Unusual Direction of Cyclocondensation of 1-(4-Chlorophenyl)-3,5-diamino-1,2,4-triazole, Pyruvic Acid, and Aldehydes

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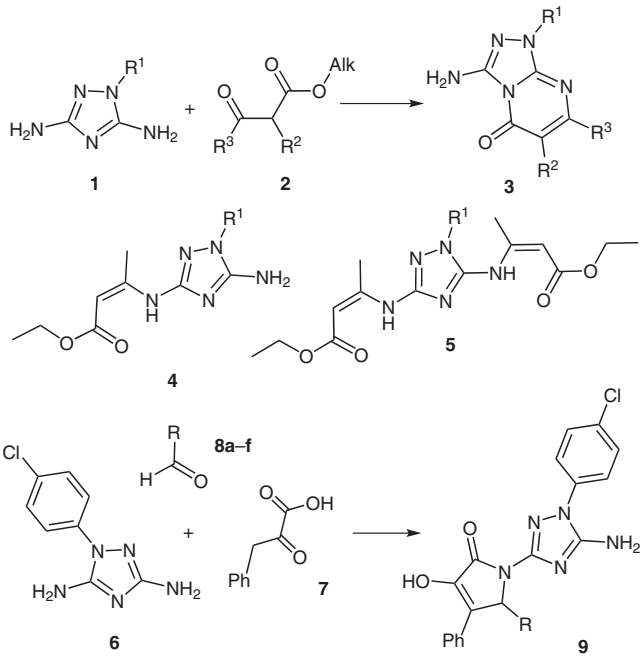
Abstract: The reactivity of 1-(4-chlorophenyl)-3,5-diamino-1,2,4-triazole in multicomponent reactions with pyruvic acid and aldehydes and in two-component reactions with arylidenepyruvic acid was studied. The unusual direction of these treatments leading to the formation of unprecedented 3-[5-amino-1-(4-chlorophenyl)-1,2,4-triazol-3-ylamino]-5-arylfuran-2-ones instead of triazolopyrimidine or triazolylpyrrolone derivatives was found and discussed.

Key words: heterocycles, multicomponent reaction, furans, nucleophiles, regioselectivity

Pyruvic acid and its derivatives play an important role in biological processes and being a part of some pharmacologically active compounds are challenging building blocks for heterocyclization reactions.[1] In our recent publications, several examples of multicomponent and sequential (linear) reactions involving pyruvic acids and polyfuctional aminoazoles were discussed from the viewpoints of their selectivity and molecular diversity.[2] In particular, the influence of temperature, catalytic system, activation method, and structural factors on the reaction directions were presented. It was shown that variation of these parameters can be effective tools to control the selectivity of processes involving pyruvic acids[2] as well as other types of heterocyclizations.[3]

Among the polyfunctional aminoazoles applied in heterocyclizations with carbonyl compounds, 3,5-diamino-1,2,4-triazole is an attractive target due to the presence of several alternative reaction centers and possibility of further modification of the cyclization products. The usual direction of multicomponent reactions of this diaminoazole with aldehydes and active methylene compounds (CH acids) is a formation of pyrimidine ring with participation of NH_2 group and one of the endocyclic nitrogen.[1,4] The second amino group is able to take part in further transformations of the heterocycles obtained.[4b] Introducing an aryl substituent at position 1 of the diaminotriazole gave rise to specific properties, which have been studied in detail by Chernyshev et al.,[5] Papini et al.,[6] and other authors.[7,8] However, the reactions of 1-aryl-substituted 3,5-diamino-1,2,4-triazoles **1** with β-keto esters **2** led to the formation of pyrimidine cycles[5a,8] (compounds **3**, Scheme 1) as it was observed for other types of (di)amino-1,2,4-triazoles.[1] On the hand, in some cases the isolation of only noncyclized compounds like **4**, **5** and similar products was described.[6] Another possible direction of heterocyclization leading to pyrrolone derivatives **9** was observed in the multicomponent reaction between phenylpyruvic acid (**7**), 1-(4-chlorophenyl)-3,5-diamino-1,2,4-triazole (**6**), and aromatic aldehydes **8a**–**f**.[2c]



Scheme 1

Thus, 1-aryl-substituted (di)amino-1,2,4-triazoles are able to participate in reactions with electrophiles with formation of several types of heterocyclic or noncyclic final compounds. In the present article, we describe a new unusual direction of the multicomponent treatment[9] of 1-(4-chlorophenyl)-3,5-diamino-1,2,4-triazole with pyruvic acid and aldehydes or its linear reactions with arylidenepyruvic acids yielding earlier undisclosed derivatives of triazolylfuranone.

It was established that three-component treatment of 1-(4-chlorophenyl)-3,5-diamino-1,2,4-triazole (**6**), aromatic aldehydes **8a**–**f**, and pyruvic acid (**10**) in boiling DMF took place in an unusual direction and unexpectedly gave

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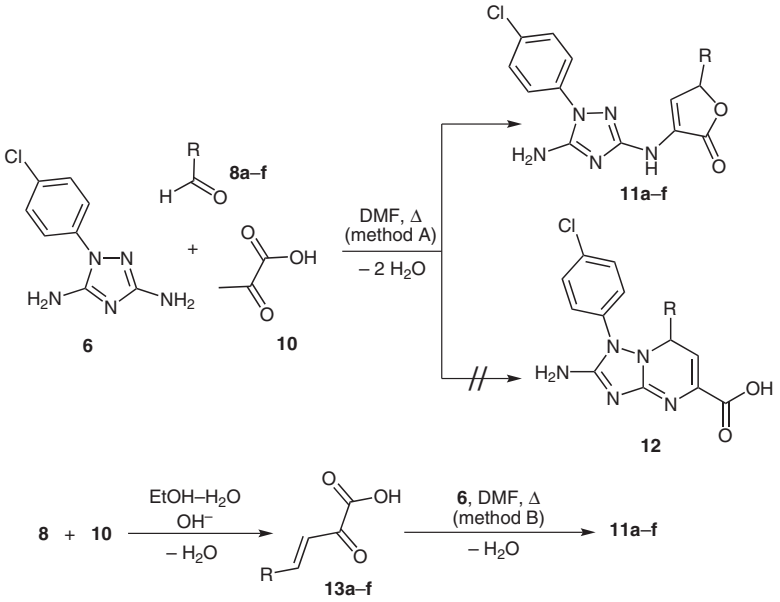


Scheme 2

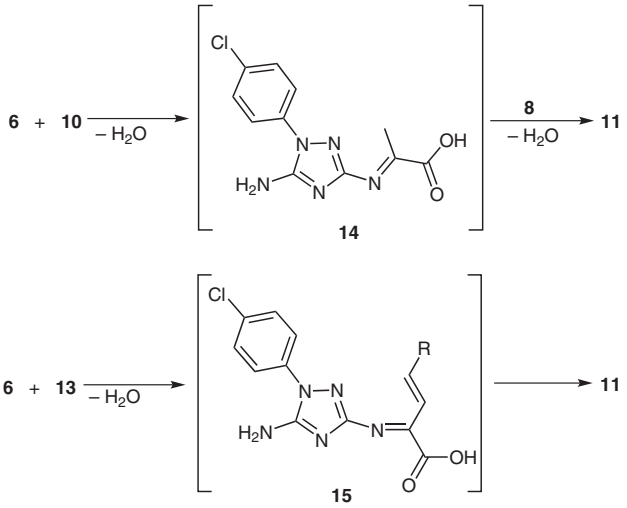
as the sole reaction product unprecedented 3-[5-amino-1-(4-chlorophenyl)-1*H*-1,2,4-triazol-3-ylamino]-5-arylfuran-2-ones **11a–f** in 50–70% yields (Method A, Scheme 2, Table 1). Surprisingly, neither triazolopyrimidines **12**, the formation of which was earlier described in the similar multicomponent treatment involving 1-unsubstituted 3-amino-1,2,4-triazole,[2a] nor pyrrolone derivatives of type **9**, which were produced in the case of phenylpyruvic acid reactions,[2c] were isolated or even chromatographically detected in the mother liquor.

Table 1 3-[5-Amino-1-(4-chlorophenyl)-1*H*-1,2,4-triazol-3-ylamino]-5-arylfuran-2-ones **11a–f**

Entry	R	Product	Yield (%)	
			Method A	Method B
1	Ph	**11a**	60	52
2	4-$MeOC_6H_4$	**11b**	63	48
3	4-BrC_6H_4	**11c**	68	50
4	4-ClC_6H_4	**11d**	70	51
5	4-$HO_2CC_6H_4$	**11e**	50	47
6	4-MeC_6H_4	**11f**	58	58

In the case of a sequential reaction via preliminary synthesis of arylidenepyruvic acids, the direction of the treatment was identical to the multicomponent procedure. It was found that refluxing aminoazole **6** and unsaturated acids **13a–f** in DMF led to the formation of the same triazolylfuranones **11a–f**, however, in smaller yields (Method B, Scheme 2, Table 1).

The most probable way for the formation of triazolylfuranones **11** in this multicomponent reaction includes attack of one of the NH_2 groups on the β-carbonyl group of pyruvic acid, formation of azomethine **14**, and further cyclization of its enamine form with an aldehyde molecule into the corresponding furanone (Scheme 3). Formation of imines like **14** in similar heterocyclizations involving aromatic or heterocyclic amines and pyruvic acids was previously described and discussed in several publications.[10] Other possible pathways, for example, via preliminary treatment of pyruvic acid with aldehyde giving arylidenepyruvic acids **13** or whole furanone nucleus are doubtful according to our earlier results obtained for analogous multicomponent reactions.[2a,c]



Scheme 3

An alternative direction of the heterocyclization leading to triazolopyrimidines **12** is connected with a loss of aromaticity by the aminoazole fragment during the reaction explaining why this pathway is disfavored (Scheme 2).

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On the other hand, isolation of triazolylpyrrolones **9** instead of furanones **11**, which was observed in the three-component heterocyclization involving phenylpyruvic acid,[2c] can be explained by the specific influence of the phenyl substituent preventing the formation of intermediate like **14**.

It seems that the reaction of aminotriazole **6** with arylidenepyruvic acid **13** can take place via formation of imine **15** and its further cyclization into final heterocycles **11** (Scheme 3).[10e]

The structure of the compounds **11a–f** was established by elemental analysis, mass spectrometry, ^{1}H and ^{13}C NMR spectroscopy with application of NOE, and X-ray diffraction study. For example, ^{1}H NMR spectra of **11a–f** exhibit doublets of two CH groups at 6.0–7.2 ppm (^3J = ~2.1–2.5 Hz), signals of aromatic protons (6.5–7.8 ppm), a singlet of NH group at ca. 9.0 ppm, a broad singlet of NH_2 group at 6.6 ppm, and appropriate signals of terminal substituents. NOE experiments, in particular, showed the presence of cross-peaks between NH_2 group and the *ortho*-proton of the *N*-aryl substituent (Figure 1) in compound **11b** that allowed to identify which exocyclic amino group was involved in the reaction. Signals of protons for both *para*-substituted aryl rings were assigned according to NOE correlations of methoxy group.

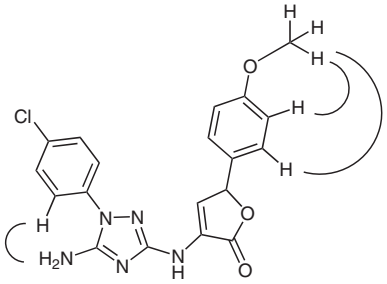

Figure 1 Some NOE correlations for compound **11b**

The regioselectivity of the reaction regarding the NH_2 groups is concerned with sterical influence of chlorophenyl substituent on amino group in position 5 hampering its participation in the treatment.

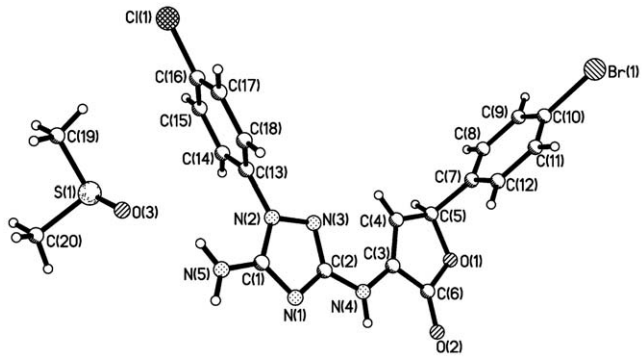

Figure 2 Molecular structure of compound **11c** (X-ray diffraction data)

The final structure assignment about structures of the compounds synthesized was made on the basis of X-ray diffraction data obtained for single crystal of heterocycle **11c** (Figure 2).

In summary, an introduction of aryl substituent in position 1 of aminotriazole affects the direction of multicomponent reactions with pyruvic acid and aldehydes. In contrast to 1-unsubstituted 3,(5)-(di)amino-1,2,4-triazoles such treatment involving 1-(4-chlorophenyl)-3,5-diamino-1,2,4-triazole proceeds in an unusual way with formation of unprecedented 3-[5-amino-1-(4-chlorophenyl)-1*H*-1,2,4-triazol-3-ylamino]-5-arylfuran-2-ones instead of triazolopyrimidine derivatives.

Melting points were obtained on a standard melting point apparatus in open capillary tubes. The ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 at 200 MHz (50 MHz for ^{13}C) on Varian Mercury VX-200 spectrometers. High-resolution mass spectra were measured on a GC-MS Varian 1200L spectrometer (ionizing voltage 70 eV). Elemental analysis was made on a EuroVector EA-3000. TLC analyses were performed on precoated (silica gel 60 HF_{254}) plates. All solvents and chemicals were obtained from standard commercial vendors and used without any purification.

3-[5-Amino-1-(4-chlorophenyl)-1*H*-1,2,4-triazol-3-ylamino]-5-arylfuran-2(5*H*)-ones 11a–f; General Procedure

Method A: A mixture containing 3,5-diamine-1-(4-chlorophenyl)-1,2,4-triazole (**6**; 100 mg, 0.5 mmol), the corresponding aldehyde **8a–f** (0.5 mmol) and pyruvic acid (**10**; 40 mg, 0.03 mL, 0.5 mmol) in DMF (0.5 mL) was refluxed for 5 min. The reaction mixture was cooled to r.t. and diluted with EtOH (10 mL). The precipitate formed was collected by filtration, washed with EtOH (2 mL), and dried.

Method B: A mixture containing 3,5-diamine-1-(4-chlorophenyl)-1,2,4-triazole (**6**; 210 mg, 1 mmol) and arylidenepyruvic acid **13a–f** (1 mmol) in DMF (0.7 mL) was refluxed for 5 min. After cooling to r.t., EtOH (10 mL) was added and the mixture was allowed to stand overnight. The precipitate formed was isolated by filtration, washed with EtOH (10 mL), and air-dried.

3-[5-Amino-1-(4-chlorophenyl)-1*H*-1,2,4-triazol-3-ylamino]-5-phenylfuran-2(5*H*)-one (11a)

Yellow solid; mp 212–214 °C.

^{1}H NMR (200 MHz, DMSO-d_6): δ = 6.16 (d, J = 2.3 Hz, 1 H, CH), 6.58 (br s, 1 H, NH_2), 7.07 (d, J = 2.3 Hz, 1 H, CH), 7.24–7.63 (m, 9 H, ArH), 9.02 (s, 1 H, NH).

^{13}C NMR (50 MHz, DMSO-d_6): δ = 81.9, 102.9, 122.2, 124.3, 127.3, 129.4, 129.9, 131.0, 132.9, 137.1, 137.7, 154.8, 157.8, 169.9.

MS (EI, 70 eV): m/z (%) = 367 (22, [M$^+$]), 323 (25), 153 (100).

Anal. Calcd for $C_{18}H_{14}ClN_5O_2$: C, 58.78; H, 3.84; N, 19.04. Found: C, 58.81; H, 3.84; N, 19.01.

3-[5-Amino-1-(4-chlorophenyl)-1*H*-1,2,4-triazol-3-ylamino]-5-(4-methoxyphenyl)furan-2(5*H*)-one (11b)

Yellow solid; mp 210–212 °C.

^{1}H NMR (200 MHz, DMSO-d_6): δ = 3.73 (s, 3 H, CH_3O), 6.11 (d, J = 2.1 Hz, 1 H, CH), 6.60 (br s, 1 H, NH_2), 7.04 (d, J = 2.1 Hz, 1 H, CH), 6.88–7.62 (m, 8 H, ArH), 9.0 (s, 1 H, NH).

^{13}C NMR (50 MHz, DMSO-d_6): δ = 55.9, 81.8, 114.9, 122.2, 124.2, 128.2, 129.1, 129.3, 129.9, 131.0, 137.0, 154.7, 157.8, 160.5, 169.9.

MS (EI, 70 eV): m/z (%) = 397 (13, [M$^+$]), 338 (20), 153 (100).

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Anal. Calcd for $C_{19}H_{16}ClN_5O_3$: C, 57.36; H, 4.05; N, 17.6. Found: C, 57.39; H, 4.02; N, 17.65.

3-[5-Amino-1-(4-chlorophenyl)-1*H*-1,2,4-triazol-3-ylamino]-5-(4-bromophenyl)furan-2(5*H*)-one (11c)
Yellow solid; mp 208–210 °C.

^{1}H NMR (200 MHz, DMSO-d_6): δ = 6.16 (d, J = 2.1 Hz, 1 H, CH), 6.55 (br s, 1 H, NH_2), 7.06 (d, J = 2.1 Hz, 1 H, CH), 7.22–7.67 (m, 8 H, ArH), 8.98 (s, 1 H, NH).

^{13}C NMR (50 MHz, DMSO-d_6): δ = 81.1, 121.7, 122.6, 124.4, 128.3, 129.5, 129.9, 131.1, 132.4, 137.1, 137.2, 154.8, 157.7, 169.7.

MS (EI, 70 eV): m/z (%) = 445 (12, [M$^+$]), 252 (20), 153 (100).

Anal. Calcd for $C_{18}H_{13}BrClN_5O_2$: C, 48.4; H, 2.93; N, 15.68. Found: C, 48.37; H, 2.9; N, 15.64.

X-ray Diffraction Analysis
The colorless crystals of **11c** ($C_{18}H_{13}BrClN_5O_2{\cdot}C_2H_6OS$) are monoclinic. At 293 K, a = 19.7450(8), b = 5.4916(3), c = 21.8240(9) Å, β = 106.709(5)°, V = 2266.5(2) Å^3, Mr = 524.82, Z = 4, space group $P2_1/n$, d_{calc} = 1.538 g/cm^3, μ(MoK$_\alpha$) = 2.056 mm^{-1}, F(000) = 1064. Intensities of 7131 reflections (3776 independent, R_{int} = 0.040) were measured on the 'Xcalibur-3' diffractometer (graphite monochromated MoK$_\alpha$ radiation, CCD detector, ω-scaning, 2θmax = 50°). The structure was solved by direct method using SHELXTL package.[11] The absorption correction was performed by multiscan method (T_{min} = 0.578, T_{max} = 0.904). Positions of the hydrogen atoms were located from electron density difference maps and refined by 'riding' model with Uiso = nUeq of the carrier atom (n = 1.5 for methyl groups and n = 1.2 for other hydrogen atoms). Full-matrix least-squares refinement against F2 in anisotropic approximation for non-hydrogen atoms using 3737 reflections was converged to $wR2$ = 0.154 [$R1$ = 0.054 for 1597 reflections with F>4σ(F), S = 0.859].[12]

3-[5-Amino-1-(4-chlorophenyl)-1*H*-1,2,4-triazol-3-ylamino]-5-(4-chlorophenyl)furan-2(5*H*)-one (11d)
Yellow solid; mp 222–224 °C.

^{1}H NMR (200 MHz, DMSO-d_6): δ = 6.18 (d, J = 2.2 Hz, 1 H, CH), 6.56 (br s, 1 H, NH_2), 7.07 (d, J = 2.2 Hz, 1 H, CH), 7.28–7.65 (m, 8 H, ArH), 9.0 (s, 1 H, NH).

^{13}C NMR (50 MHz, DMSO-d_6): δ = 81.1, 121.7, 124.3, 128.4, 129.2, 129.5, 129.9, 131.1, 134.2, 136.7, 137.1, 154.7, 157.7, 169.7.

MS (EI, 70 eV): m/z (%) = 401 (16, [M$^+$]), 357 (20), 194 (27), 153 (100).

Anal. Calcd for $C_{18}H_{13}Cl_2N_5O_2$: C, 53.75; H, 3.26; N, 17.63. Found: C, 53.71; H, 3.22; N, 17.61.

4-{4-[5-Amino-1-(4-chlorophenyl)-1*H*-1,2,4-triazol-3-ylamino]-5-oxo-2,5-dihydrofuran-2-yl}benzoic Acid (11e)
Yellow solid; mp 258–260 °C.

^{1}H NMR (200 MHz, DMSO-d_6): δ = 6.26 (d, J = 1.8 Hz, 1 H, CH), 6.59 (br s, 1 H, NH_2), 7.1 (d, J = 1.8 Hz, 1 H, CH), 7.33–8.07 (m, 8 H, ArH), 9.1 (s, 1 H, NH), 12.99 (br s, 1 H, CO_2H).

^{13}C NMR (50 MHz, DMSO-d_6): δ = 81.2, 122.0, 124.3, 127.4, 128.1, 129.9, 130.5, 130.9, 131.8, 136.9, 142.4, 154.6, 157.7, 167.5, 169.8.

MS (EI, 70 eV): m/z (%) = 411 (2, [M$^+$]), 367 (5), 209 (61).

Anal. Calcd for $C_{19}H_{14}ClN_5O_4$: C, 55.42; H, 3.43; N, 17.01. Found: C, 55.38; H, 3.39; N, 17.05.

3-[5-Amino-1-(4-chlorophenyl)-1*H*-1,2,4-triazol-3-ylamino]-5-*p*-tolylfuran-2(5*H*)-one (11f)
Yellow solid; mp 216–218 °C.

^{1}H NMR (200 MHz, DMSO-d_6): δ = 2.28 (s, 3 H, CH_3), 6.11 (d, J = 2.1 Hz, 1 H, CH), 6.59 (br s, 1 H, NH_2), 7.04 (d, J = 2.1 Hz, 1 H, CH), 7.16–7.59 (m, 8 H, ArH), 9.0 (s, 1 H, NH).

^{13}C NMR (50 MHz, DMSO-d_6): δ = 21.4, 81.9, 122.2, 122.3, 124.3, 127.4, 128.1, 129.9, 130.0, 134.6, 137.1, 139.0, 154.7, 157.8, 169.9.

MS (EI, 70 eV): m/z (%) = 381 (37, [M$^+$]), 337 (47), 194 (43).

Anal. Calcd for $C_{19}H_{16}ClN_5O_2$: C, 59.77; H, 4.22; N, 18.34. Found: C, 59.73; H, 4.19; N, 18.31.

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(12) The final atomic coordinates, and crystallographic data for molecule **11c** have been deposited to with the Cambridge Crystallographic Data Centre, 12 Union Road, CB2 1EZ, UK [fax: +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk] and are available on request quoting the deposition number CCDC 793788.

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