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1-(N,N-Dimethylamino)-2-(N-phenylcarbamoyl)-1-buten-3-one as a Building Block for the Synthesis of Heterocyclic Compounds

by T.A. Elmaati[1*], S. Said[2], N.A. Elenein[2], M. Sofan[2] and N. Khodeir[2]

[1]*Faculty of Specific Education, Mansoura University, New Damietta, P.O.Box. 34517, Egypt*
[2]*Faculty of Science, Mansoura University, New Damietta, Egypt*

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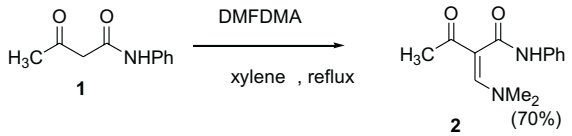
Acetoacetanilide **1** reacted with DMF-DMA to give the enaminone **2**. Compound **2**, when treated with hydrazines gives the pyrazoles **4a** and **4b** respectively, and with pyrazole derivatives **5a** and **5b** the pyrazolopyrimidines **7**. On the other hand, in reaction of **2** with benzimidazole and benzimidazole-2-acetonitrile, the pyrimidobenzimidazole **14** and the pyridobenzimidazole **17** were formed. **2** reacts with hippuric acid in boiling acetic anhydride to afford the pyridine **20**. In the reaction of **2** with malononitrile, cyanoacetamide or malononitrile dimer compounds **21**, **22** and **24** were formed. Compound **22** was further reacted with arylidenemalononitriles to give the benzopyridine derivatives **28**. Pyridone **22** treated with S-DMF mixture gives thienopyridine **29**, while refluxed with DMFDMA yielded the pyridopyridine **30**.

Key words: acetoacetanilide, DMFDMA, pyrazolopyrimidines, pyrimidobenzimidazole, thienopyrimidine

Formamide acetals are useful reagents [1–3] for functional group transformations. They may also be applied as one carbon synthons in the construction of carbon skeletons. The reaction of dimethylformamide dimethylacetal with acetoacetanilide **1** gave previously unknown 1-(N,N-dimethylamino)-2-(N-phenylcarbamoyl)-1-buten-3-one **(2)**.

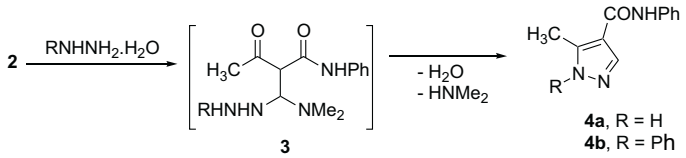
In this work we report on the application of **2** as a building block for the synthesis of heterocyclic compounds.



We investigated the reactions of enaminone **2** with some nitrogen nucleophiles. Thus, treatment of compound **2** with hydrazine hydrate in acetic acid under reflux afforded 3-methyl-2,3-dihydro-1H-pyrazole-4-carboxylic acid phenylamide (**4a**) and with phenylhydrazine corresponding 2-phenyl derivative (**4b**) (Scheme 1).

*Author for correspondence.

Scheme 1

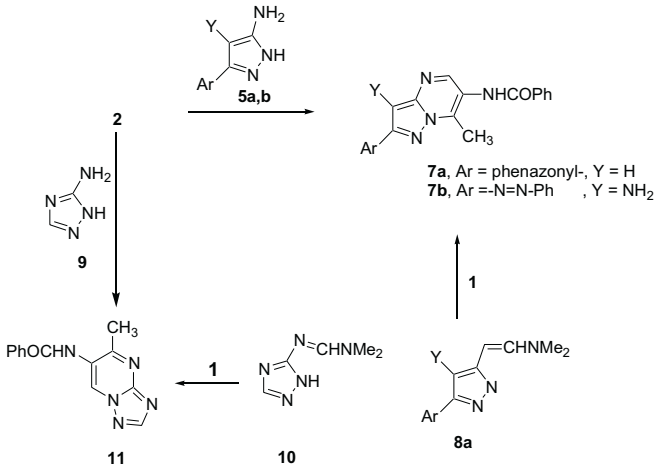


The compounds **4a** and **4b** are formed *via* Michael addition of the amino group of hydrazines to the enamine double bond in **2**, followed by cyclization of intermediate **3**, accompanied with elimination of dimethylamine and water molecules.

RESULTS AND DISCUSSION

Enaminones react with heterocyclic amines to give fused heterocyclic systems [4,5]. Thus, compound **2** was treated with 5-amino-3-aryl-1H-pyrazoles **5a,b** in refluxing acetic acid. In both cases, a single products identified as pyrazolo[1,5-a]pyrimidines (**7a,b)** were isolated (Scheme 2). To confirm the proposed structure, compound **7a** was synthesized from 3-phenazonyl-1H-pyrazole **8a** and acetoacetanilide. Similary, compound **2** reacted with 3-amino-1,2,4-triazole (**9**) to produce triazolo[1,5-a]pyrimidine **11** (Scheme 2). The structure of compound **11** was analogous to that synthesized from imino-1,2,4-triazole derivative **10** and compound **1**.

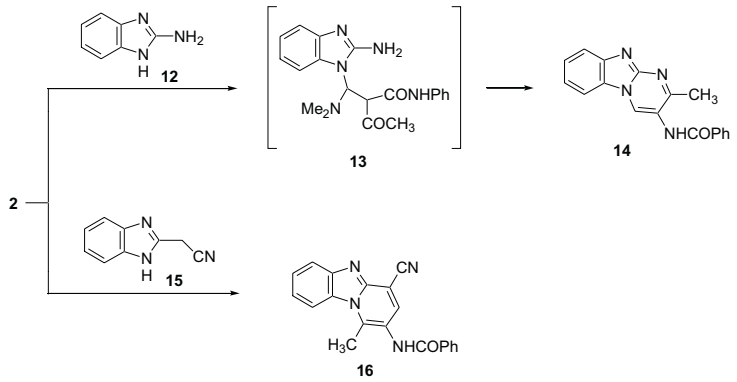
Scheme 2



In contrast to the behaviour of **2** towards 5-amino-3-arylpyrazoles **5a,b** and 3-amino-1,2,4-triazole (**9**), 2-aminobezimidazole (**12**) reacted with **2** under the same conditions and afforded the pyrimido[1,2-a]benzimidazole **14** (Scheme 3). The Mi-

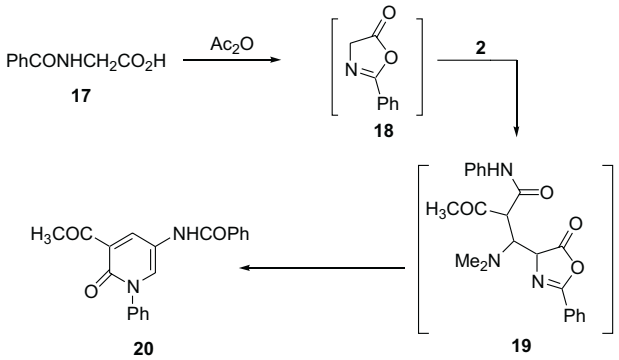
chael addition of **12** to **2** lead to the nonisolable adduct **13**, which subsequently cyclized into **15**. Although the ring nitrogen in compounds **5a,b** is the most nucleophilic centre [6,7], it is also the most hindered site. Therefore, addition takes place at the NH_2 group to afford the pyrazolopyrimidine derivative **7a,b**, which is in contrast to previously reported results [8]. However, in case of the reaction of **2** with 2-aminobenzimidazole (**12**), the formation of the adduct **13** takes place *via* the attack of the endocyclic nitrogen of the imidazole ring into the activated double bond of the enaminonitrile **2**, followed by an intramolecular cyclization to afford the pyrimido[1,2-a]benzimidazole derivative **14**. The reaction of **2** with 1H-benzimidazole-2-acetonitrile (**15**) afforded pyrido[1,2-a]benzimidazole derivative **16**.

Scheme 3



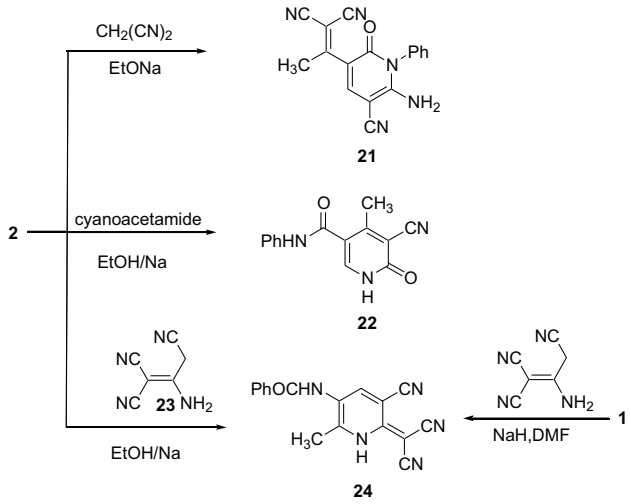
Reaction of **2** with hippuric acid (**17**) in refluxing acetic anhydride produced the pyridine derivative **20**. It is assumed that hippuric acid is cyclized into the oxazolone derivative **18**, which then reacted with **2** yielding the final isolable **20** through the intermediate **19** (Scheme 4).

Scheme 4



Compound **2** reacted with malononitrile in refluxing ethanolic sodium ethoxide to give 2-[1-(6-amino-5-cyano-2-oxo-1-phenyl-1,2-dihydropyridine-3-yl)-ethylidene] malononitrile (**20**). In contrast to the behaviour of **2** towards malononitrile, it reacted with cyanoacetamide under the same conditions to yield the pyridine **21** (Scheme 5).

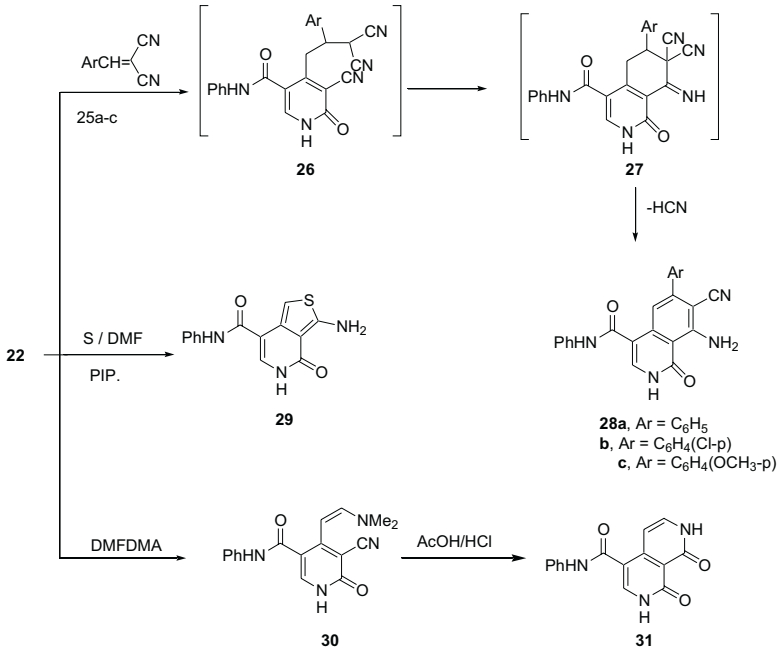
Scheme 5



When **2** was treated with malononitrile dimer (**22**) in ethanolic sodium ethoxide, compound **24** was produced. Compound **24** found to be identical with the product obtained from reaction of the dimer **23** with **1** and DMF-DMA [3]. The reaction of **22** with arylidenemalononitriles **25a–c** afforded the expected isoquinoline **28a–c** (Scheme 6) most probably involving intermediate adduct **26**, which then cyclized into **27**. Final loss of HCN yields aromatic **28**. The spectral data for compounds **28a–c** were in agreement with the proposed structure.

The compound **22** reacts with sulphur in DMF in the presence of piperidine to yield the thienopyridazine-6-ones **29** in good yields. Compound **22** condensed with DMF-DMA to give the enaminone **30**, which cylized to **31** on reflux with acetic acid / hydrochloric acid mixture.

Scheme 6



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. Mass spectra were measured on GC/MS INCOS XL Finnigan MAT. Micoroanalysis were performed on LECO CHNS-932.

Preparation of 1-(*N*,*N*-dimethylamino)-2-(*N*-phenylcarboxamido)-1-buten-3-one (2). Dimethylformamide dimethylacetal (1.19 g, 10 mmol) and acetoacetanilide (1.77 g, 10 mmol) were refluxed in p-xylene (50 mL) for 2 hours. The removal of the solvent under reduced pressure yielded the crude product, which was crystallized from ethanol to give **2** as yellow crystals; m.p. 154°C; yield 70%; ν_{max}: 3480 (NH), 1710 (CO) and 1680 (CO). ^{1}H NMR ([$^{2}H_6$] DMSO) δ_H: 2.3 (s, 3H, CH_3); 2.47 (s, 6H, 2 CH_3), 7.00–7.64 (m, 6H, arom-H + 1H CH), 9.36 (br s, 1H, NH). ^{13}C NMR ([$^{2}H_6$] DMSO) δ_C: 195.5 (CO), 163.8 (CO-amide), 157.8, 113.8 (vinyl), 138.2, 128.7, 128.7, 124.1, 120.4, 120.4 (aromatic), 40.8, 40.8 (methyl). Anal. for $C_{13}H_{16}N_2O_2$ (233.29); Calcd. C, 66.92; H, 7.34; N, 12.01%. Found: C, 66.95; H, 7.31; N, 11.99%.

General procedure for the preparation of compounds 4a,b; 7a,b and 11. Method A: A mixture of each of hydrazine hydrate, phenyl hydrazine, aminopyrazole derivative **5a,b** or aminotriazole **9** (10 mmol) and compound **2** (2.33 g, 10 mmol) in acetic acid (15 mL) was heated under reflux for 6 hours, then left to cool and triturated with ethanol. The solid product, so formed, was collected by filtration and crystallized from ethanol. **Method B:** A mixture of the enamine **8a** or **10** (10 mmol) and acetoacetanilide (1.77 g, 10 mmol) in xylene (50 mL) was heated under reflux for 6 h, then left to cool and triturated with ethanol. The solid product was collected by filtration and crystallized from ethanol.

5-Methyl-1H-pyrazole-4-carboxylic acid phenylamide (4a) was obtained as yellow crystals; m.p. 265°C; yield 87%; ν_{max}: 3350–3000 (NH) and 1687 (CO). ^{1}H NMR ([$^{2}H_6$] DMSO) δ_H: 1.20 (d, 3H, CH_3); 3.48 (q, 1H, CH); 6.89 (s, 1H, CH); 7.00–7.92 (m, 6H, arom-H and NH); 9.2 (br s, 1H, NH). MS: m/z

(201). ^{13}C NMR ([$^2H_6$] DMSO) δ_C: 163.8 (CO amide), 141.7, 113.8 (vinyl), 138.2, 128.7, 128.7, 124.1, 120.4, 120.4 (aromatic), 55.8 (methylene), 15.6 (methyl). Anal. for $C_{11}H_{13}N_3O$ (201.22); Calcd. C, 65.60; H, 5.51; N, 20.88%. Found: C, 65.12; H, 5.50; N, 20.39%.

3-Methyl-2-phenyl-1H-pyrazole-4-carboxylic acid phenylamide (4b) was obtained as yellowish brown crystals; m.p. 250°C; yield 77%; ν_{max}: 3375 (NH) and 1680 (CO). ^{1}H NMR ([$^2H_6$] DMSO) δ_H: 1.33 (d, 3H, CH_3); 3.48 (q, 1H, CH); 6.89 (s, 1 H, CH); 6.66–7.64 (m, 10 H, arom-H); 8.2 (br s, 1H, NH). MS: m/z (277). Anal. for $C_{17}H_{17}N_3O$ (277.32); Calcd. C, 73.63; H, 5.45; N, 15.15%. Found: C, 73.00; H, 5.30; N, 15.23%.

3-Amino-7-methyl-2-phenazonyl[1,5-*a*]pyrimidine-6-carboxylic acid phenylamide (7a) was obtained as yellow crystals; m.p. 149°C; yield 80%; ν_{max}: 3308 (NH), 1690 (CO-amide) and 1650 (CO-phenazonyl). ^{1}H NMR ([$^2H_6$] DMSO) δ_H: 1.93 (s, 3H, CH_3); 2.35 (s, 3H, CH_3); 2.47 (s, 3H, CH_3); 6.2 (s, 1H, 3H-pyrazole); 6.66–7.18 (m, 10H, arom-H); 9.16 (s, 1H, 4H-pyridine); 9.40 (br s, 1H, NH). ^{13}C NMR ([$^2H_6$] DMSO) δ_C: 167.9, 156.4, 126.8 (pyrimidine); 165.2, 160.7 (CO-amide); 167.9, 154.5 (vinyl); 142.2, 138.2, 129, 129, 128.7, 128.7, 126.8, 124.1, 120.4, 120.4, 118.9, 112, 112 (aromatic); 133, 133, 105 (pyrazol); 35.6, 17.4, 9.0 (methyl). MS: m/z (438). Anal. for $C_{25}H_{17}N_7O$ (371.40); Calcd. C, 64.68; H, 4.61; N, 26.40%. Found: C, 64.40; H, 4.18; N, 26.34%.

3-Amino-7-methyl-2-phenylazopyrazolo[1,5-*a*]pyrimidine-6-carboxylic acid phenyl amide (7b) was obtained as red crystals; m.p. 235°C; yield 70%; ν_{max}: 3330 (NH), 3200 (NH_2), 1690 (CO) and 1660 (N=N). ^{1}H NMR ([$^2H_6$] DMSO) δ_H: 1.93 (s, 3H, CH_3); 5.9 (br s, 2H, NH_2); 6.64–7.26 (m, 10H, arom-H); 8.72 (s, 1H, 4H-pyridine); 9.35 (br s, 1H, NH). MS: m/z (371). Anal. for $C_{20}H_{17}N_7O$ (371.40); Calcd. C, 64.68; H, 4.61; N, 26.40%. Found: C, 64.60; H, 4.30; N, 26.67%.

***N*-(5-Methyl-[1,2,4]triazol[1,5-*a*]pyrimidine-6-yl-)benzamide (11)** was obtained as yellow crystals; m.p. 209°C; ν_{max}: 3380 (NH) and 1685 (CO-amide). ^{1}H NMR ([$^2H_6$] DMSO) δ_H: 1.93 (s, 3H, CH_3); 6.46–7.01 (m, 5H, arom-H); 8.27 (s, 1H, CH); 8.76 (s, 1H, 4H-pyrimidine); 9.40 (br s, 1H, NH). MS: m/z (253). Anal. for $C_{13}H_{11}N_5O$ (253.26); Calcd. C, 61.65; H, 4.38; N, 27.65%. Found: C, 61.60; H, 4.03; N, 27.55%.

Preparation of compounds 14 and 16. To a solution of compound **2** (2.33 g, 10 mmol) in absolute ethanol (30 mL) containing catalytic amount of piperidine, 1H-benzimidazole (**12**, 10 mmol) or benzimidazole-2-acetonitrile (**15**) was added. The reaction mixture was heated under reflux for 4 hours, then left to cool. The formed precipitate was collected by filtration and recrystallized from ethanol-dioxane.

***N*-(2-Methylbenzo[4,5]imidazo[1,2-*a*]pyrimidine-3-yl)-benzamide (15)** was obtained as orange crystals; m.p. 244°C; yield 85%; ν_{max}: 3330 (NH) and 1690 (CO-amide). ^{1}H NMR ([$^2H_6$] DMSO) δ_H: 2.35 (s, 3H, CH_3); 6.46–7.10 (m, 9H, arom-H); 8.53 (s, 1H, CH); 9.35 (br s, 1H, NH). ^{13}C NMR ([$^2H_6$] DMSO) δ_C: 165.2 (amide); 151.0, 144.7, 142.3 (pyrimidine); 141.5, 137.9, 137.9, 122.9, 122.9, 115.4, 115.4 (benzimidazole); 133.5, 131.9, 128.6, 127.3, 127.3 (aromatic); 11.8 (CH_3). Anal. for $C_{18}H_{14}N_4O$ (302.33); Calcd. C, 71.51; H, 4.67; N, 18.53%. Found: C, 71.00; H, 4.10; N, 18.90%.

4-Cyano-1-methylbenzo[4,5]imidazo[1,2-*a*]pyridine-2-carboxylic acid phenyl amide (16) was obtained as yellow crystals; m.p. > 300°C; yield 80%; ν_{max}: 3338 (NH); 2220 (CN) and 1690 (CO-amide). ^{1}H NMR ([$^2H_6$] DMSO) δ_H: 2.55 (s, 3H, CH_3); 6.46–7.10 (m, 9H, arom-H); 8.31 (s, 1H, CH); 10.4 (br s, 1H, NH). Anal. for $C_{21}H_{15}N_3O$ (313.33); Calcd. C, 72.83; H, 4.18; N, 17.08%. Found: C, 72.50; H, 4.70; N, 17.00%.

Preparation of compound 20: A solution of compound **2** (2.33 g, 10 mmol) and hippuric acid (1.79 g, 10 mmol) in acetic anhydride (45 ml) was refluxed for 3–4 hours, left to cool and then poured into water. After complete decomposition of excess acetic anhydride the remaining oil was separated and triturated with ethanol. The solid product was collected by filtration and crystallized from ethanol/DMF. Compound **20** was obtained as deep brown crystals; m.p. > 300°C; yield 77%; ν_{max}: 3300 (NH); 1710 (CO) and 1685 (CO). ^{1}H NMR ([$^2H_6$] DMSO) δ_H: 2.30 (s, 3H, CH_3); 6.71 (s, 1H, CH); 7.00–7.95 (m, 10H, arom-H); 8.15 (s, 1H, CH); 9.25 (br s, 1H, NH). ^{13}C NMR ([$^2H_6$] DMSO) δ_C: 196.5 (CO); 164.3, 158.4 (CO-amide), 138.2, 138.1, 133.5, 131.9, 128.7, 128.7, 128.6, 128.6, 127.3, 127.3, 124.1, 120.4 (aromatic); 147.4, 138.1, 114.9, 106.9 (vinyl); 21.7 (CH_3). Anal. for $C_{20}H_{16}N_2O_3$ (332.35); Calcd. C, 72.28; H, 4.85; N, 8.43 %. Found: C, 72.00; H, 5.00; N, 8.43%.

Reaction of 2 with malononitrile, cyanoacetamide and malononitrile dimer. Preparation of compounds 21, 22 and 24. Method A: A mixture of compound **2** (2.33 g, 10 mmol) and malononitrile, cyanoacetamide or malononitrile dimer (10 mmol) in ethanolic sodium ethoxide (30 mL) was refluxed for

30 min. The reaction mixture was poured into water and acidified with dil. HCl. The precipitate formed was collected by filtration and crystallized from ethanol.

Method B (for compound 24): A mixture of acetoacetanilide (1.77 g, 10 mmol), dry *N*,*N*-dimethylformamide dimethylacetal (1.19 g, 10 mmol) was stirred under an inert atmosphere at r.t. for 24 h. In a second flask a mixture of dry DMF (10 mL), sodium hydride (0.48 g, 20 mmol) and malononitrile dimer (1.45 g, 10 mmol) was stirred under an inert atmosphere at r.t. for 10 min.The content of the second flask were transferred by a syring into the first flask and the resulting mixture was stirred for 24 h. A mixture of ethanol (25 mL) and water (25 mL) was added, the mixture was acidified with conc. HCl to pH 4 and stirring was continued for 24 h. The product was recovered by filtration and crystallized from ethanol.

2-[1-(6-Amino-5-cyano-2-oxo-1-phenyl-1,2-dihydropyridine-3-yl)-ethylidene]malononitrile (21) was obtained as yellow crystals; m.p. 210°C; yield 75%; $\nu_{max.}$ 3285 (NH_2), 2210, 2200 (CN) and 1690 (CO). ^{1}H NMR ([$^2H_6$] DMSO) δ_H: 1.71 (s, 3H, CH_3); 6.97 (s, 1H, CH); 7.00–8.20 (m, 6H, arom-H and NH_2). ^{13}C NMR ([$^2H_6$] DMSO) δ_C: 158.4, 138.2, 137.4, 135.7, 128.7, 128.7, 124.1, 120.4 (aromatic); 117.2, 117.2, 117.2 (nitrile); 174.7, 167.9, 137.4, 135.7 (vinyl); 11.6 (CH_3). Anal. for $C_{17}H_{11}N_5O$ (301.30); Calcd. C, 67.77; H, 3.68; N, 23.24%. Found: C, 67.80; H, 4.00; N, 23.30%.

5-Cyano-4-methyl-6-oxo-1,6-dihydropyridine-3-carboxylic acid phenylamide (22) was obtained as yellow crystals; m.p. > 300°C; yield 77%; $\nu_{max.}$ 3322, 3200 (NH); 2220 (CN) and 1680 (CO). ^{1}H NMR ([$^2H_6$] DMSO) δ_H: 1.71 (s, 3H, CH_3); 7.00–7.64 (m, 5H, arom-H); 8.20 (s, 1H, CH); 9.20 (s, 1H, NH); 14.20 (br s, 1H, NH). ^{13}C NMR ([$^2H_6$] DMSO) δ_C: 163.8, 162.2 (CO-amide); 166.3, 138.2, 128.7, 128.7, 124.1, 120.4, 120.4 (aromatic-carbons); 130.1, 118.6, 99.3 (vinyl); 117.2 (CN); 11.3 (CH_3). Anal. for $C_{14}H_{11}N_3O$ (237.26); Calcd. C, 70.87; H, 4.67; N, 17.71%. Found: C, 70.90; H, 4.56; N, 17.65%.

5-Cyano-6-dicyanomethylene-1,2-methyl-1,6-dihydropyridine-3-carboxylic acid phenylamide (24) was obtained as orange crystals; m.p. 180°C; yield 60%; ν_{max}: 3300, 3280 (NH); 2220, 2215 (CN) and 1690 (CO-amide). ^{1}H NMR ([$^2H_6$] DMSO) δ_H: 1.71 (s, 3H, CH_3); 6.46–7.01 (m, 5H, arom-H); 8.29 (s, 1H, CH); 8.79 (s, 1H, NH); 14.1 (s, 1H, NH). Anal. for $C_{17}H_{11}N_5O$ (301.30); Calcd. C, 67.77; H, 3.68; N, 23.24%. Found: C, 67.80; H, 4.00; N, 23.30%.

Preparation of compounds 28a–c. In a 100 ml flask, a solution of compound **22** (2.53 g, 10 mmol) in pyridine (30 mL) was treated with an arylidenemalononitrile (10 mmol). The reaction mixture was refluxed for 4-6 h, left to cool to r.t., poured into ice-cold water, and neutralized with HCl (10%). The solid product was filtered off and crystallized from ethanol.

8-Amino-7-cyano-1-oxo-6-phenyl-1,2-dihydroisoquinoline-4-carboxylic acid phenylamide (28a) was obtained as brown crystals; m.p. 290°C; yield 60%; ν_{max}: 3448, 3290 (NH_2 and NH); 2221 (CN) and 1660 (CO). ^{1}H NMR ([$^2H_6$] DMSO) δ_H: 6.16 (s, 1H, CH); 6.80–7.64 (m, 11H, arom-H and NH_2); 8.02 (s, 1H, CH); 9.40 (br s, 1H, NH); 12.21 (br s, 1H, NH). Anal. for $C_{23}H_{16}N_4O_2$ (380.41); Calcd. C, 72.62; H, 4.24; N, 14.73 %. Found: C, 72.00; H, 4.80; N, 8.42%.

8-Amino-7-cyano-1-oxo-6-(p-chlorophenyl)-1,2-dihydroisoquinoline-4-carboxylic acid phenylamide (28b) was obtained as yellow crystals; m.p. 190°C; yield 70%; $\nu_{max.}$ 3448, 3290 (NH_2 and NH); 2221 (CN) and 1660 (CO). ^{1}H NMR ([$^2H_6$] DMSO) δ_H: 6.16 (s, 1H, CH); 6.80–7.64 (m, 11H, arom-H and NH_2); 8.02 (s, 1H, CH); 9.40 (br s, 1H, NH); 12.21 (br s, 1H, NH). Anal. for $C_{23}H_{15}ClN_4O_2$ (414.86); Calcd. C, 70.23; H, 4.42; N, 13.65%. Found: C, 66.00; H, 4.18; N, 13.65%.

8-Amino-7-cyano-1-oxo-6-(p-methoxyphenyl)-1,2-dihydroisoquinoline-4-carboxylic acid phenylamide (28c) was obtained as brown crystals; m.p. 100°C; yield 75%; $\nu_{max.}$ 3448, 3290 (NH_2 and NH); 2221 (CN) and 1660 (CO). ^{1}H NMR ([$^2H_6$] DMSO) δ_H: 3.2 (s, 3H, CH_3); 6.16 (s, 1H, CH); 6.80–7.64 (m, 11H, arom-H and NH_2); 8.02 (s, 1H, CH); 9.40 (br s, 1H, NH); 12.21 (br s, 1H, NH). Anal. for $C_{24}H_{18}N_4O_3$ (410.42); Calcd. C, 69.89; H, 4.89; N, 13.58%. Found: C, 69.90; H, 5.00; N, 13.70%.

3-Amino-4-oxo-4,5-dihydrothieno[3,4-*a*]pyridine-7-carboxylic acid phenylamide (29): A solution of compound **22** (10 mmol) in DMF (10 mL) was treated with elemental sulphur (0.32 g, 10 mmol) and piperidine (0.2 mL). The reaction mixture was refluxed for 4 h, then poured into water, the solid product, so formed, was collected by filtration and crystallized from ethanol-DMF. Compound **29** was obtained as brown crystals; m.p. 255°C; yield 67%; $\nu_{max.}$ 3400, 3280 (NH_2 and NH); 1680 (CO). ^{1}H NMR ([$^2H_6$] DMSO) δ_H: 6.4 (s, 1H, thiophene-H); 7.00–8.30 (m, 7H, arom-H and NH_2); 8.18 (s, 1H, CH); 9.24 (s, 1H, NH); 12.4 (br s, 1H, NH). ^{13}C NMR ([$^2H_6$] DMSO) δ_C: 163.8 (CO); 163.3 (CO); 138.2, 120.4, 128.7, 124.1, 128.7, 120.4 (aromatic); 122, 133, 142, 138 (thiophene); 117.5 (vinyl). Anal. for $C_{14}H_{11}N_3O_2S$ (285.32); Calcd. C, 58.93; H, 3.89; N, 14.73%. Found: C, 59.00; H, 4.10; N, 14.80%.

5-Cyano-4-(2-dimethylaminovinyl)-6-oxo-1,6-dihydropyridine-3-carboxylic acid phenylamide (30): A solution of **22** (2.53 g, 10 mmol) in xylene (30 mL) was treated with *N*,*N*-dimethylformamide dimethylacetal (1.2 g, 10 mmol). The reaction mixture was refluxed for 2 h, left to cool at r.t. The resulting solid product was collected by filtration and crystallized from ethanol – DMF. Compound **30** was obtained as yellow crystals; m.p. 195°C; yield 60%; ν_{max}: 3380 (NH) and 2220 (CN). ^{1}H NMR ([$^2H_6$] DMSO) δ_H: 4.50 (d, 1H, vinyl-H); 5.72 (d, 1H, vinyl-H); 7.00–7.92 (m, 6H, arom-H and vinyl-H); 9.23 (br s, 1H, NH). MS (m /z) 308. Anal. for $C_{17}H_{16}N_4O_2$ (308.35); Calcd. C, 66.22; H, 5.23; N, 18.17%. Found: C, 65.80; H, 6.00, N, 18.12%.

1,8-Dioxo-1,2,7,8-tetrahydro[2,7]naphthyridine-4-carboxylic acid phenylamide (31): A solution of **30** (0.5 g) in AcOH – HCl (5 mL, 3:1 by volume) was refluxed for 1 h, then allowed to cool at r.t. The solid product, so formed, was collected by filtration and crystallized from ethanol – DMF. Compound **31** was obtained as yellow crystals; m.p. 220°C; yield 60%; ν_{max}: 3390–3350 (NH) and 1680 (CO). ^{1}H NMR ([$^2H_6$] DMSO) δ_H: 4.99 (d, 1H, vinyl-H); 7.00–7.64 (m, 6H, arom-H and vinyl-H); 7.92 (s, 1H, vinyl-H); 9.30 (br s, 1H, NH); 12.40 (br s, 1H, NH); 13.06 (br s, 1H, NH). MS (m /z) 281. Anal. for $C_{15}H_{11}N_3O_3$ (281.27); Calcd. C, 64.05; H, 3.94; N, 14.44%. Found: C, 63.71; H, 4.00; N, 14.57%.

REFERENCES

1. Granik V.G., Zhik A.M. and Glushkov G.R., *Chem. Rev.*, **46**, 361 (1977).
2. Abdulla R.F. and Brinkmeyer R.S., *Tetrahedron*, **35**, 1675 (1979).
3. Abu-Shanab F.A., Redhouse A.D., Hompson J.R. and Wakefield B.J., *Synthesis*, 557 (1995).
4. Elnagdi M.H., Abdel-All F.A. and Elgemeie G.E.H., *Heterocycles*, **23**, 3121 (1985).
5. Dawood K.M., Farag A.M. and Kandeel Z.E., *J. Chem. Res. (s)*, 88 (1999).
6. Fathi N.M., Abdel Motti F.M. and Elgemeie G.E.H., *Arch. Pharm. (Weinheim*), **321**, 509 (1998).
7. Elnagdi M.H., Taha N.H., Abdel All F.A., Abdel Motaleb R.M. and Mahmoud F.F., *Collect. Czech. Chem. Commun.,* **54**, 1082 (1989).
8. Sherief S.M. and Hussien A.M., *Monatsh. Chem.,* **128**, 687 (1997).