REACTIONS WITH HETEROCYCLIC AMIDINES: NEW ROUTES FOR THE SYNTHESIS OF NOVEL AZOLO[1,5-*a*]PYRIMIDINE, BENZO[4,5]IMIDAZO[1,2-*a*]PYRIMIDINE, SOME PYRIDINE, PYRAN AND PYRAZOLE DERIVATIVES CONTAINING THE ANTIPYRINE MOIETY†

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†This paper is dedicated to the soul of Prof. Zaghloul E. Kandeel

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Abstract

Some novel pyrazolo[1,5-*a*]pyrimidines **5a,e**, 1,2,4-triazolo[1,5-*a*]pyrimidine **10** and benzo[4,5]imidazo[1,2-*a*]pyrimidine **15** could be synthesized by reacting 3-dimethylamino-2-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazole-4-carbonyl)-acrylonitrile (**2**) with 5-amino-3,4-substituted-1*H*-pyrazoles **3a-e**, 3-amino-1,2,4-triazole **9** and 2-aminobenzimidazole **12** respectively. The reaction of **2** with 2-benzimidazolylacetonitrile (**17**) afforded the benzo[4,5]imidazo[1,2-*a*]pyridine **18**. On the other hand, the reaction of **2** with hydrazine, phenylhydrazine, malononitrile dimer and ethyl cyanoacetate dimer produced the pyrazoles **22**, **23**, the pyridine **26** and the pyrone **28**, respectively.

Introduction

1-Phenyl-2,3-dimethyl-3-pyrazoline-5-one (antipyrine or phenazone) has attracted a great deal of interest due to its wide applications in the field of pharmaceuticals.[1-5] In continuation of our interest in the development of new and simple methods for the synthesis of polyfunctionally substituted heterocycles with anticipated biologiacal activity that could be used as biodegradable agrochemicals,[6-12] we report here on the reactivity of phenazonylacetonitrile (**1**) towards some nitrogen containing compounds. The work has resulted in the formation of a variety of heterocyclic compounds incorporating an antipyrine moiety. Also, the biological activity reported for pyrazolo[1,5-*a*]pyrimidines have stimulated chemists to develop the chemistry of this class of compounds.[9,13-15] Enaminones have recently been reported as useful precursors for the synthesis of pyrazolo[1,5-*a*]pyrimidines.[16-18] Therefore in continuation of our previous interest[20,21] in the synthesis of a variety of heterocyclic systems from the readily obtainable inexpensive starting materials for biological screening program in our laboratory, we report here on the behavior of the hitherto unreported 3-dimethylamino-

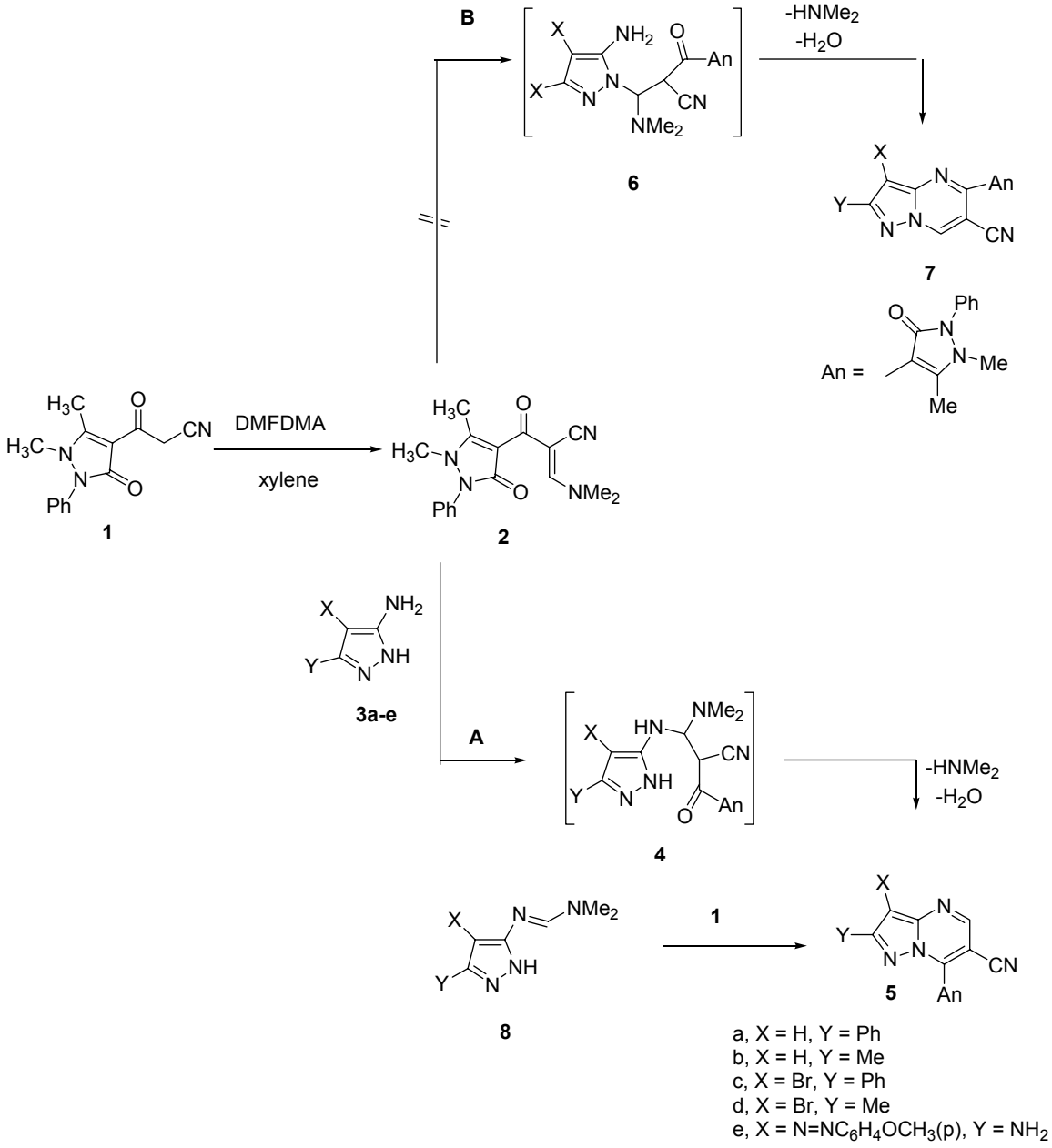
2-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazole-4-carbonyl)acrylonitrile (**2**) towards some nitrogen nucleophiles.

Results and discussion

It seemed much better to prepare compound **2** by heating an equimolar amounts of phenazonylacetonitrile (**1**) and *N*,*N*-dimethylformamide dimethyl acetal (DMFDMA) in dry xylene under gentle reflux for a short time rather than following a recently reported procedure by Kappe et al.[19] The structure of compound **2** was elucidated on the basis of its elemental analysis and spectral data (Scheme **1**).

Compound **2** reacted with some substituted 5-amino-1*H*-pyrazole derivatives **3a-e** in ethanol in the presence of piperidine as a catalyst to afford the substituted pyrazolo[1,5-*a*]pyrimidine derivatives **5a-e**. Structure of the latter products was confirmed on the basis of their correct elemental and spectral data (*cf.* experimental). The formation of compounds **5a-e** assumed to take place *via* an initial Michael addition of the exocyclic amino group in compound **3** to the activated double bond in **2** to give the acyclic non-isolable intermediate **4** (route A), which undergo cyclization and aromatization *via* loss of both dimethylamine and water molecules producing the final isolable products **5a-e**. Although the endocyclic imino group in compounds **3a-e** is the most nucleophilic center,[20-22] nevertheless, it is the most sterically hindered site[23] therefore, the reaction is assumed to take place *via* route A rather than route B as shown in Scheme **1**. Structure **5** was further confirmed *via* an independent synthesis of compound **5a** by reacting equimolar amounts of **8a** with **1** in ethanol under reflux to provide a product identical in all aspects (m.p., TLC, and spectra) with those of the proposed structure **5**.

Similarly, compound **2** reacted with 3-amino-1,2,4-triazole (**9**) to yield the triazolopyrimidine **10** in good yield (Scheme **2**). The structure of compound **10** was assigned by means of its spectral properties. Furthermore, the structure of compound **10** was confirmed by an independent synthesis of the same compound *via* reacting an equimolar amount of compound **11** with **1** in ethanol containing catalytic amount of piperidine under reflux to afford a product identical in all aspects to compound **10**.

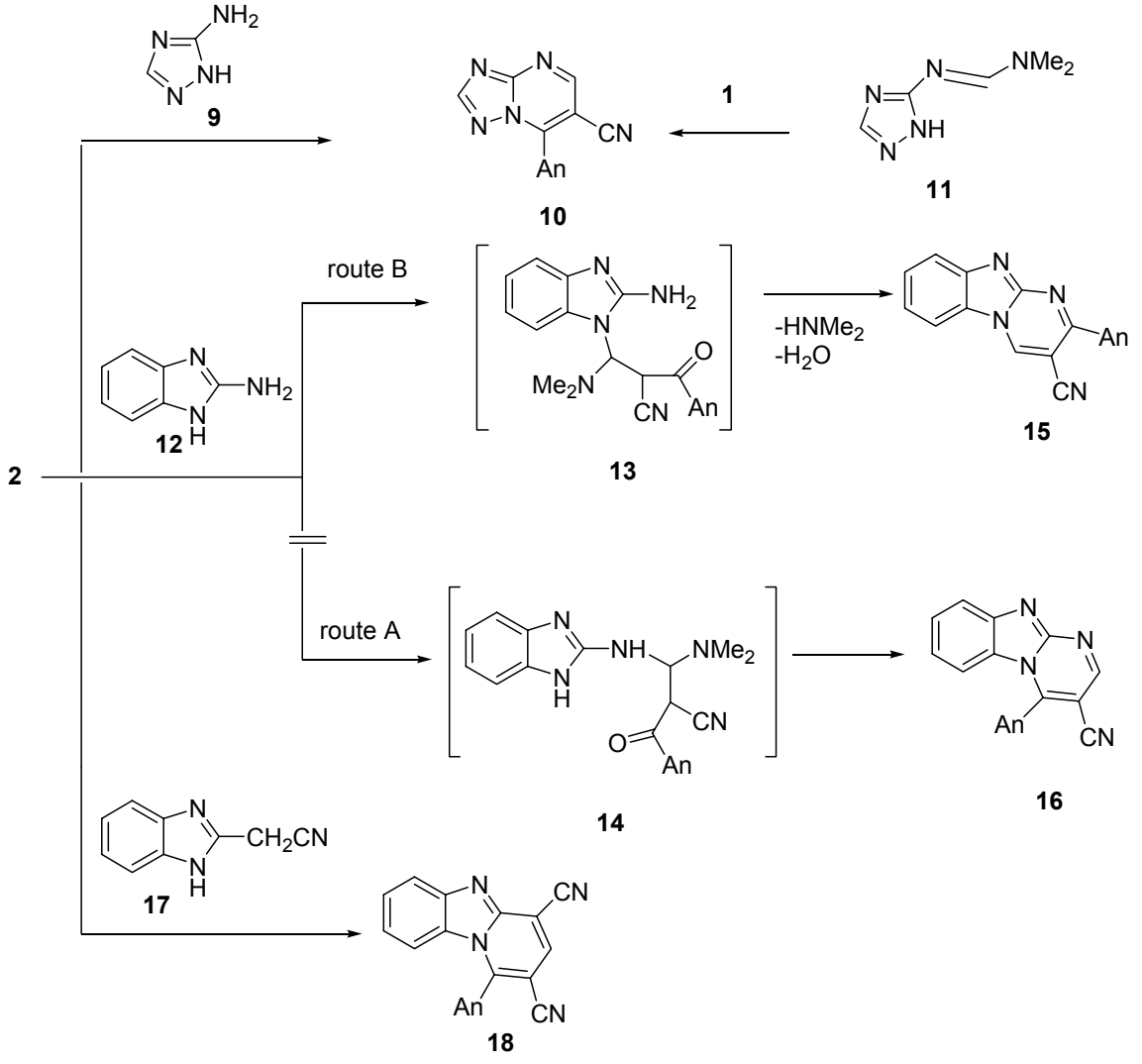


Scheme 1

In contrast to its behavior towards compounds **5** and **10**, compound **2** reacted with 2-aminobenzimidazole **12** under the same experimental conditions to afford the benzo[4,5]imidazo[1,2-*a*]pyrimidine derivative **15** (Scheme **2**). The structure of compound **15** was established on the basis of elemental analysis and spectral data of the isolated reaction product. Formation of **15** is assumed to proceed *via* an initial Michael addition of the imino function in compound **12** to the activated double bond in **2** to form the non-isolable acyclic intermediate **13** (route B) that undergoes cyclization and

aromatization affording **15**. The discrepancy in the behavior of compounds **5**, **10** and **15** can be explained on the basis of steric factors. Thus if the final product proceeds according to route A, the formation of compound **16** would be difficult due to steric interaction of the antipyrinyl moiety and the benzene ring of benzimidazole nucleus.

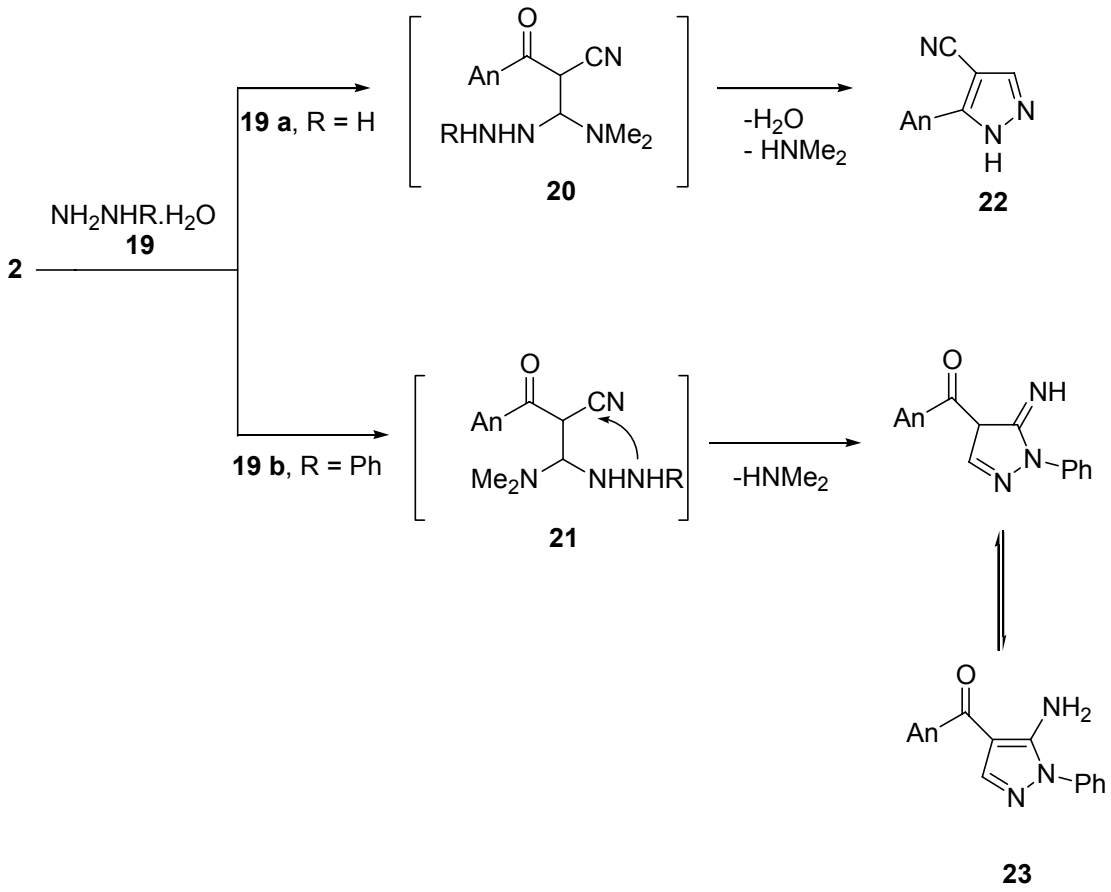
In a similar manner, compound **2** was subjected to react with 2-benzimidazolylacetonitrile (**17**), under the same experimental conditions and afforded a yellow crystalline product, which was identified as **18** on the basis of its elemental analysis and spectral data (Scheme **2**).



Scheme 2

Also, compound **2** underwent cyclocondensation on treatment with hydrazine hydrate or its derivatives **19** to afford the non-readily available pyrazole **22**. Structure of

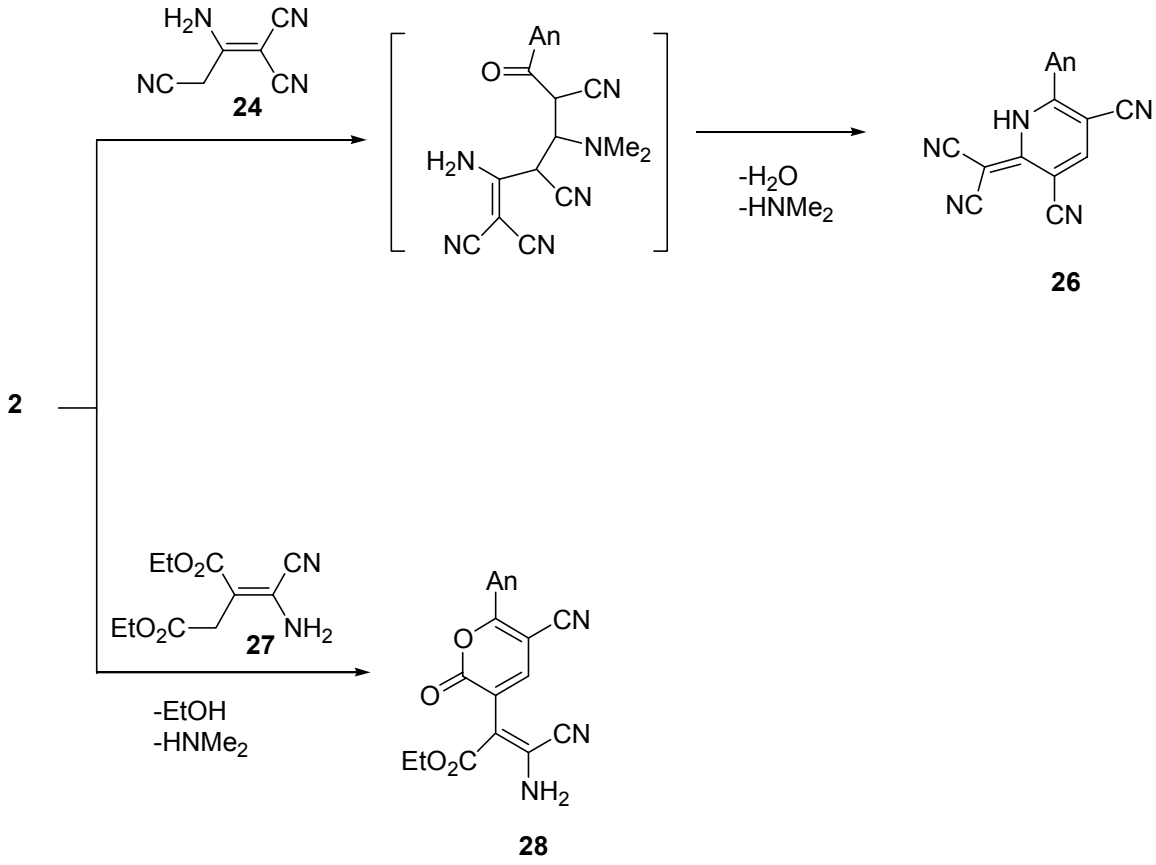
22 was established on the basis of elemental analysis and spectral data of the isolated reaction product. On the other hand, compound **2** reacted with phenylhydrazine (**19b**) under the same experimental conditions and afforded the pyrazolone derivative **23**. Formation of compounds **22** and **23** is assumed to proceed *via* addition of the amino function in hydrazine hydrate (**19a**) or phenylhydrazine (**19b**) to the activated double bond in **2** to form the non-isolable acyclic hydrazine derivatives **20** and **21** that underwent cyclization *via* either loss of one water molecule and dimethylamine providing **22** or addition of the NH- group to the cyano function yielding **23**, respectively (Scheme **3**).



Scheme 3

In addition, compound **2** was allowed to react with malononitrile dimer (**24**) to give the pyridine derivative **26**. Compound **26** was assigned as a reaction product in accordance with elemental analysis and spectral data (*cf.* experimental). Following the same manner, compound **2** reacted with ethyl cyanoacetate dimer (**27**) to afford the pyrone derivative **28**. Formation of the compound **28** is thought to proceed *via* initial

addition of the active methylene group in **27** to the activated double bond in **2** followed by elimination of ethanol and dimethylamine molecules producing the final isolable product **28** (Scheme 4).



Scheme 4

Experimental

All melting points are uncorrected. IR spectra were recorded in KBr disks using a Shimadzu IR-740 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Ac-80 spectrometer with [$^{2}H_6$] DMSO as solvent and TMS as internal standard; chemical shifts are reported in δ units (ppm). Mass spectra were measured on Gs/MS INCOS XL Finnigan MAT. Microanalysis was performed on LECOCHNS-932.

3-Dimethylamino-2-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazole-4-carbonyl)acrylonitrile (2).

A mixture of phenazonylacetonitrile **1** (0.01 mol), xylene (10 ml) and *N*,*N*-dimethylformamide dimethylacetal (0.01 mol) was heated under reflux for 2 hours, cooled and the solid product that deposited was filtered off and recrystallized from EtOH to give **2** as yellow crystals, yield 85%, m.p. 205-207 °C. IR (cm^{-1}): 2202 (CN), 1700 (CO), 1639 (CO-antipyrinyl). ^{1}H NMR δ_H: 3.15 (s, 3H, CH_3), 3.20 (s, 3H, CH_3), 3.25 (s, 3H, CH_3), 3.36 (3H, CH_3), 7.22-7.42 (m, 5H, Ph), 7.9 (s, 1H, ylidenic H). ^{13}C NMR δ_C: 187.0 (CO), 160.0 (CO-amide), 176.0, 174.0, 112.7, 91.5 (vinylic-carbons), 142.0, 129.0, 118.9, 117.2, 112.0, 112.0 (aromatic-carbons), 40.7, 40.7, 35.3, 17.3 (aliphatic-carbons). Anal.Calcd. for $C_{17}H_{18}N_4O_2$ (310.34). C, 65.79; H, 5.85; N, 18.05. Found: C, 65.60; H, 5.67; N, 18.23. MS: 310 m^+/z.

The preparation of compounds 5a-e.

Method (A):

A solution of **2** (0.01 mol) in abs. ethanol (30ml) was mixed with the appropriate pyrazole derivative **3a-e** (0.01 mol) and a few drops of piperidine. The reaction mixture was heated under reflux for 3 hours, and the solvent was evaporated *in vacuo*. The remaining product was collected by filtration and recrystallized to give **5a-e**.

Method (B):

A solution of compound **8a** (0.01 mol) in abs. ethanol (30ml) was treated with the the enamine **1** (0.01 mol). The reaction mixture was heated under reflux for 3 hours, and the solvent was evaporated *in vacuo*. The remaining product was collected by filtration and recrystallized to give **5a**.

7-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)-2-phenyl pyrazolo[1,5-*a*]pyrimidine-6-carbonitrile (5a). Compound **5a** was obtained as yellow crystals from ethanol, yield 80%, m.p. 265-267 °C. IR (cm^{-1}): 2229 (CN), 1656 (CO-antipyrinyl). ^{1}H NMR δ_H: 2.38 (s, 3H, CH_3), 3.38 (s, 3H, CH_3), 7.05 (s, 1H, CH), 7.39-7.94 (m, 10H, 2Ph), 8.49 (s, 1H, CH). ^{13}C NMR δ_c: 160.7 (CO-amide), 165.9, 161.8, 105.3 (pyrimidine-carbons), 150.4, 134.4, 103.7 (pyrazole-carbons), 154.5, 107.9 (vinyle-carbons), 118.7 (nitrile-carbon), 142.0, 136.0, 129.0, 129.0, 129.0, 129.0, 128.5,

127.0, 127.0, 118.9, 112.0, 112.0 (aromatic-carbons), 35.6, 17.4 (aliphatic-carbons). Anal. Calcd. for $C_{24}H_{18}N_6O$ (406.15) C,70.92; H, 4.46; N, 20.68. Found: C, 70.60; H, 4.67; N, 20.23. MS: 406 m^+/z.

7-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)-2-methyl pyrazolo[1,5-*a*]pyrimidine-6-carbonitrile (5b). Compound **5b** was obtained as yellow crystals from ethanol, yield 70%, m.p. 225-227 °C. IR (cm^{-1}): 2229 (CN), 1656 (CO-antipyrinyl). ^{1}H NMR δ_H: 2.36 (s, 3H, CH_3), 2.51 (s, 3H,CH_3), 3.33 (s, 3H, CH_3), 6.79 (s, 1H, CH), 7.43-7.60 (m, 5H, Ph), 8.73 (s, 1H, CH). ^{13}C NMR δ_c: 161.0 (CO-amide), 166.0, 161.9, 105.5 (pyrimidine-carbons), 144.4, 135.8, 105.3 (pyrazole-carbons), 154.5, 108.0 (vinyle-carbons), 118.2 (nitrile-carbon), 142.2, 129.0, 129.0, 118.9, 112.0, 112.0 (aromatic-carbons), 35.5, 17.2, 13.9 (aliphatic-carbons). Anal. Calcd. for $C_{19}H_{16}N_6O$ (344.37) C,66.27; H, 4.68; N, 24.40. Found: C, 66.60; H, 4.67; N, 24.23. MS: 344 m^+/z.

7-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)-3-bromo-2-phenyl pyrazolo[1,5-*a*]pyrimidine-6-carbonitrile (5c). Compound **5c** was obtained as yellow crystals from aq. ethanol, yield 63%, m.p. 185-187 °C. IR (cm^{-1}): 2220 (CN), 1640 (CO-antipyrinyl). ^{1}H NMR δ_H: 2.39 (s, 3H, CH_3), 3.39 (s, 3H, CH_3), 7.04-7.85 (m, 10H, 2 Ph), 8.48 (s, 1H, CH). ^{13}C NMR δ_c: 160.9 (CO-amide), 165.7, 161.6, 105.1 (pyrimidine-carbons), 150.7, 134.7, 90.9 (pyrazole-carbons), 154.4, 107.7 (vinyle-carbons), 118.0 (nitrile-carbon), 142.3, 136.0, 129.1, 129.1, 129.1, 129.1, 128.7, 127.2, 127.2, 118.8, 112.2, 112.2 (aromatic-carbons), 35.6, 17.6 (aliphatic-carbons). Anal. Calcd. for $C_{24}H_{17}BrN_6O$ (484.34) C,59.39; H, 3.53; N, 17.32. Found: C, 59.60; H, 3.67; N, 17.23. MS: 484 m^+/z.

7-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)-3-bromo-2-methylpyrazolo[1,5-*a*]pyrimidine-6-carbonitrile (5d). Compound **5d** was obtained as yellow crystals from ethanol, yield 70%, m.p.194-196 °C. IR (cm^{-1}): 2224 (CN), 1645 (CO-antipyrinyl). ^{1}H NMR δ_H: 2.39 (s, 3H, CH_3), 2.57 (s, 3H,CH_3), 3.39 (s, 3H, CH_3), 7.04-7.85 (m, 5H, Ph), 8.48 (s, 1H, CH). ^{13}C NMR δ_c: 160.7 (CO-amide), 165.7, 161.6, 105.1 (pyrimidine-carbons), 144.7, 135.1, 92.5 (pyrazole-carbons), 154.4, 107.7 (vinyle-carbons), 118.0 (nitrile-carbon), 142.2, 129.0, 129.0, 118.9, 112.0, 112.0 (aromatic-

carbons), 35.6, 17.6, 6.1 (aliphatic-carbons). Anal. Calcd. for $C_{19}H_{15}BrN_6O$ (423.27) C, 53.91; H, 3.57; N, 19.86. Found: C, 53.80; H, 3.67; N, 19.90. MS: 423 m^+/z.

2-Amino-7-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)-3-(4-methoxyphenylazo)-pyrazolo[1,5-*a*]pyrimidine-6-carbonitrile (5e). Compound **5e** was obtained as reddish brown crystals from aq. ethanol, yield 75%, m.p. 245-247 °C. IR (cm^{-1}): 3411-3263 (NH_2), 2219 (CN), 1656 (CO-antipyrinyl), 1616 (N=N). ^{1}H NMR) δ_H: 2.35 (s, 3H, CH_3), 3.32 (s, 3H, CH_3), 3.80 (s, 3H, OCH_3), 7.29-7.41 (m, 10H, 2 Ph), 8.55 (s, 1H, CH). ^{13}C NMR δ_c: 160.9 (CO-amide), 165.7, 161.6, 105.1 (pyrimidine-carbons), 154.1, 132.7, 91.9 (pyrazole-carbons), 154.5, 107.9 (vinyle-carbons), 118.3 (nitrile-carbon), 159.0, 142.3, 143.2, 129.0, 129.0, 123.3, 123.3, 118.9, 114.6, 114.6, 112.2, 112.2 (aromatic-carbons), 56.2, 35.5, 17.4 (aliphatic-carbons). Anal. Calcd. for $C_{25}H_{21}N_9O_2$ (479.49) C, 62.62; H, 4.41; N, 26.29. Found: C, 62.60; H, 4.67; N, 26.00. MS: 479 m^+/z.

Reaction of 2 with 3-amino-1,2,4-triazole, 2-aminobenzimidazole, benzimidazole-2-acetonitrile, hydrazine hydrate and phenylhydrazine: Formation of compounds 10, 15, 18, 22 /and 23.

A solution of **2** (0.01 mol) and 0.01 mol of compounds **9**, **12**, **17**, hydrazine and / or hydrazine hydrate in absolute ethanol (30 ml) containing catalytic amount of piperidine was heated under reflux for 8 hours. The reaction mixture was cooled and the solid product formed, was collected by filtration and recrystallized to give **10**, **15**, **16**, **22** and **23,** respectively.

7-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)-1,2,4-triazolo [1,5-*a*]pyrimidine-6-carbonitrile (10). Compound **10** was obtained as yellow crystals from ethanol/DMF, yield 60%, m.p. 247-249 °C. IR (cm^{-1}): 2245 (CN), 1664 (CO-antipyrinyl). ^{1}H NMR) δ_H: 2.56 (s, 3H, CH_3), 3.26 (s, 3H, CH_3), 7.20-7.40 (m, 5H, Ph), 8.45 (s, 1H, CH). ^{13}C NMR δ_C: 165.9, 161.8, 105.3 (pyrimidine-carbons), 160.7 (CO-amide), 147.9, 147.9 (triazole-carbons), 154.5, 107.9 (vinyle-carbons), 142.2, 129.0, 129, 119.0, 112.0, 112.0 (aromatic-carbons), 118.2 (nitrile-carbons), 35.6, 17.5 (aliphatic-carbons). Anal. Calcd. for $C_{17}H_{13}N_7O$ (331.33) C,61.62; H, 3.95; N, 29.59. Found: C, 61.60; H, 3.67; N, 29.40. MS: 331 m^+/z.

1-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)benzo[4,5] imidazo[1,2-*a*]pyrimidine-3-carbonitrile (15). Compound **15** was obtained as yellow crystals from ethanol, yield 80%, m.p. 223-225°C. IR (cm^{-1}): 2205 (CN), 1641(CO-antipyrinyl). ^{1}H NMR δ_H: 2.56 (s, 3H, CH_3), 3.26 (s, 3H, CH_3), 7.20-7.40 (m, 9H, Ph + benzoimidazolyl H), 8.45 (s, 1H, CH). ^{13}C NMR δ_C: 166.7, 161.0, 105.3 (pyrimidine-carbons), 160.8 (CO-amide), 154.5, 107.9 (vinyl-carbons), 141.5, 137.9, 137.9, 122.9, 122.9, 115.4, 115.4 (benzimdazole-carbons), 142.5, 129.1, 129, 119.5, 112.2, 112.0 (aromatic-carbons) 118.2 (nitrile-carbon), 35.4, 17.2 (aliphatic-carbons). Anal. Calcd. for $C_{22}H_{16}N_6O$ (380.39) C, 69.46; H, 4.24; N, 22.09. Found: C, 69.60; H, 4.37; N, 22.00. MS: 380 m^+/z.

1-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)benzo[4,5] imidazo[1,2-*a*]pyridin-2,4-dicarbonitrile (18). Compound **18** was obtained as yellow crystals from ethanol, yield 72%, m.p. 273-275 °C. IR (cm^{-1}): 2231 (CN), 1670 (CO-antipyrinyl). ^{1}H NMR δ_H: 2.42 (s, 3H, CH_3), 3.36 (s, 3H, CH_3), 7.51-8.01 (m, 9H, arom-H). ^{13}C NMR δ_C: 163.5, 145.5, 109.3, 108.1 (pyridine-carbons), 160.6 (CO-amide), 154.2, 111.9 (vinyl-carbons), 141.8, 137.3, 137.3, 123.9, 123.9, 115.6, 115.6 (benzimdazole-carbons), 143.5, 129.5, 129.5, 119.4, 112.6, 112.6 (aromatic-carbons) 118.5, 118.5 (nitrile-carbons), 35.6, 17.5 (aliphatic-carbons). Anal. Calcd. for $C_{24}H_{16}N_6O$ (404.42) C, 71.28; H, 3.99; N, 20.78. Found: C, 71.34; H, 3.67; N, 20.70. MS: 404 m^+/z.

1`,5`-Dimethyl-3`-oxo-2`-phenyl-2`,3`-dihydro-2*H*,1`*H*-[3,4`]bipyrazolyl-4-carbonitrile (22). Compound **22** was obtained as yellow crystals from ethanol, yield 90%, m.p. 275-278 °C. IR (cm^{-1}): 3300 (NH), 2189 (CN), 1652 (CO-antipyrinyl). ^{1}H NMR δ_H: 2.41(s, 3H, CH_3), 3.14 (s, 3H, CH_3), 7.28 (s, 1H, CH), 7.29-7.45 (m, 5H, Ph), 9.12 (s, 1H, NH). ^{13}C NMR δ_C: 133.3, 133.3, 104.7 (pyrazole-carbons), 160.8 (CO-amide), 154.5, 118.0 (vinyl-carbons), 142.5, 129.2, 129.2, 119.3, 112.1, 112.1 (aromatic-carbons), 118.0 (nitrile-carbon), 35.4, 17.3 (aliphatic-carbons). Anal. Calcd. for $C_{15}H_{13}N_5O$ (279.29) C, 64.51; H, 4.69; N, 25.08. Found: C, 64.60; H, 4.63; N, 25.18. MS: 279 m^+/z.

4-(5-Amino-1-phenyl)-1*H*-pyrazole-4-carbonyl)-1,5-dimethyl-2-phenyl-1,2-dihydropyrazole-3-one (23). Compound **23** was obtained as yellow crystals from ethanol, yield 80%, m.p. 282-284 °C. IR (cm^{-1}): 3340-3256 (NH_2), 2200 (CN), 1650 (CO-antipyrinyl). ^1H NMR δ_H: 2.31(s, 3H, CH_3), 3.24 (s, 3H, CH_3), 5.63 (s, 2H, NH_2), 6.32 (s, 1H, CH), 6.66-7.45 (m, 10H, 2Ph). ^{13}C NMR δ_C: 147.0, 139.0, 94.0 (pyrazole-carbons), 187.1 (CO), 160.8 (CO-amide), 166.5, 105.4 (vinyl-carbons), 142.5, 142.5, 139.7, 129.2, 129.2, 129.0, 129.0, 126.0, 118.3, 118.3, 112.0, 112.0 (aromatic-carbons), 35.5, 17.3 (aliphatic-carbons). Anal. Calcd. for $C_{21}H_{19}N_5O_2$ (373.40) C, 67.55; H, 5.13; N, 18.76. Found: C, 67.60; H, 5.23; N, 18.20. MS: 373 m^+/z .

Reaction of 2 with malononitrile dimer and ethyl cyanoacetate dimer: Formation of compounds 26 / and 28.

A solution of compound **2** (0.01 mol) and (0.01 mol) of malononitrile dimer or ethyl cyanoacetate dimer in dry pyridine (30 ml) was heated under reflux for 8 hours. The solvent was evaporated *in vacuo* and the product that deposited after cooling was collected by filtration and identified as **26** and **28** respectively.

2-Dicyanomethylene-6-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)-1,2-dihydropyridine-3,5-dicarbonitrile (26). Compound **26** was obtained as brown crystals from aq. ethanol, yield 60%, m.p. 220-222 °C. IR (cm^{-1}): 3300 (NH), 2192-2164 (CN), 1630 (CO-antipyrinyl). ^1H NMR δ_H: 2.52 (s, 3H, CH_3), 3.30 (s, 3H, CH_3), 7.19-7.46 (m, 6H, Ph and NH), 7.70 (s, 1H,CH). ^{13}C NMR δ_C: 175.7, 154.2, 152.5, 144.1, 112.8, 109.0, 82.8, 52.1 (vinyl-carbons), 160.7 (CO-amide), 142.5, 129.2, 129.2, 119.3, 112.1, 112.1 (aromatic-carbons), 117.5, 117.5, 117.5, 117.5 (nitrile-carbons), 35.5, 17.3 (aliphatic-carbons). Anal. Calcd. for $C_{21}H_{13}N_7O$ (379.36) C, 66.48; H, 3.45; N, 25.84. Found: C, 66.60; H, 3.22; N, 25.26. MS: 379 m^+/z.

3-Amino-3-cyano-2-[5-cyano-6-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)-2-oxo-2H-pyran-3-yl]acrylicacidethylester (28). Compound **28** was obtained as yellow crystals from ethanol, yield 75%, m.p. 192-194 °C. IR (cm^{-1}): 3300-3228 (NH_2), 2208 (CN), 1630 (CO-antipyrinyl). ^1H NMR δ_H: 1.3 (t, 3H, CH_3), 2.52 (s, 3H, CH_3), 3.00 (s, 2H, NH_2), 3.30 (s, 3H, CH_3), 4.19 (q, 2H, CH_2), 6.71-7.25 (m, 6H, Ph and CH-4). ^{13}C NMR ([$^2H_6$] DMSO) δ_C: 162.5, 152.5, 139.7, 134.5, 128.4, 127.2, 109.3,

85.1 (vinyl-carbons), 165.2, 161.2 (CO-carbons), 160.7 (CO-amide), 142.5, 129.2, 129.2, 119.3, 112.1, 112.1 (aromatic-carbons), 117.2, 117.2 (nitrile-carbons), 60.0, 35.5, 17.3, 13.7 (aliphatic-carbons). Anal. Calcd. for $C_{23}H_{19}N_5O_5$ (445.43) C, 62.02; H, 4.30; N, 15.72. Found: C, 62.00; H, 4.13; N, 15.66. MS: 445 m^+/z.

References and Notes

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Povzetek

Sintetizirali smo nove derivate pirazolo[1,5-*a*]pirimidina, 1,2,4-triazolo[1,5-*a*]pirimidina in benzo[4,5]imidazo[1,2-*a*]pirimidina iz ustrezno substituiranih pirazolov, triazolov oziroma iz 2-aminobenzimidazola.