Studies with 2-arylhydrazononitriles: further investigations on the utility of 2-arylhydrazononitriles as precursors to 1,2,3-triazole amines

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3-Oxo-2-arylhydrazonobutanenitriles react with hydroxylamine hydrochloride in ethanolic sodium acetate to yield either amidoximes or isoxazolamines depending on the nature of the substituent. The amidoximes cyclise in refluxing DMF containing piperidine to form 2-aryl-1,2,3-triazol-5-amines. The isoxazolamines rearranged into 1,2,3-triazolamines on refluxing in DMF. Amidoxime **2c** cyclised in acetic anhydride to give 2-arylhydrazono-1,2,4-oxadiazole **9c**, which rearranged to acetylamino-1,2,3-triazole **8c**. The prepared acetyl-1,2,3-triazolamines **8b,c** were utilised as precursors to triazolopyridines and pyrazolyltriazoles.

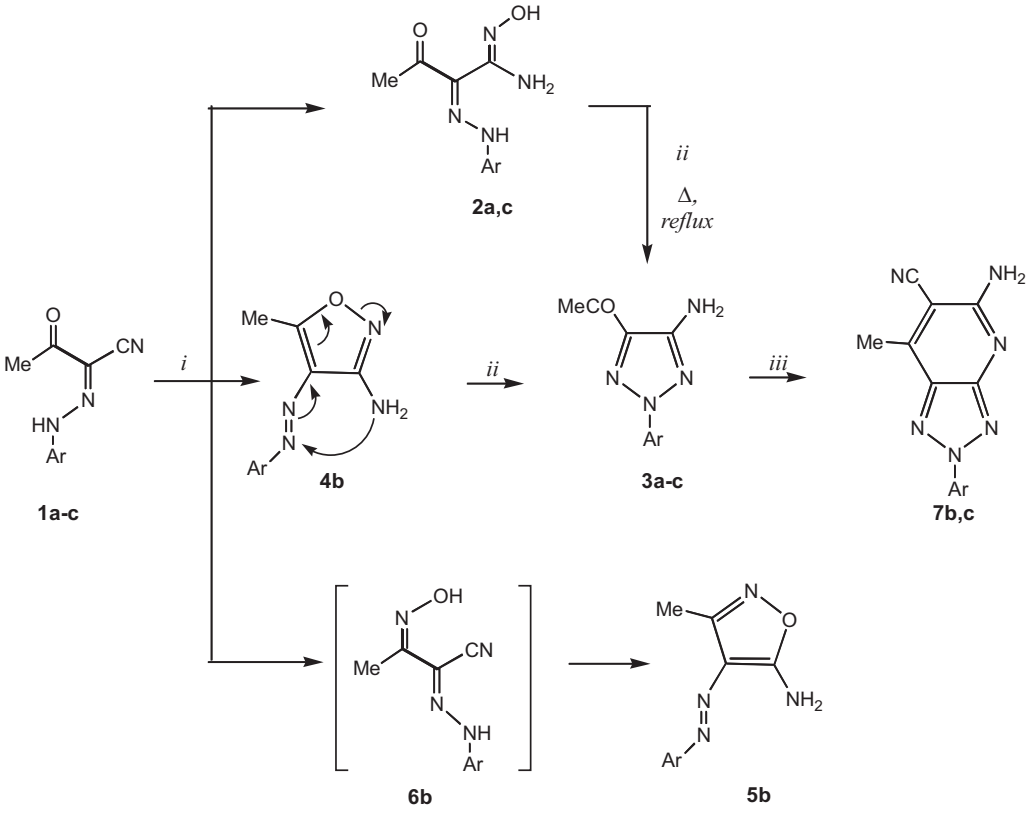
Keywords: arylhydrazones, amidoximes, ketonitriles, isoxazoleamines, pyrazoles, 1,2,3-triazoleamines, fused 1,2,3-triazoles, fused pyridines

The synthetic potentialities of 2-arylhydrazononitriles have recently been reviewed.[1] Elnagdi *et al.* showed that these readily obtainable[2-4] versatile starting materials are excellent precursors to pyrazolamines, 1,2,4-triazolamines,[5] 1,2,3-triazolamines,[6] isoxazol-3-amines[7] and pyridazin-6-imines.[8] Recently Elnagdi *et al.* have reported that 2-phenylhydrazono-3-oxobutanenitrile **1a** reacted with hydroxylamine hydrochloride in ethanolic sodium acetate to yield amidoxime **2a** that cyclised readily into 4-acetyl-2-phenyl-1,2,3-triazol-5-amine **3a** upon reflux in DMF in presence of piperidine.[9]

Results and discussion

As part of this work, we subjected **1b** to hydroxylamine hydrochloride in ethanolic sodium acetate. Unexpectedly, a condensation product with elimination of water was obtained. We had expected that an intermediately formed amidoxime **2b** would cyclise readily to **3b** in a way similar to that reported recently from our laboratories.[10] However, ^{13}C NMR of the reaction product indicated that this was not the case, as it indicated the absence of the carbonyl carbon in the range δ = 180–200 ppm. We therefore considered the formation of isomeric isoxazoles **4b** and/or **5b**. While **4b** can be produced *via* cyclisation of the initially formed **2b**, formation of **5b** can take place only *via* intermediacy of the initial product of condensation of the keto carbonyl of **1b** with hydroxylamine, yielding **6b,** that could then cyclise to **5b** (Scheme 1).

The subsequent chemical behaviour of the reaction product led us to conclude that **4b** is the correct structure. Thus, when it was heated in DMF in the presence of piperidine it rearranged readily into **3b**, which reacted readily with malononitrile to yield the triazolo[4,5-*b*]pyridine **7b** (Scheme 1).



Scheme 1 *Reagents: i*, $NH_2OH.HCl$, EtOH, NaOAc; *ii*, DMF/piperidine; *iii*, $CH_2(CN)_2$, EtOH

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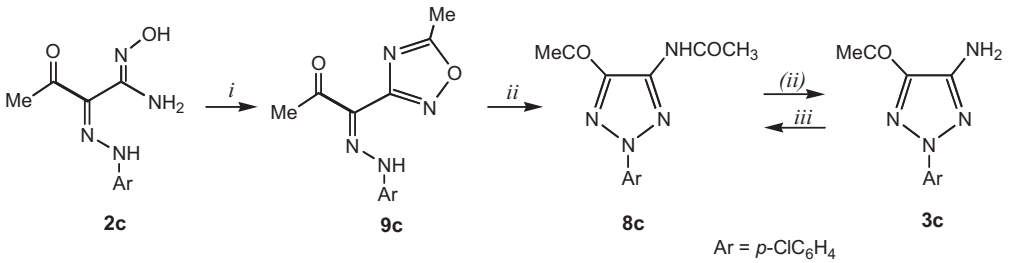
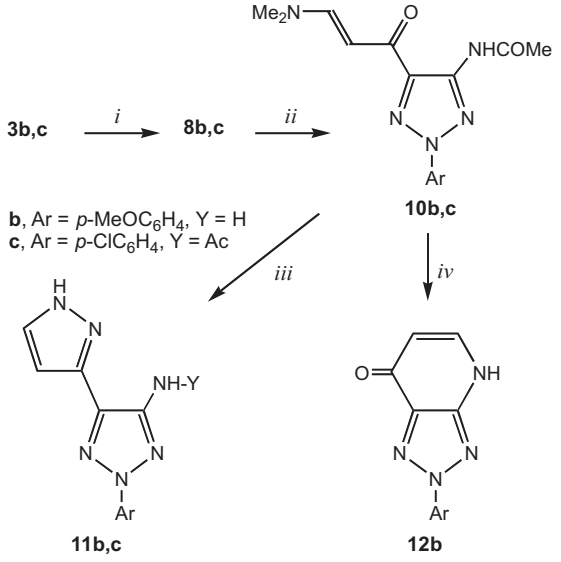


Scheme 2 *Reagents: i,* Ac_2O; *ii,* reflux, DMF; *iii,* $AcOH/Ac_2O$.



Scheme 3 *Reagents: i,* $Ac_2O/AcOH$*; ii,* DMFDMA, xylene; *iii,* $N_2H_4.H_2O/EtOH$; *iv,* DMF, piperidine.

To our knowledge, this is the first reported rearrangement of arylazoisoxazol-3-amines into 1,2,3-triazole derivatives. In contrast to **1b**, compound **1c** reacted with hydroxylamine hydrochloride in ethanolic sodium acetate yielding **2c** that cyclised into **3c** on refluxing in DMF in the presence of piperidine. The latter also condensed with malononitrile, yielding **7c** (Scheme 1).

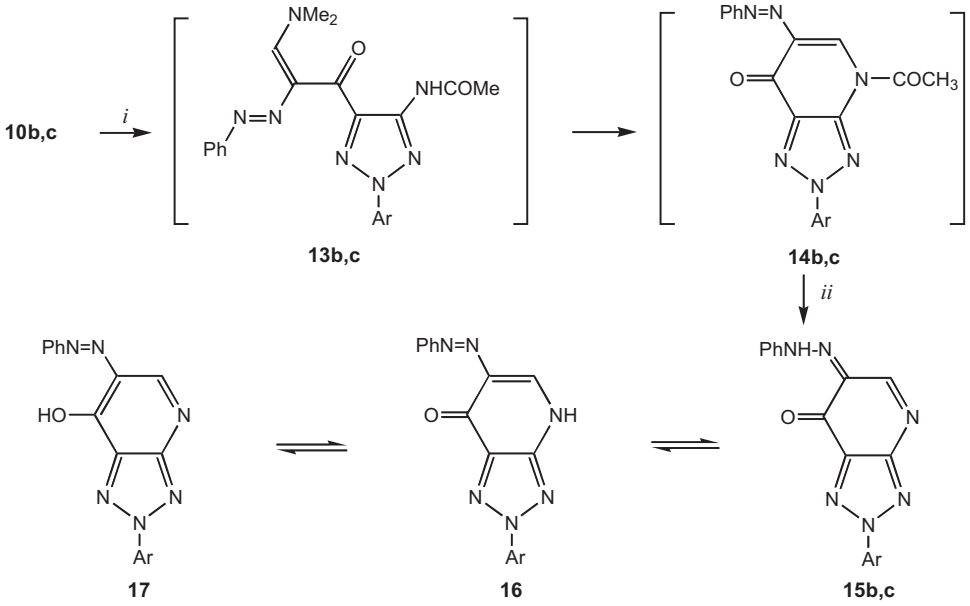
In an attempt to cyclise **2c** to the 1,2,3-triazole derivative **3c** *via* refluxing in acetic anhydride, an acylated product was formed. Initially we thought that this product is acetyl derivatives of **3c** (compounds **8c**). However, **8c** proved to be different from the product of reaction **2c** with acetic anhydride. The latter was thus assigned structure **9c**. Heating **9c** in DMF gives **3c**. We believe that initially a Katritzky–Boulton[11] rearrangement of **9c** into **8c** occurred and that **8c** was then deacetylated under the reaction conditions.

We have investigated the potential utility of **8b,c** for synthesis of azolyl-1,2,3-triazoles as well as 1,2,3-triazoloazines. Refluxing **8b,c** with dimethylformamide dimethylacetal (DMFDMA) afforded the *trans*-enaminones **10b,c** based on their ^{1}H NMR. Thus, the ^{1}H NMR of **10b** revealed two olefinic protons at δ = 5.85 and 7.13 ppm with the coupling constant J = 12 Hz. A smaller J would be expected for *cis* olefinic protons.

Compounds **10b,c** were refluxed with hydrazine hydrate in ethanol to yield the pyrazolyl-1,2,3-triazole **11b,c**. Refluxing **10b** in DMF in the presence of piperidine gave 1,2,3-triazolo-[4,5-*b*]pyridine **12b** (Scheme 3).

Coupling of **10b,c** with benzenediazonium chloride gave **15b,c** *via* intermediacy of the nonisolable **13b,c**, or their hydrolysis products **14b,c**. Enaminones are known to react readily with aromatic diazonium salts to yield arylazo (or arylhydrazono) derivatives.[12] This is thus a further application of this reaction.

Although **15b,c** can also, at least in theory, exist as **16** or **17** or other tautomers, ^{13}C NMR as well as NOE difference experiment supported the proposed hydrazone structure **15b,c** (Scheme 4).



Scheme 4 *Reagents: i,* $PhN_2^+Cl^-$; *ii,* (deacetylation).

Experimental

IR spectra were recorded in KBr and were determined on a Perkin-Elmer 2000 FT-IR system. NMR spectra were determined on a Bruker DPX spectrometer, at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR, in $CDCl_3$ or DMSO-d_6 as solvent and TMS as internal standard; chemical shifts are reported in δ (ppm). Mass spectra were measured on VG Autospec QMS 30 and MS 9 (AEI) spectrometers, with EI 70 eV. Elemental analyses were measured using a LEO CHNS-932 Elemental Analyser in the Analytical Laboratory of Kuwait University.

Synthesis of hydrazono-nitriles **1b,c**: *general procedure*
A cold solution of aryldiazonium salt (0.01 mol) was prepared by adding sodium nitrite (0.7 g) in H_2O (5 ml) to a cold solution of an arylamine hydrochloride (0.01 mol of arylamine in 5 ml concentrated HC1) with stirring. The resulting aryldiazonium salt solution was then dropped into a cold solution of 3-aminocrotononitrile (0.82 g, 0.01 mol) in ethanol (10 ml) and subsequently sodium acetate (2 g) was added. The reaction mixture was then kept at room temperature for 1 h. The resulting solid product which separated was filtered off and dissolved in acetic acid (20 ml). Concentrated hydrochloric acid (12 ml) was added, and the mixture was refluxed for 15 min, allowed to cool, and then poured into ice-water. A yellow solid was obtained, which was isolated and recrystallised from ethanol.

2-[2-(4-Methoxyphenyl)hydrazono]-3-oxobutanenitrile (**1b**): Yellow plates (90%), m.p. 130–132°C. IR: ν_{max} 3198 (NH), 2213 (CN), 1667 cm^{-1} (CO). NMR: δ_H ($CDCl_3$) 2.5 (s, 3H, CH_3), 3.8 (s, 3H, OCH_3), 6.9 (d, 2H, *J* = 8 Hz, Ar–H), 7.3 (d, 2H, *J* = 8 Hz, Ar–H), 9.6 (s, 1H, NH, D_2O exchangeable); δ_C (DMSO-d_6) 193.5 (CO), 157.9, 136.4, 130.3, 119.1 (2CH), 115.6 (2CH), 112.2, 56.2, 25.5 (CH_3). MS: *m/z* (%) 217 (M^+, 98), 122 (65), 107 (80), 77 (50). Anal. Calcd for $C_{11}H_{11}N_3O_2$ (217.2): C, 60.8; H, 5.1; N, 19.3. Found: C, 60.6; H, 4.9; N, 19.3%.

2-[2-(4-Chlorophenyl)hydrazono]-3-oxobutanenitrile (**1c**): Yellow plates (82%), m.p. 220–222°C. IR (KBr): ν_{max} 3236 (NH), 2211 (CN), 1667 cm^{-1} (CO). NMR (DMSO-d_6): δ_H 2.4 (s, 3H, CH_3), 7.4 (d, 2H, *J* = 8 Hz, Ar–H), 7.5 (d, 2H, *J* = 8 Hz, Ar–H), 12.3 (s, 1H, NH, D_2O-exchangeable); δ_C 193.5 (CO), 141.9, 130.3 (2CH), 129.9, 118.8 (2CH), 115.2, 111.8 56.2, 25.5 (CH_3). MS: *m/z* (%) 221 (M^+, 100), 139 (40), 111 (85), 75 (15). Anal. Calcd for $C_{10}H_8ClN_3O$ (221.6): C, 54.1; H, 3.6; N, 18.9. Found C, 54.0; H, 3.6; N, 19.0%.

2-[2-(4-Chlorophenyl)hydrazono]-N-hydroxy-3-oxobutanamidine (**2c**)
The nitrile **1c** (2.21 g, 0.01 mol), hydroxylamine hydrochloride (0.69 g; 0.01 mol), and sodium acetate (0.82 g, 0.01 mol) in ethanol (20 ml) were refluxed for 4 h. After cooling, the mixture was poured onto ice-water. The solid which separated was collected by filtration and crystallised from ethanol to give yellow needles (yield 75%), m.p. 207–208°C. IR: ν_{max} 3478 (OH), 3340, 3285 (NH_2), 3155 (NH), 1697 cm^{-1} (CO). NMR: δ_H ($CDCl_3$) 2.5 (s, 3H, CH_3), 6.1 (br, 1H, OH, D_2O-exchanged), 6.5 (br, 2H, NH_2, D_2O-exchanged), 7.2 (d, 2H, *J* = 8 Hz, Ar–H) 7.3 (d, 2H, *J* = 8 Hz, Ar–H), 13.4 (s, 1H, NH, D_2O-exchanged); δ_C (DMSO-d_6) 199.4 (CO), 152.1, 142.4, 130.5 (2CH), 128.4, 127.8, 117.1 (2CH), 27.4 (CH_3). MS: *m/z* (%) 254 (M^+, 95), 237 (80), 221 (40), 195 (10), 141 (20), 127 (60), 111 (40), 90 (15), 69 (45). Anal. Calcd for $C_{10}H_{11}ClN_4O_2$ (254.6): C, 47.1; H, 4.3; N, 22.0. Found C, 47.5; H, 4.2; N, 22.0%.

1-(5-Amino-2-(4-chlorophenyl)-2H-1,2,3-triazol-4-yl)ethanone (**3c**)
The amidoxime **2c** (2.54 g, 0.01 mol) was refluxed for 6–8 h in *N*, *N*-dimethylformamide (10 ml) containing a few drops of piperidine. The solution was cooled and then poured onto ice-water. The solid which separated was collected by filtration and crystallised from petroleum ether (b.p. 60–80°C) to give yellow granules (66%), m.p. 117–118°C. IR: ν_{max} 3479, 3384 (NH_2), 1676 cm^{-1} (CO). NMR ($CDCl_3$): δ_H 2.6 (s, 3H, CH_3), 5.1 (s, 2H, NH_2, D_2O-exchanged), 7.4 (d, 2H, *J* = 8 Hz, Ar–H) 7.9 (d, 2H, *J* = 8 Hz, Ar–H); δ_C 194.6 (CO), 154.6, 138.3, 133.9, 130.7 (2CH), 120.7 (2CH), 117.5, 27.2 (CH_3). MS: *m/z* (%) 236 (M^+, 100), 194 (15), 125 (10), 111 (65), 90 (20), 75 (10). Anal. Calcd for $C_{10}H_9ClN_4O$ (236.6): C, 50.8; H, 3.8; N, 23.6. Found C, 51.2; H, 3.9; N, 23.3%.

4-(4-Methoxyphenyl)-5-methylisoxazol-3-amine (**4b**)
The nitrile **1b** (2.17 g, 0.01 mol), hydroxylamine hydrochloride (0.69 g; 0.01 mol), and sodium acetate (0.82 g, 0.01 mol) were heated to reflux for 2 h in ethanol (20 ml). After cooling, the mixture was poured into ice-water. The solid which separated was collected by filtration and crystallised from petroleum ether (60–80°C) to give yellow needles (83%), m.p. 165–166°C. IR: ν_{max} 3430, 3274 cm^{-1} (NH_2). NMR ($CDCl_3$): δ_H 2.7 (s, 3H, CH_3), 3.9 (s, 3H, OCH_3), 5.3 (s, 2H, NH_2, D_2O-exchanged), 6.9 (d, 2H, *J* = 8 Hz, Ar–H), 7.7 (d, 2H, *J* = 8 Hz, Ar–H); δ_C 171.6, 162.2, 156.5, 147.2, 125.4 (2CH), 118.2, 115.65 (2CH), 56.22 (CH_3), 11.9 (CH_3). MS: *m/z* (%) 232 (M^+, 95), 221 (30), 189 (20), 147 (30), 135 (25), 121 (80), 107 (40), 73 (35), 55 (35). Anal. Calcd for $C_{11}H_{12}N_4O_2$ (232.2): C, 56.9; H, 5.2; N, 24.1. Found C, 56.8; H, 5.1; N, 23.8%.

1-[5-Amino-2-(4-methoxyphenyl)-2H-1,2,3-triazol-4-yl]ethanone (**3b**)
Compound **4b** (2.32 g, 0.01 mol) in *N*,*N*-dimethylformamide (10 ml) containing a few drops of piperidine was heated under reflux for 4 h, cooled, and then poured into ice-water. The solid which separated was collected by filtration and crystallised from ethanol to give yellow plates(yield 75%), m.p. 143–145°C. IR: ν_{max} 3452, 3355 (NH_2), 1660 cm^{-1} (CO). NMR: δ_H ($CDCl_3$) 2.6 (s, 3H, CH_3), 3.8 (s, 3H, CH_3), 6.3 (s, 2H, NH_2, D_2O-exchanged), 7.1 (d, 2H, *J* = 8 Hz, Ar–H), 8.8 (d, 2H, *J* = 8 Hz, Ar–H); δ_C (DMSO-d_6) 193.7 (CO), 159.7, 155.3, 133.4, 132.3, 120.7 (2CH), 115.7 (2CH), 80.1, 56.5 (CH_3), 27.6 (CH_3). MS: *m/z* (%) 232 (M^+, 100), 189 (15), 148 (15), 121 (85). Anal. Calcd for $C_{11}H_{12}N_4O_2$ (232.2): C, 56.9; H, 5.2; N, 24.1. Found C, 57.1; H, 5.2; N, 24.1%.

Synthesis of triazolopyridines **7b,c**, *general procedure*
Equimolecular amounts of compound **3b,c** (0.01 mol) and malononitrile (0.66 g, 0.01 mol) in *N*,*N*-dimethylformamide (10 ml) were treated with a few drops of piperidine. The reaction mixture was heated to reflux for 3 h. After cooling, the mixture was poured onto ice-water. The solid, so formed, was collected by filtration and crystallised from ethanol.

5-Amino-2-(4-methoxyphenyl)-7-methyl-2H-[1,2,3]triazolo[4,5-b]pyridine-6-carbonitrile (**7b**): Yellow fibrous crystals (yield 62%), m.p. 277–278°C. IR: ν_{max} 3469, 3366 (NH_2), 2218 cm^{-1} (CN). NMR: δ_H ($CDCl_3$) 2.9 (s, 3H, CH_3), 3.9 (s, 3H, CH_3), 5.4 (s, 2H, NH_2, D_2O-exchanged), 7.1 (d, 2H, *J* = 8 Hz, Ar–H), 8.2 (d, 2H, *J* = 8 Hz, Ar–H); δ_C (DMSO-d_6) 160.9, 159.3, 157.0, 149.2, 133.7, 133.4, 122.2 (2CH), 116.3, 115.9 (2CH), 97.5, 56.67 (OCH_3), 17.17 (CH_3). MS: *m/z* (%) 280 (M^+, 80), 265 (20), 232 (40), 221 (50), 207 (20), 147 (20), 121 (30), 97 (40), 81 (50), 69 (95), 57 (80). Anal. Calcd for $C_{14}H_{12}N_6O$ (280.3): C, 59.9; H, 4.3; N, 29.9. Found C, 59.9; H, 4.3; N, 29.5%.

5-Amino-2-(4-chlorophenyl)-7-methyl-2H-[1,2,3]triazolo[4,5-b]pyridine-6-carbonitrile (**7c**): Yellow crystals (yield 58%), m.p. 289–290°C. IR: ν_{max} 3390, 3386 (NH_2), 2230 cm^{-1} (CN). NMR: δ_H ($CDCl_3$) 2.9 (s, 3H, CH_3), 5.5 (s, 2H, NH_2, D_2O-exchanged), 7.5 (d, 2H, *J* = 8 Hz, Ar–H), 8.2 (d, 2H, *J* = 8 Hz, Ar–H). δ_C (DMSO-d_6) 159.4, 157.1, 149.5, 138.9, 134.6, 134.1, 130.8 (2CH), 122.2 (2CH), 116.1, 98.6, 17.2 (CH_3). MS: *m/z* (%) 284 (M^+, 65), 235 (95), 218 (50), 193 (15), 138 (30), 124 (75), 110 (80), 90 (30), 69 (35). Anal. Calcd for $C_{13}H_9ClN_6$ (284.7): C, 54.8; H, 3.1; N, 29.5. Found C, 54.6; H, 3.2; N, 29.2%.

Synthesis of triazoles **8b,c**: *general procedure*
Equimolar amounts of amine **3b,c** (0.01 mol) and acetic anhydride (1.02 g, 0.01 mol) in glacial acetic acid (20 ml) were heated to reflux for 2 h. After cooling, the reaction mixture was poured into ice-water. The solid so formed was collected by filtration and crystallised from petroleum ether (b.p. 60–80°C) to give yellow crystals.

N-[5-Acetyl-2-(4-methoxyphenyl)-2H-1,2,3-triazol-4-yl]acetamide (**8b**): Yellow granules (70%), m.p. 126–127°C. IR: ν_{max} 3321 (NH), 1716 (CO), 1670 cm^{-1} (CO). NMR (DMSO-d_6): δ_H 2.1 (s, 3H, CH_3), 2.5 (s, 3H, CH_3), 3.38 (s, 3H, OCH_3), 7.1 (d, 2H, *J* = 8 Hz, Ar–H), 7.9 (d, 2H, *J* = 8 Hz, Ar–H), 10.1 (br, 1H, NH, D_2O-exchanged); δ_C 192 (CO), 169.4 (CO), 145.4, 138.9, 133.8, 130.9 (2CH), 130.7, 121.5 (2CH), 56.8 (OCH_3), 28.8 (CH_3), 24.2 (CH_3). MS: *m/z* (%) 274 (M^+, 60), 232 (100), 217 (10), 189 (25), 135 (15), 121 (40), 107 (25), 92 (15), 77 (15), 64 (10). Anal. Calcd for $C_{13}H_{14}N_4O_3$ (274.3): C, 56.9; H, 5.1; N, 20.4. Found C, 56.8; H, 5.2; N, 20.3%.

N-[5-Acetyl-2-(4-chlorophenyl)-2H-1,2,3-triazol-4-yl]acetamide (**8c**): Yellow solid (63%), m.p. 160–162°C. IR: ν_{max} 3287 (NH), 1693 (CO), 1674 cm^{-1} (CO). NMR (DMSO-d_6): δ_H 2.1 (s, 3H, CH_3), 2.6 (s, 3H, CH_3), 7.6 (d, 2H, *J* = 8 Hz, Ar–H), 8.1 (d, 2H, *J* = 8 Hz, Ar–H), 10.2 (br, 1H, NH, D_2O-exchanged); δ_C 192 (CO), 169.4 (CO), 145.4, 138.2, 133.9, 130.8 (2CH), 125.3, 121.1 (2CH), 28.7 (CH_3), 19.5 (CH_3). MS: *m/z* (%) 278 (M^+, 30), 236 (95), 194 (25). Anal. Calcd for $C_{12}H_{11}ClN_4O_2$ (278.7): C, 51.7; H, 3.9; N, 20.1. Found C, 51.6; H, 4.0; N, 19.0%

1-[2-(4-Chlorophenyl)hydrazono]-1-(5-methyl-1,2,4-oxadiazol-3-yl)propan-2-one (**9c**)
Equimolecular amounts of the amidoxime **2c** (2.54 g, 0.01 mol) and acetic anhydride (1.02 g, 0.01 mol) in glacial acetic acid (20 ml) was

heated for 2 h under reflux. After cooling, the mixture was poured into ice-water. The solid so formed was collected by filtration and crystallised from petroleum ether (b.p. 60–80°C) to give faintly yellow fibrous crystals (62%), m.p. 170–172°C. IR): ν_{max} 3327 (NH), 1677 cm^{-1} (CO). NMR: δ_H ($CDCl_3$) 2.3 (s, 3H, CH_3), 2.7 (s, 3H, CH_3), 7.4 (d, 2H, *J* = 8 Hz, Ar–H), 8.1 (d, 2H, *J* = 8 Hz, Ar–H), 9.3 (br, 1H, NH, D_2O-exchanged); δ_C (DMSO-d_6) 195.5 (CO), 167.8, 147.1, 138.1, 134.8, 130.3 (2CH), 122.2 (2CH), 118.3, 27.6 (CH_3), 25.1 (CH_3). MS: *m/z* (%) 278 (M^+, 20), 236 (100), 221 (20), 194 (20), 139 (20), 125 (40), 111 (70), 90 (20). Anal. Calcd for $C_{12}H_{11}ClN_4O_2$ (278.7): C, 51.7; H, 3.9; N, 20.1. Found C, 51.7; H, 4.0; N, 20.2%.

Synthesis of the enaminoketones **10b,c**, *general procedure*
The acetmidotriazole **8b,c** (0.01 mol) and *N*,*N*-dimethylformamide dimethylacetal (1.19 g, 0.01 mol) were heated to reflux for 6 h in xylene (20 ml). The reaction mixture was evaporated under reduced pressure to yield a crude product which from toluene formed dark yellow crystals.

N-[5-[3-(Dimethylamino)acryloyl]-2-(4-methoxyphenyl)]-2H-1,2,3-triazol-4-yl]acetamide (**10b**): Yellow granules (70%), m.p. 173–175°C. IR ν_{max} 3254 (NH), 1681 (CO), 1639 cm^{-1} (CO). NMR: δ_H (DMSO-d_6) 2.1 (s, 3H, CH_3), 2.9 (s, 3H, NCH_3), 3.2 (s, 3H, NCH_3), 3.8 (s, 3H, OCH_3), 5.8 (d, 1H, *J* = 12 Hz, CH), 7.1 (d, *J* = 8 Hz, 2H, Ar–H), 7.8 (d, 1H, *J* = 12, CH), 7.9 (d, *J* = 8, 2H, Ar–H), 10.1 (br, 1H, NH, D_2O-exchanged); δ_C ($CDCl_3$) 186.4 (CO), 167.3 (CO), 155.5, 145.5, 142.0, 134.9, 130.9 (2CH), 128.3, 121.5 (2CH), 92.4, 56.8 (OCH_3), 46.0 (NCH_3), 38.1 (NCH_3), 25.1 (CH_3). MS: *m/z* (%) 329 (M^+, 95), 312 (25), 285 (30), 243 (80), 121 (10), 98 (40), 70 (15). Anal. Calcd for $C_{16}H_{19}N_5O_3$ (329.4): C, 58.3; H, 5.8; N, 21.2. Found C, 58.1; H, 5.8; N, 21.3%.

N-[2-(4-Chlorophenyl)-5-(3-(dimethylamino)acryloyl)-2H-1,2,3-triazol-4-yl]acetamide (**10c**): Yellow crystals (65%), m.p. 186–188°C. IR: ν_{max} 3265 (NH), 1686 (CO), 1637 cm^{-1} (CO). NMR: δ_H (DMSO-d_6) 2.1 (s, 3H, CH_3), 2.9 (s, 3H, NCH_3), 3.3 (s, 3H, NCH_3), 5.8 (d, 1H, *J* = 12 Hz, CH), 7.6 (d, *J* = 8 Hz, 2H, Ar–H), 7.8 (d, 1H, *J* = 12 Hz, CH), 8.1 (d, *J* = 8 Hz, 2H, Ar–H), 10.2 (br, 1H, NH, D_2O-exchanged); δ_C ($CDCl_3$): 180.1 (CO), 167.3 (CO), 155.5, 146.3, 142.0, 138.4, 132.9, 130.5 (2CH), 120.9 (2CH), 91.9, 45.6 (CH_3), 38.1 (CH_3), 24,5 (CH_3). MS: *m/z* (%) 333 (M^+, 80), 316 (40), 292 (90), 263 (40), 247 (80), 221 (40), 111 (20), 98 (95), 70 (20). Anal. Calcd for $C_{15}H_{16}ClN_5O_2$ (333.7): C, 53.9; H, 4.8; N, 20.9. Found C, 53.9; H, 4.8; N, 20.7%.

Synthesis of pyrazolyltriazoles **11b,c**, *general procedure*
Equimolecular amounts of **10b**,**c** (0.01 mol) and hydrazine hydrate (0.5 g, 0.01 mol) in *N*,*N*-dimethylformamide (20 ml) were refluxed for 5 h. After cooling, the reaction mixture was poured into ice-water. The solid so formed was collected by filtration and crystallised from ethanol.

2-(4-Methoxyphenyl)-5-(1H-pyrazol-3-yl)-2H-1,2,3-triazol-4-amine (**11b**): Yellow granules (70%), m.p. 149–150°C. IR: ν_{max} 3433, 3387 (NH_2), 3313 cm^{-1} (NH). NMR: δ_H ($CDCl_3$) 3.8 (s, 3H, OCH_3), 4.8 (br, 2H, NH_2, D_2O-exchanged), 6.8 (d, 1H, *J* = 8 Hz, CH), 6.9 (d, 2H, *J* = 8 Hz, Ar–H), 7.6 (d, 1H, *J* = 8 Hz, CH), 7.9 (d, 2H, *J* = 8 Hz, Ar–H), 10.3 (br, 1H, NH, D_2O-exchanged); δ_C (DMSO-d_6) 158.2, 151.7, 134.2, 130.7, 122.2, 119.2 (2CH), 115.7, 115.6 (2CH), 102.8, 56.4 (CH_3). MS: *m/z* (%) 256 (M^+, 100), 241 (30), 121 (20), 107 (20), 92 (20), 77 (20). Anal. Calcd for $C_{12}H_{12}N_6O$ (256.3): C, 56.2; H, 4.7; N, 32.7. Found C, 55.9; H, 4.9; N, 32.5%.

N-[2-(4-Chlorophenyl)-5-(1H-pyrazol-3-yl)-2H-1,2,3-triazol-4-yl)acetamide (**11c**): Yellow crystals (68%), m.p. 251–252°C. IR ν_{max} 3258 (NH), 3200 (NH), 1668 cm^{-1} (CO). NMR: δ_H ($CDCl_3$) 2.1 (s, 3H, CH_3), 6.6 (d, 1H, *J* = 8 Hz, CH), 7.6 (d, 2H, *J* = 8 Hz, Ar–H), 7.8 (d, 1H, *J* = 8 Hz, CH), 8.0 (d, 2H, *J* = 8 Hz, Ar–H), 10.0 (br, 1H, NH, D_2O-exchanged), 13.2 (br, 1H, NH, D_2O-exchanged); δ_C (DMSO-d_6) 170.0 (CO), 142.8, 142.1, 140.8, 138.7, 132.6, 130.7 (2CH), 120.5 (2CH), 105.9, 104.5, 19.5 (CH_3). MS: *m/z* (%) 302 (M^+, 70), 260 (95), 125 (40), 111 (25), 94 (30), 75 (15). Anal. Calcd for $C_{13}H_{11}ClN_6O$ (302.7): C, 51.5; H, 3.6; N, 27.7. found C, 51.6; H, 3.6; N, 27.7%.

Synthesis of the triazolopyridines **15b,c**, *general procedure*
Benzenediazonium chloride solution was prepared by the standard literature procedure from aniline (0.93 g, 0.01 mol), concentrated hydrochloric acid, and sodium nitrite. Compound **10b,c** (0.01 mol) in ethanol (50 ml) was stirred with sodium acetate (5 g), and the diazonium salt solution was added gradually to the mixture. After the addition was complete, the reaction mixture was kept at room temperature for 1 h. The solid which separated was collected by filtration and crystallised from ethanol to give a dark yellow powder.

2-(4-Methoxyphenyl)-6-(2-phenylhydrazono)-2H-[1,2,3]triazolo[4,5-b]pyridin-7(6H)-one (**15b**): Yellow solid (79%), m.p. 253–255°C. IR: ν_{max} 3435 (NH), 1626 cm^{-1} (CO). NMR: δ_H (DMSO-d_6) 3.8 (s, 3H, OCH_3), 7.1 (d, 2H, *J* = 8 Hz, Ar–H), 7.4-7.8 (m, 5H, Ar–H), 8.1 (d, 2H, *J* = 8 Hz, Ar–H), 8.4 (s, 1H, CH), 15.8 (br, 1H, NH, D_2O-exchanged); δ_C ($CDCl_3$) 169.3 (CO), 161.0, 159.4, 141.4, 140.2, 135.8, 132.9, 130.4 (2CH), 130.0 (2CH), 130, 129.7, 119.3 (2CH), 115.0 (2CH), 56.6 (CH_3). MS: *m/z* (%) 346 (M^+, 100), 269 (15), 241 (75), 158 (25), 107 (25), 72 (25), 77 (70). Anal. Calcd for $C_{18}H_{14}N_6O_2$ (346.35): C, 62.4 H, 4.0; N, 24.2. Found C, 62.2; H, 3.9; N, 24.4%.

((Z)-2-(4-Chlorophenyl)-6-(2-phenylhydrazono)-2H-[1,2,3]triazolo[4,5-b]pyridin-7(6H)-one (**15c**): yellow solid (70%), m.p. 192–94°C. IR: ν_{max} 3355 (NH), 1629 cm^{-1} (CO). NMR: δ_H (DMSO-d_6) 7.3–7.8 (m, 7H, Ar–H), 8.2 (d, 2H, *J* = 8 Hz, Ar–H), 8.5 (s, 1H, CH), 16.0 (br, 1H, NH, D_2O-exchanged); δ_C ($CDCl_3$) 169.4 (CO), 161.0, 159.4, 141.4, 140.2, 135.8, 132.9, 130.4 (2CH), 130.2 (2CH), 130, 129.7, 122.3 (2CH), 120.0 (2CH). MS: *m/z* (%) 350 (M^+, 100), 273 (30), 245 (45), 210 (15), 182 (25), 162 (30), 125 (20), 111 (70), 93 (20), 77 (98). Anal. Calcd for $C_{17}H_{11}ClN_6O$ (350.7): C, 58.2; H, 3.1; N, 23.9. Found C, 58.2; H, 3.0; N, 23.7%.

The authors are grateful to Kuwait University Research Administration for financial support through project No. SC11/02 and for SAF facilities projects GS01/01; GS03/01.

Received 9 August 2007 ; accepted 3 September 2007
Paper 07/4783 doi: 10.3184/030823407X244869

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