MS: 187 (73, M^+), 116 (100), 172 (12), 159 (42), 145 (72), 130 (66), 90 (85), 77 (58), 65 (49), 58 (14).

*4-(2-Methylpropanoyl)-1-phenyl-1*H-*1,2,3-triazole* (**6**): IR: 3138, 3067, 2971, 2932, 2870, 1678, 1597, 1528, 1506, 1466. ^{1}H-NMR: 9.08 (*s*, H–C(5)); 8.04–7.96, 7.72–7.5 (2*m*, 2 + 3 arom. H); 3.78 (*sept.*, *J* = 7.2, Me_2CH); 1.24 (*d*, *J* = 7.2, 2 Me). ^{13}C-NMR: 18.71; 37.62; 121.46; 125.59; 130.01; 130.69; 137.50; 148.01; 198.48. EI-MS: 215 (57, M^+), 186 (22), 172 (50), 158 (72), 144 (94), 130 (57), 116 (88), 104 (57), 89 (88), 77 (100), 63 (33), 58 (28).

*4-(3-Methylbutanoyl)-1-phenyl-1*H-*1,2,3-triazole* (**7**): IR: 3135, 3069, 2953, 2926, 2872, 1678, 1530, 1507, 1468. ^{1}H-NMR: 9.07 (*s*, H–C(5)); 8.04–7.98, 7.72–7.5 (2*m*, 2 + 3 arom. H); 3.0 (*d*, *J* = 6.6, CH_2); 2.33 (*m*, Me_2CH); 1.01 (*d*, *J* = 6.7, 2 Me). ^{13}C-NMR: 22.86; 25.53; 48.88; 121.54; 125.16; 130.07; 137.57; 149.22; 194.51. EI-MS: 229 (26, M^+), 214 (25), 200 (27), 186 (50), 172 (47), 159 (93), 144 (58), 132 (100), 117 (60), 104 (56), 89 (33), 77 (60), 57 (65).

*4-(1-Naphthoyl)-1-phenyl-1*H-*1,2,3-triazole* (**8**): IR: 3123, 3050, 1642, 1511, 1466*w*. ^{1}H-NMR: 9.27 (*s*, H–C(5)); 8.5–8.35 (*m*, 1 arom. H); 8.23–8.25 (*m*, 1 arom. H); 8.1–8.02 (*m*, 3 arom. H); 7.72–7.54 (*m*, 7 arom. H). ^{13}C-NMR: 121.84; 125.40; 126.18; 127.27; 128.04; 128.28; 129.40; 130.17; 130.65; 130.76; 131.60; 133.08; 134.80; 135.89; 137.80; 149.6; 186.77. EI-MS: 299 (66, M^+), 270 (72), 254 (20), 243 (66), 230 (85), 215 (27), 168 (56), 155 (79), 140 (41), 127 (55), 104 (29), 77 (100), 89 (16), 63 (24).

*4-(4'-Chlorobenzoyl)-1-phenyl-1*H-*1,2,3-triazole* (**9**): IR: 3104, 1669, 1611, 1597, 1520, 1506, 1466*w*, 1429*w*. ^{1}H-NMR: 9.24 (*s*, H–C(5)); 8.47 (*AA'* of *AA'XX'*, ^3J = 8.7, H–C(3'), H–C(5')); 8.04 (*XX'* of *AA'XX'*, ^3J = 7.4, H–C(2'), H–C(6')); 7.73–7.52 (*m*, Ph). ^{13}C-NMR: 121.83; 128.22; 129.54; 130.32; 130.83; 132.93; 140.0; 149.0; peaks for 2 arom. C and the CO peak not observed. EI-MS: 285 (7, M^+), 283 (19, M^+), 254 (55), 227 (40), 214 (95), 192 (12), 165 (46), 152 (40), 141 (59), 123 (24), 111 (100), 104 (38), 89 (55), 77 (61), 63 (28).

*4-(3',4'-Dichlorobenzoyl)-1-phenyl-1*H-*1,2,3-triazole* (**10**): IR: 3137, 3056, 1635, 1581, 1523, 1464. ^{1}H-NMR: 9.23 (*s*, H–C(5)); 8.64 (*d*, ^4J = 2, H–C(2')); 8.41 (*dd*, ^3J = 8.54, ^4J = 1.93, H–C(5')); 7.81 (*d*, ^3J = 8.34, H–C(6')); 8.05–7.98, 7.72–7.54 (*m*, 2 + 3 arom. H). ^{13}C-NMR: 121.89; 123.52; 128.54; 130.45; 130.90; 131.78; 133.11; 149.78; peaks for 4 arom. C and the CO peak not observed. EI-MS: 321 (9, M^+), 319 (43, M^+), 317 (55, M^+), 293 (18), 292 (30), 291 (71), 290 (71), 289 (85), 288 (76), 261 (80), 248 (100), 226 (17), 199 (52), 186 (51), 175 (68), 157 (31), 145 (89), 123 (22), 109 (38), 104 (50), 89 (19), 77 (77), 63 (10).

*4-(2',4'-Dichlorobenzoyl)-1-phenyl-1*H-*1,2,3-triazole* (**11**): IR: 3125, 3065, 1666, 1580, 1550, 1468. ^{1}H-NMR ($CDCl_3$, 100 MHz): 8.53 (*s*, H–C(5)); 7.75–7.1 (*m*, 8 arom. H). ^{13}C-NMR ($CDCl_3$, 67.8 MHz): 119.7; 124.46; 125.86; 128.61; 128.89; 129.34; 130.25; 132.07; 134.29; 135.07; 136.56; 146.61; 184.8. EI-MS: 321 (2.5, M^+), 319 (13, M^+), 317 (19, M^+), 292 (14), 290 (44), 288 (55), 282 (22), 261 (62), 254 (81), 248 (82), 226 (22), 199 (38), 186 (45), 175 (100), 157 (29), 145 (83), 123 (35), 109 (48), 104 (68), 89 (29), 77 (90), 63 (22).

*4-(2',4'-Dibromobenzoyl)-1-phenyl-1*H-*1,2,3-triazole* (**12**): IR: 3127, 3075, 1669, 1575, 1545, 1468. ^{1}H-NMR: 9.29 (*s*, H–C(5)); 7.52–8.08 (*m*, 8 arom. H). ^{13}C-NMR: 121.01; 121.64; 125.36; 127.73; 130.32; 130.77; 131.47; 132.12; 136.28; 137.45; 147.90; peak for 1 arom. C and the CO peak not observed. EI-MS: 409 (6, M^+), 407 (13, M^+), 405 (6, M^+), 378 (35), 351 (36), 338 (56), 300 (72), 298 (72), 263 (96), 235 (46), 219 (20), 191 (24), 167 (19), 154 (16), 144 (53), 116 (16), 104 (49), 77 (100), 63 (25).

*4-(2',4',6'-Trimethylbenzoyl)-1-phenyl-1*H-*1,2,3-triazole* (**13**): IR: 3130, 3068, 1640, 1586, 1566, 1526, 1510, 1484, 1468. ^{1}H-NMR: 9.15 (*s*, H–C(5)); 8.05–7.95, 7.70–7.51 (2*m*, 2 + 3 arom. H); 6.95 (*s*, H–C(3'), H–C(5')); 2.32 (*s*, Me–C(4')); 2.15 (*s*, Me–C(2'), Me–C(6')). ^{13}C-NMR: 19.50; 21.12; 121.58; 124.74; 126.64; 129.06; 130.16; 130.74; 134.87; 138.36; peaks for 2 arom. C and the CO peak not observed. EI-MS: 291 (100, M^+), 263 (43), 248 (59), 234 (100), 220 (95), 204 (15), 171 (21), 160 (27), 147 (57), 132 (41), 119 (43), 104 (49), 91 (53), 77 (79), 65 (34).

*4-(Ethoxycarbonyl)-1*H-*1,2,3-triazole* (**14**): IR: 3437, 3170, 2997, 2924, 1709, 1535*w*, 1472*w*, 1458*w*. ^{1}H-NMR: 8.34 (*s*, H–C(5)); 4.37 (*q*, *J* = 7.12, CH_2); 2.8–3.4 (disapp. on deut., NH); 1.36 (*t*, *J* = 7.12, Me). ^{13}C-NMR: 14.48; 61.4; 132.95 (br.); 161.4. EI-MS: 141 (71, M^+), 126 (12), 114 (96), 97 (88), 85 (22), 69 (100), 57 (17).

*4-Acetyl-1*H-*1,2,3-triazole* (**15**): IR: 3460, 3108, 2936, 1680, 1491. ^{1}H-NMR: 8.30 (*s*, H–C(5)); 2.6–3.7 (disapp. on deut., NH); 2.58 (*s*, Me). ^{13}C-NMR: 27.32; 130.61; 131.2 (sh-like); 180.8. EI-MS: 111 (100, M^+), 96 (76), 83 (25), 78 (5), 69 (74), 63 (7), 58 (20).

*4-(2',4'-Dichlorobenzoyl)-1*H-*1,2,3-triazole* (**16**): IR: 3430, 3420, 3171, 3104, 2920, 1649, 1584, 1476*w*, 1464*w*. ^{1}H-NMR: 8.53 (*s*, H–C(5')); 7.7 (*d*, ^3J = 8.58, H–C(6')); 7.67 (*d*, ^4J = 1.71, H–C(3')); 7.57 (*dd*, ^4J = 1.89, ^3J = 8.31, H–C(5')); 2.9–3.5 (dissap. on deut., NH). ^{13}C-NMR: 124.7; 128.04; 130.55; 131.99; 132.81; 133.03; 137.36; peak for 1 arom. C and the CO peak not observed. EI-MS: 247 (9, M^+), 245 (45, M^+), 243 (63, M^+), 208 (87), 185 (12), 173 (100), 157 (9), 145 (49), 123 (34), 109 (42), 96 (62), 85 (22), 74 (36), 68 (57), 58 (16).

*4-(2',4'-Dibromobenzoyl)-1*H-*1,2,3-triazole* (**17**): IR: 3428, 3420, 3169, 3101, 2972, 2920, 1645, 1574, 1476*w*, 1460*w*. ^{1}H-NMR: 8.55 (*s*, H–C(5)); 7.97 (*d*, ^4J = 1.48, H–C(3')); 7.76 (*dd*, ^4J = 1.39, ^3J = 8.10, H–C(5')); 7.59 (*d*, ^3J = 8.35, H–C(6')); 2.6–3.3 (disapp. on deut., NH). ^{13}C-NMR: 120.62; 125.20; 131.44; 131.94; 132.71 (br.); 136.20; 136.74; CO peak not observed. EI-MS: 333 (35, M^+), 331 (92, M^+), 329 (36, M^+), 275 (11), 261 (100), 252

(55), 235 (99), 224 (22), 194 (21), 182 (6), 167 (41), 154 (53), 143 (8), 130 (7), 114 (28), 96 (58), 87 (30), 74 (94), 68 (53), 62 (18).

*4-(Ethoxycarbonyl)-1-hydroxy-1*H*-1,2,3-triazole* (**18**): IR: 3263, 2997, 1723, 1447, 1406. ^{1}H-NMR: 8.27 (*s*, H–C(5')); 4.25 (*q*, J = 7.12, CH_2); 3.02 (disapp. on deut., OH); 1.28 (*t*, J = 7.23, Me). ^{13}C-NMR: 14.28; 62.07; 139.23; peak for 1 arom. C and the CO peak not observed. EI-MS: 160 (45, $[M + 3]^+$), 143 (19), 132 (83), 125 (36), 114 (100), 98 (56), 87 (49), 79 (84), 71 (80), 63 (52).

*1-Hydroxy-4-[1-(hydroxyimino)ethyl]-1*H*-1,2,3-triazole* (**21**): IR: 3410, 3250, 3181, 2961, 2926, 2849, 1639*w*, 1578*w*, 1422. ^{1}H-NMR: 8.45 (*s*, H–C(5)); 2.9–3.3 (disapp. on deut., OH); 2.27 (*s*, Me). ^{13}C-NMR: 17.26; 122.62; peak for 1 arom. C and the oxime-C peak not observed. EI-MS: 142 (7, $M^{+\cdot}$), 126 (17), 110 (6), 108 (8), 97 (100), 79 (19), 71 (17), 66 (15), 58 (30).

*4-[(2',4'-Dibromobenzoyl)(hydroxyimino)methyl]-1-hydroxy-1*H*-1,2,3-triazole* (**22**): IR: 3268, 3240, 3183, 3057, 2861, 1672, 1637, 1582, 1547, 1472, 1441. ^{1}H-NMR: 8.62 (*s*, H–C(5)); 7.88 (*d*, ^4J = 2.10, H–C(3')); 7.67 (*dd*, ^4J = 2.02, ^3J = 8.18, H–C(5')); 7.39 (*d*, ^3J = 8.26, H–C(6')); 2.8–3.4 (disapp. on deut., OH). ^{13}C-NMR: 123.0; 123.26; 125.49; 131.18; 134.17; 135.42; 136.59; 136.79; 148.61. EI-MS: 365 (20, $[M + 1]^+$), 364 (22, $M^{+\cdot}$), 363 (39, $[M + 1]^+$), 362 (39, $M^{+\cdot}$), 361 (22, $[M + 1]^+$), 360 (20, $M^{+\cdot}$), 349 (12), 348 (28), 347 (31), 346 (52), 345 (27), 344 (31), 343 (8), 330 (42), 328 (70), 326 (42), 319 (69), 317 (100), 315 (69), 302 (79), complex fragmentation continues.

*4-(Ethoxycarbonyl)-1-ureido-1*H*-1,2,3-triazole* (**19**): IR: 3407, 3270, 3194, 3131, 2994, 1719, 1696, 1595, 1549, 1480. ^{1}H-NMR ((D_6)DMSO): 10.48 (*s*, disapp. on deut., NH); 8.80 (*s*, H–C(5)); 6.55 (br. *s*, disapp. on deut., NH_2); 4.32 (*q*, J = 7.09, CH_2); 1.31 (*t*, J = 7.13, Me). ^{13}C-NMR ((D_6)DMSO): 14.06; 60.51; 131.28; 137.29; 155.93; 159.95. EI-MS: 399 (2), 356 (4), 353 (4), 310 (10), 267 (7), 255 (8), 229 (7), 211 (11), 201 (92), 183 (54), 172 (35), 158 (100). CI-MS: 200 (13, $[M + 1]^+$), 199 (6, $M^{+\cdot}$), 157 (22), 119 (10), 93 (20), 89 (100).

*4-[1-(Semicarbazono)ethyl]-1-ureido-1*H*-1,2,3-triazole* (**23**): IR: 3424, 3317, 3214, 1713, 1703, 1671*w*, 1638*w*, 1589, 1489, 1435. ^{1}H-NMR ((D_6)DMSO): 10.36 (*s*, disapp. on deut., NH); 9.32 (*s*, disapp. on deut., NH); 8.63 (*s*, H–C(5)); 6.46 (br. *s*, disapp. on deut., 2 NH_2); 2.24 (*s*, Me). ^{13}C-NMR ((D_6)DMSO): 17.28; 124.65; 129.69; 156.16; 157.17. EI-MS: 302 (21), 289 (28), 287 (25), 285 (42), 256 (13), 243 (18), 241 (28), 239 (38), ..., 78 (99), 63 (100). CI-MS: 249 (7), 234 (7), 227 (20, $[M + 1]^+$), 184 (38), 167 (11), 157 (16), 152 (100), 141 (37), 126 (34), 124 (35), 109 (9), 102 (12), 98 (15), 84 (50), 80 (69).

*4-Acetyl-1-ureido-1*H*-1,2,3-triazole* (**20**; as mixture with **23**). ^{1}H-NMR ((D_6)DMSO): 2.55 (*s*, Me). ^{13}C-NMR ((D_6)DMSO): 26.84; 137.90; 145.60.

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