Scope and Limitations of a Novel Synthesis of 3-Arylazonicotinates

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Abstract: The reaction of 3-oxo-3-phenyl-2-phenylhydrazonal with functionally substituted and heteroaromatic substituted acetonitrile to yield arylazonicotinic acid derivatives and 5-arylsubstituted pyridines was established. In some cases the produced nicotinates could not be isolated as they underwent thermally induced 6π-electrocyclization yielding polynuclear pyridine derivatives.

Keywords: 3-oxo-3-phenyl-2-phenylhydrazonal; arylazonicotinic acid; pyridine; electrocyclization; heteroaromatics

1. Introduction

3-oxo-3-Substituted-2-arylhazrazonals 1 are versatile, readily obtainable reagents [1] that have been extensively utilized in the synthesis of polyfunctional substituted aromatics and heteroaromatics [2,3]. In the past we have reported novel synthesis of polyfunctional pyridazines 4 via heating 1 with dimethyl acetylenedicarboxylate (2) as well as acrylonitrile (3) in presence of triphenylphosphine or a tertiary amine base [4,5] (Scheme 1). We have also reported that condensing active methylene nitriles 5 with 1 affords products that were believed to be the pyridazine imines 6 [6]. Recently however Al-Mousawi et al. [7,8] realized that this structure cannot be correct as reported 13C-NMR data for the
product lacked a carbonyl carbon at $\delta < 175$ ppm. It was revealed that the products of condensing 1 with ethyl cyanoacetate are really the arylationenicicotinates 7 (cf. Scheme 1), as clearly revealed by the X-ray crystal structure (Figure 1).

**Scheme 1.** Chemical reactivities of 3-oxo-3-substituted-2-arylhydrazonals 1.

**Figure 1.** X-ray structure of compound 7.
However, in some cases pyridazinones 8 were the reaction products rather than nicotinates. In light of the enormous potential of arylazonicotinates both as new pyridone dyes [9] and as biologically active compounds with anticonvulsant activity that act due to synaptic and non-synaptic mechanisms and some studies that have proved their antitumor and antimicrobial activities [10], we were interested in defining further the behavior of 1 toward 5 to see if the reaction would afford 7 or 8. In the present article we report on the reactivity of 1a–d toward a variety of derivatives of 5 where we noted that this reaction may produce derivatives of 7 or 8 depending on the nature of 5. Distinguishing between 7 and 8 could be easily accomplished based on 13C-NMR data as the absence of a carbonyl carbon signal would mean that the product is not an arylpyridazine derivative. Also with some derivatives of 7 electrocyclization and loss of hydrogen leading to novel 6-aryl-6H-pyrido[3,2-c]cinnolin-2-ones 9 seems probable.

2. Results and Discussion

Compounds 1a–d reacted with malononitrile 5b yielding the arylazonicotinonitriles 7b,h, respectively as indicated by the absence of carbonyl carbon absorptions in the 13C-NMR of the products. Similar to their behavior toward malononitrile compounds, 1a–d condensed with 5a,c–k to yield phenylazonicotinates 7a,c–g (Scheme 2).

Scheme 2. Syntheses of phenylazonicotinates 7a,c–g.

Phenylazonicotinates 7a,b were converted to aminopyridinones 10a,b by reduction using Zn/AcOH (Scheme 3).
The reaction of 1a,b with 5c,d,k in ethanolic piperidine solution resulted in the formation of 12a–c. It is believed that the initially formed derivative of 7 readily underwent a $6\pi$ electrocyclization yielding 11a–c that then aromatized to the final products 12a–c (Scheme 4).

We believe that the decreased aromaticity of the thiophene ring as compared to benzene is behind this ready electrocyclization, and in support of this conclusion we have found that 1c also afforded 14b–d,g,k upon reaction with 5b–d,g,k; again the initially formed derivative of 7 underwent electro-cyclization to 13 and then aromatized to yield 14b–d,g,k (Scheme 5).
Scheme 5. Syntheses of compounds 14b–d,g,k.

Similar to this behavior compound 1d reacted with 5c–e,g–k to afford compounds 16c–e,g–k under the same reaction conditions (Scheme 6).

Scheme 6. Syntheses of compounds 16c–e,g–k.
In summary, we could clearly demonstrate that the structures of the products obtained by reacting 1a–d with active methylenes can be readily concluded via inspection of position of the carbonyl carbon signals in the corresponding 13C-NMR spectra. When an arylhydrazone moiety in the intermediates cyclises via addition to a CN function subsequent hydrolysis of the formed imine usually occurred leading to pyridazinones.

3. Experimental Section

3.1. General

Melting points are reported uncorrected and were determined with a Sanyo (Gallenkamp) instrument. Infrared spectra were recorded using KBr pellets and a Perkin-Elmer 2000 FT-IR instrument. 1H- and 13C-NMR spectra were determined using a Bruker DPX instrument at 400 MHz for 1H-NMR and 100 MHz for 13C-NMR and DMSO-d6 solutions with TMS as internal standard. Chemical shifts are reported in δ (ppm). Mass spectra were measured using a VG Autospec Q MS 30 and MS 9 (AEI) spectrometers, using the EI (70 EV) mode. Elemental analyses were carried out using a LEO CHNS-932 Elemental Analyzer

3.2. General Procedure for the Synthesis of Compounds 7a–g

A mixture of 1a–d (0.01 mmol), and active methylenenitrile derivatives 5a–l (0.01 mmol) in the presence of piperidine (5 drops) and ethanol (10 mL) as a solvent was refluxed for 1–2 h. The reaction mixture was evaporated. The solid product, so formed, was crystallized from a suitable solvent.

3-(4-Oxo-4,5-dihydrothiazol-2-yl)-6-phenyl-5-phenylazo-1H-pyridin-2-one (7a). Red crystals from ethanol, yield 95%; m.p. up 300 °C; Anal. Calcd. for C20H14N4O2S (374) calcd: C, 64.16; H, 3.77; N, 14.96. Found: C, 64.00; H, 3.54; N, 14.83; IR (KBr) $\nu_{max}$: 1,629 (CN), 1,670 (CO); 1H-NMR (DMSO-d6): δ = 1.3 (s, 2H, CH$_2$); 7.0–8.1 (m, 10H, Ph-H); 10.0 (br, 1H, NH, D$_2$O exchangeable); 13C-NMR (DMSO-d6): δ = 163.7, 162.9, 143.0, 137.0, 134.9, 129.0, 128.4, 127.7, 126.2, 124, 100.0, 39.0; MS: m/z (%) 373 (M+, 10), 299 (85), 224 (5), 140 (20).

2-Oxo-6-phenyl-5-phenylazo-1,2-dihydropyridine-3-carbonitrile (7b). Dark yellow crystals from ethanol, yield 95%; m.p. 153 °C; Anal. Calcd. for C18H12N4O (300): C, 71.99; H, 4.03; N, 18.66. Found: C, 71.80; H, 3.99; N, 18.53; IR (KBr): $\nu_{max}$: 3,264 (NH), 1,660 (CO); 13C-NMR (DMSO-d6): δ = 162.9, 156.9, 137, 134.9, 129.0, 128.4, 127.7, 126.2, 117.2, 106.7, 100.0; MS: m/z (%) 301 (M+, 10), 299 (85), 224 (5), 140 (20).

2-Oxo-6-phenyl-5-phenylazo-1,2-dihydropyridine-3-carboxylic acid amide (7d). Orange crystals from ethanol, yield 98%, m.p. 190 °C; Anal. Calcd. for C18H14N4OS (334): C, 64.65; H, 4.22; N, 16.75. Found: C, 64.59; H, 4.21; N, 16.62; IR (KBr): $\nu_{max}$: 3,399–3,266 (NH$_2$), 1,614(CN), 1,680 (CO); 1H-NMR (DMSO-d6): δ = 7.4–7.9 (m, 10H, Ph-H); 10.6 (br, 2H, NH$_2$, D$_2$O exchangeable); 13C-NMR (DMSO-d6): δ = 164.7, 135.7, 133.0, 130.3, 128.1, 126.4; MS: m/z (%) 334 (M+, 100), 105 (30), 77 (25).
6-Biphenyl-4-yl-2-oxo-5-phenylazo-1,2-dihydropyridine-3-carbonitrile (7e). Green crystals from AcOH, yield 95%; m.p. 145 °C; Anal. Calcd. for C_{24}H_{16}N_{4}O (376.13): C, 76.58; H, 4.28; N, 14.88. Found: C, 76.57; H, 4.21; N, 14.62; IR (KBr): \( \nu_{\text{max}} \) 3,343 (NH), 2,202 (CN), 1,655 (CO); \( ^{13} \text{C-NMR} \) (DMSO-\( \text{d}_6 \)): \( \delta = 162.0, 156.9, 137.0, 136.6, 135.8, 132.8, 129.0, 127.4, 126.7, 117.2, 106.7, 100.0 \); MS: \( m/z \) (%) 377 (M\(^+\), 90), 244 (20), 152 (50), 77 (30).

6-Biphenyl-4-yl-2-oxo-5-phenylazo-1,2-dihydropyridine-3-carboxylic acid hydrazide (7f). Buff crystals from ethanol, yield 95%; m.p. 237 °C; Anal. Calcd. For C_{24}H_{19}N_{5}O_{2} (409): C, 70.40; H, 4.68; N, 17.10. found: C, 70.39; H, 4.61; N, 17.02; IR (KBr): \( \nu_{\text{max}} \) 3,412–3,331 (NH\(_2\)), 1,660 (CO); \( ^{13} \text{C-NMR} \) (DMSO-\( \text{d}_6 \)): \( \delta = 165.9, 162.9, 148.5, 137.0, 136.6, 135.8, 133.8, 131.3, 129.0, 127.4, 126.7, 100.0 \); MS: \( m/z \) (%) 409 (M\(^+\), 50) 324 (80), 181 (75), 77 (70).

3-Benzothiazol-2-yl-5-phenylazo-6-thiophen-2-yl-1H-pyridin-2-one (7g). Yellow crystals from ethanol/AcOH, yield 98%; m.p. 242 °C; Anal. Calcd. for C_{22}H_{14}N_{4}OS_{2} (414): C, 63.75; H, 3.40; N, 13.52. Found: C, 63.71; H, 3.31; N, 13.42; IR (KBr): \( \nu_{\text{max}} \) 3,264 (NH), 1,680 (CO); \( ^{1} \text{H-NMR} \) (DMSO-\( \text{d}_6 \)): \( \delta = 7.2–7.3 \) (t, 3H, thiol-H); 7.6–8.2 (m, 9H, Ph-H); 8.6 (br, 1H, NH, D\(_2\)O exchangeable); 9.0 (s, 1H, nicotine-H); \( ^{13} \text{C-NMR} \) (DMSO-\( \text{d}_6 \)): \( \delta = 162.9, 156.0, 153.0, 137.7, 136.6, 133.0, 130.0, 129.0, 127.8, 126.4, 125.0, 124.0, 123.0, 122.0, 106 \); MS: \( m/z \) (%) 413(M\(^+\), 100), 304 (25), 111 (40), 77 (10).

6-Furan-2-yl-2-oxo-5-phenylazo-1,2-dihydropyridine-3-carbonitrile (7h). Green crystals from ethanol, yield 95%; m.p. 214 °C; Anal. Calcd. for C_{16}H_{10}N_{4}O_{2} (290): C, 66.20; H, 3.47; N, 19.30. Found: C, 66.19; H, 3.31; N, 19.30; IR(KBr): \( \nu_{\text{max}} \) 3,322 (NH), 1,631 (CO); \( ^{1} \text{H-NMR} \) (DMSO-\( \text{d}_6 \)): \( \delta = 6.7–7.4 \) (m, 3H, furan-H); 7.6 (m, 2H, Ph-H); 8.1 (m, 1H, Ph-H); 8.1 (m, 1H, Ph-H); \( ^{13} \text{C-NMR} \) (DMSO-\( \text{d}_6 \)): \( \delta = 149.1, 148.7, 133.3, 130.4, 129.9, 126.1, 123.3, 112.8, 79.1 \); MS: \( m/z \) (%) 289 (M\(^+\), 100), 197 (5), 130 (5), 77 (50).

Synthesis of 5-Amino-3-(4-oxo-thiazolidin-2-yl)-6-phenyl-1H-pyridin-2-one (10a). A mixture of 7a (3.6 g, 0.1 mol) and Zn powder (2 gm) in acetic acid (20 mL) was refluxed for 2 h. then filtered while hot. The reaction mixture was cooled to room temperature and then poured onto ice-water. The solid thus formed was collected by filtration and crystallized from AcOH to give black crystals, yield 70%; m.p. up 300 °C; Anal. Calcd. for C_{14}H_{10}N_{4}O_{2} (290): C, 66.20; H, 3.47; N, 19.30. Found: C, 66.19; H, 3.31; N, 19.30; IR(KBr): \( \nu_{\text{max}} \) 3,322 (NH), 1,631 (CO); \( ^{1} \text{H-NMR} \) (DMSO-\( \text{d}_6 \)): \( \delta = 6.7–7.4 \) (m, 3H, furan-H); 7.6 (m, 2H, Ph-H); 8.1 (m, 2H, Ph-H); 8.1 (m, 1H, Ph-H); \( ^{13} \text{C-NMR} \) (DMSO-\( \text{d}_6 \)): \( \delta = 149.1, 148.7, 133.3, 130.4, 129.9, 126.1, 123.3, 112.8, 79.1 \); MS: \( m/z \) (%) 289 (M\(^+\), 100), 197 (5), 130 (5), 77 (50).

Synthesis of 5-Amino-2-oxo-6-phenyl-1,2-dihydropyridine-3-carbonitrile (10b). A mixture of 7b (0.1 mol) and and Zn powder (2 gm) in acetic acid (20 mL) was refluxed for 2 h. then filtered while hot. The reaction mixture was cooled to room temperature and then poured onto ice-water. The solid thus formed was collected by filtration and crystallized from AcOH to give pale brown crystals, yield 70%; m.p. 190 °C; Anal. Calcd. for C_{12}H_{9}N_{3}O (211): C, 68.24; H, 4.29; N, 19.89. Found: C, 68.20; H, 4.19; N, 19.83; IR (KBr): \( \nu_{\text{max}} \) 3,432, 3,312, (NH\(_2\)), 1,640 (CO); \( ^{13} \text{C-NMR} \) (DMSO-\( \text{d}_6 \)): \( \delta = 162.0, 162.9, 134.9, 128.4, 127.7, 126.2, 121.0, 108.0, 51.4, 39.0 \); MS: \( m/z \) (%) 287 (M\(^+\), 50), 207 (10), 93 (65), 55 (40).
6-Phenyl-3-(4-phenylthiazol-2-yl)-6H-pyrido[3,2-c]cinnolin-2-one (12a). Deep red crystals from ethanol. Yield 98%; m.p. 150 °C; Anal. Calcd. for C_{26}H_{16}N_{4}OS (432): C, 72.20; H, 3.73; N, 12.95. Found: C, 72.19; H, 3.61; N, 12.92; IR (KBr): ν_{max}: 1,614 (CN), 1,680 (CO); 1H-NMR (DMSO-d_{6}): δ = 7.2 (s, thiazole-H); 7.3–8.1 (m, Ph-H); 8.3 (s, nicotine-H); 13C-NMR (DMSO-d_{6}): δ = 157.2, 154.9, 149.2, 141.1, 140.6, 136.1, 134.3, 133.3, 133.2, 131.1, 130.8, 130.7, 130.1, 129.3, 128.8, 128.5, 127.0, 126.6, 121.3, 120.9; MS: m/z (%) 433 (M^+, 100), 329 (10), 105 (20), 77 (15).

2-Oxo-6,8-diphenyl-2,6-dihydropyrido[3,2-c]cinnoline-3-carboxylic acid amide (12b). Red crystals from ethanol. Yield 90%; m.p. 230 °C; Anal. Calcd. for C_{24}H_{16}N_{4}O_{2} (392): C, 73.46; H, 4.11; N, 14.28. Found: C, 73.35; H, 4.00; N, 14.11; IR (KBr): ν_{max}: 3,267, 3,189 (NH_{2}); 13C-NMR (DMSO-d_{6}): δ = 165.0, 150.0, 144.2, 139.8, 136.6, 130.0, 129.4, 127.4, 119.5, 118.0, 117.0; MS: m/z (%) 393 (M^+, 100), 181 (75), 77 (50).

2-Oxo-6,8-diphenyl-2,6-dihydropyrido[3,2-c]cinnoline-3-carboxthioic acid amide (12c). Orange crystals from AcOH. Yield 95%; m.p. 170 °C; Anal. Calcd. for C_{24}H_{16}N_{4}OS (408): C, 70.57; H, 3.95; N, 13.72. Found: C, 70.49; H, 3.71; N, 13.52; IR (KBr): ν_{max} 3,399, 3,298 (NH_{2}), 1670 (CO); 13C-NMR (DMSO-d_{6}): δ = 164.0, 150.0, 144.2, 139.8, 136.6, 130.0, 129.4, 127.4, 119.5, 118.0, 116.9; MS: m/z (%) 391 (M^+, 25), 385 (50), 151 (40), 51 (50).

8-Oxo-4-phenyl-4,8-dihydro-1-thia-4,5,9-triazacyclopenta[a]naphthalene-7-carbonitrile (14b). Yellow crystals from ethanol. Yield 97%; m.p. 270 °C; Anal. Calcd. for C_{16}H_{8}N_{4}OS (304): C, 63.15; H, 2.65; N, 18.14. Found: C, 63.05; H, 2.52; N, 18.11. IR (KBr): ν_{max} 3,400, 3,312 (NH_{2}), 1,615 (CO); 1H-NMR (DMSO-d_{6}): δ = 7.2–7.5 (m, thiazole-H); 7.6–7.7 (m, Ph-H); 13C-NMR (DMSO-d_{6}): δ = 141.4, 138.7, 138.4, 136.8, 136.9, 135.8, 134.9, 132.7, 131.7, 129.7, 129.0, 128.2, 127.8, 126.1, 117.2, 79.16; MS: m/z (%) 305 (M^+, 80), 195 (5), 83 (15), 77 (25).

8-Oxo-4-phenyl-4,8-dihydro-1-thia-4,5,9-triazacyclopenta[a]naphthalene-7-carboxylic acid amide (14c). Orange crystals from ethanol. Yield 98%; m.p. 200 °C; Anal. Calcd. for C_{16}H_{8}N_{4}O_{2}S (322): C, 59.62; H, 3.13; N, 17.83. Found: C, 59.59; H, 3.11; N, 17.80. IR (KBr): ν_{max} 3,400, 3,312 (NH_{2}), 1,615 (CN), 1,680 (CO); 1H-NMR (DMSO-d_{6}): δ = 7.2–7.2 (t, thiol-H); 7.6–8.0 (m, 5H, Ph-H); 8.1 (s, nicotine-H); 13C-NMR (DMSO-d_{6}): δ = 147.5, 139.3, 139.0, 138.1, 137.2, 136.2, 133.3, 133.0, 130.3, 129.9, 128.8, 128.2, 126.1, 115.0, 114.2; MS: m/z (%) 323 (M^+, 100), 306 (15), 111 (90), 77 (30).

8-Oxo-4-phenyl-4,8-dihydro-1-thia-4,5,9-triazacyclopenta[a]naphthalene-7-carboxthioic acid amide (14d). Brown crystal from ethanol/AcOH. Yield 90%; m.p. 230 °C; Anal. Calcd. for C_{16}H_{10}N_{4}O_{2}S (338): C, 56.79; H, 2.98; N, 16.56. Found: C, 56.65; H, 2.82; N, 16.41. IR (KBr): ν_{max} 3,400, 3,312 (NH_{2}), 1,620 (CN); 13C-NMR (DMSO-d_{6}): δ = 164.15, 146.7, 144.0, 141.0, 129.3, 127.0, 126.0, 118.5, 115.1; MS: m/z (%) 339 (M^+, 25), 111 (75), 77 (50).

7-(1H-Benzimidazol-2-yl)-4-phenyl-4H-1-thia-4,5,9-triazacyclopenta[a]naphthalen-8-one (14g). Yellow crystals from ethanol. Yield 95%; m.p. 230 °C; Anal. Calcd. for C_{22}H_{13}N_{3}OS (395): C, 66.82; H, 3.31;
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N, 17.71. Found: C, 66.70; H, 3.21; N, 17.68; IR (KBr): \(\nu_{\text{max}}\) 1,670 (CO), 1,620 (CN); \(^1\text{H-NMR (DMSO-d}_6\)): \(\delta = 7.2–7.3\) (t, 1H, NH, D\(_2\)O exchangeable); 7.2–7.3 (m, 2H, thiol-H); 7.5–8.1 (m, 9H, Ph-H); 8.4 (s, 1H, nicotine-H); \(^1\text{C-NMR (DMSO-d}_6\)): \(\delta = 151.9, 147.0, 138.5, 136.9, 136.0, 129.1, 128.9, 128.4, 128.1, 126.5, 123.3, 121.0); MS: \(m/z\) (%) 396 (M\(^+\), 100), 286 (25), 195 (15), 111 (90), 77 (30).

4-Phenyl-7-(4-phenylthiazol-2-yl)-4H-l-thia-4,5,9-triazacyclopenta[a]naphthalen-8-one (14K). Yellow crystals from ethanol, yield 95%; m.p. 200 °C; Anal. Calcd. for C\(_{24}\)H\(_{14}\)N\(_4\)O\(_2\)S (438): C, 65.73; H, 3.22; N, 12.78. Found: C, 65.70; H, 3.11; N, 12.68; IR (KBr): \(\nu_{\text{max}}\) 1,680 (CO), 1,620 (CN); \(^1\text{H-NMR (DMSO-d}_6\)): \(\delta = 7.2–7.4\) (t, 2H, thiol-H); 7.4–8.1 (m, 10H, Ph-H); 8.41 (s, 1H, thiazole-H); 8.6 (s, 1H, nicotine-H); \(^1\text{C-NMR (DMSO-d}_6\)): \(\delta = 154.4, 140.2, 138.5, 137.0, 136.2, 133.8, 130.7, 130.3, 129.7, 128.9, 128.3, 128.1, 126.6, 126.1, 121.0, 119.52); MS: \(m/z\) (%) 439 (M\(^+\), 100), 368 (5), 236 (10), 111 (20).

8-Oxo-4-phenyl-4,8-dihydro-1-oxa-4,5,9-triazacyclopenta[a]naphthalene-7-carboxylic acid amide (16c). Yellow crystals from ethanol, yield 95%; m.p. 288 °C; Anal. Calcd. for C\(_{16}\)H\(_{10}\)N\(_4\)O\(_3\) (306): C, 62.74; H, 3.29; N, 18.29. Found: C, 62.74; H, 3.29; N, 17.32. IR (KBr): \(\nu_{\text{max}}\) 1,685 (CO), 1,620 (CN); \(^1\text{H-NMR (DMSO-d}_6\)): \(\delta = 6.7–6.7\) (m, 2H, furan-H); 7.0 (s, 1H, nicotine-H); 7.5–8.4 (m, 5H, Ph-H), 8.7 (br, 2H, NH\(_2\), D\(_2\)O exchangeable); \(^1\text{C-NMR (DMSO-d}_6\)): \(\delta = 162.6, 149.0, 148.9, 139.9, 130.4, 129.8, 127.2, 126.5, 123.1, 112.7); MS: \(m/z\) (%) 307 (M\(^+\), 100), 290 (15), 95 (50), 77 (25).

8-Oxo-4-phenyl-4,8-dihydro-1-oxa-4,5,9-triazacyclopenta[a]naphthalene-7-carbothioic acid amide (16d). Deep brown crystal from ethanol, yield 95%; m.p. 220 °C; Anal. Calcd. for C\(_{16}\)H\(_{10}\)N\(_4\)O\(_2\)S (322): C, 59.62; H, 3.13; N, 17.38. Found: C, 59.60; H, 3.44; N, 17.32. IR (KBr): \(\nu_{\text{max}}\) 1,638 (CO), 1,620 (CN); \(^1\text{C-NMR (DMSO-d}_6\)): \(\delta = 164.0, 155.0, 146.7, 143.0, 141.0, 129.3, 118.5, 115.1, 110.0); MS: \(m/z\) (%) 323 (M\(^+\), 25), 305 (75), 289 (60), 95 (80), 51 (40).

7-(1H-Benzimidazol-2-yl)-4-phenyl-4H-l-thia-4,5,9-triazacyclopenta[a]naphthalen-8-one (16g). Yellow crystals from ethanol, yield 98%; m.p. 278 °C; Anal. Calcd. for C\(_{22}\)H\(_{13}\)N\(_5\)O\(_2\) (379): C, 69.65; H, 3.45; N, 18.46. Found: C, 69.59; H, 3.41; N, 18.42. IR (KBr): \(\nu_{\text{max}}\) 1,614 (CN), 1,670 (CO); \(^1\text{C-NMR (DMSO-d}_6\)): \(\delta = 151.9, 149.1, 148.7, 146.9, 143.0, 141.0, 129.3, 118.5, 115.1, 110.0); MS: \(m/z\) (%) 380 (M\(^+\), 100), 286 (25), 195 (25), 95 (50), 77 (20).

7-Benzo thiazol-2-yl-4-phenyl-4H-l-oxa-4,5,9-triazacyclopenta[a]naphthalen-8-one (16h). Orange crystals from ethanol, yield 98%; m.p. 258 °C; Anal. Calcd. for C\(_{18}\)H\(_{14}\)N\(_4\)O\(_3\) (396): C, 66.6; H, 3.05; N, 14.13. Found: C, 66.59; H, 3.00; N, 14.12. IR (KBr): \(\nu_{\text{max}}\) 1,614 (CN), 1,680 (CO); \(^1\text{H-NMR (DMSO-d}_6\)): \(\delta = 6.7\) (s, 1H, furan-H); 7.3 (s, 1H, furan-H); 7.4–7.7 (m, 9H, Ph-H); 8.6 (s, 1H, nicotine-H); \(^1\text{C-NMR (DMSO-d}_6\)): \(\delta = 158.8, 151.4, 151.4, 149.0, 148.9, 148.8, 140.1, 140.0, 137.8, 131.0, 130.4, 129.8, 126.6, 126.6, 125.7, 123.3, 123.1, 122.1, 121.6, 112.8); MS: \(m/z\) (%) 397 (M\(^+\), 100), 303 (5), 212 (10), 95 (40), 77 (10).

4-Phenyl-7-(4-phenylthiazol-2-yl)-4H-l-oxa-4,5,9-triazacyclopenta[a]naphthalen-8-one (16k). Yellow crystals from ethanol, yield 98%; m.p. 230 °C; Anal. Calcd. for C\(_{24}\)H\(_{14}\)N\(_4\)O\(_2\)S (422): C, 68.23; H, 3.34; N, 13.26. Found: C, 68.19; H, 3.21; N, 13.12. IR (KBr): \(\nu_{\text{max}}\) 1,614 (CN), 1,680 (CO); \(^1\text{C-NMR
(DMSO-$d_6$): δ = 164.0, 155.0, 146.7, 143.0, 139.0, 136.2, 129.3, 128.0, 127.0, 118.0, 115.1, 114.0, 110.0; MS: m/z (%) 423 (m$^+$, 100), 329 (5), 238 (5), 95 (25), 77 (10).

8-Oxo-4-phenyl-4,8-dihydro-1-oxa-4,5,9-triazacyclopenta[a]naphthalene-7-carboxylic acid benzylidene hydrazide (16l). Orange crystals from ethanol, yield 98%; m.p. 266 °C; Anal. Calcd. for C$_{23}$H$_{15}$N$_5$O$_3$ (409): C, 67.48; H, 3.69; N, 17.11. Found: C, 67.45; H, 3.59; N, 17.00; IR (KBr): $\nu$$_{max}$: 1,559 1,614 (CN), 1,680 (CO); $^1$H-NMR (DMSO-$d_6$): δ = 6.7 (s, 1H, CH); 7.2 (s,1H, nicotine-H); 7.4–7.5 (t, 2H, furan-H); 7.7–8.3 (m, 10H, Ph-H); $^{13}$C-NMR (DMSO-$d_6$): δ = 130.5, 128.8, 127.4, 112.8, 106.4, 55.8, 18.9; MS: m/z (%) 410 (M$^+$, 50), 291 (10), 105 (5), 77 (10).

4. Conclusions

In conclusion it has been found that 5 condenses with 1a to yield pyridazinones 7 as indicted from the presence of a carbonyl carbon as δ = 165 ppm in the $^{13}$C-NMR. Initially formed imines 6 in this case are readily hydrolysed under the reaction conditions to yield the final products. In fact this finding supports our belief that heterocyclic imines like 6 are difficult to isolate as they readily afford the more stable aromatic derivative.

Supplementary Materials

Supplementary materials can be accessed at: http://www.mdpi.com/1420-3049/17/5/5924/s1.

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*Sample Availability:* Samples of the all compounds are available from the authors.

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