2-Arylhydrazononitriles in heterocyclic synthesis: a novel route to 1,3-diaryl-1,2,4-triazol-5-amines *via* a Tiemann rearrangement of arylhydrazonoamidoximes

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Abstract

2-Arylhydrazononitriles react with hydroxylamine hydrochloride in refluxing ethanolic sodium acetate to yield amidoximes that cyclized into 1,2,3-triazol-5-amines or 1,2,4-triazol-5-amines depending on the nature of the substituents on hydrazone linkage. NOE difference experiments could successfully be utilized to distinguish 1,2,3-triazoles from isomeric 1,2,4-triazoles.

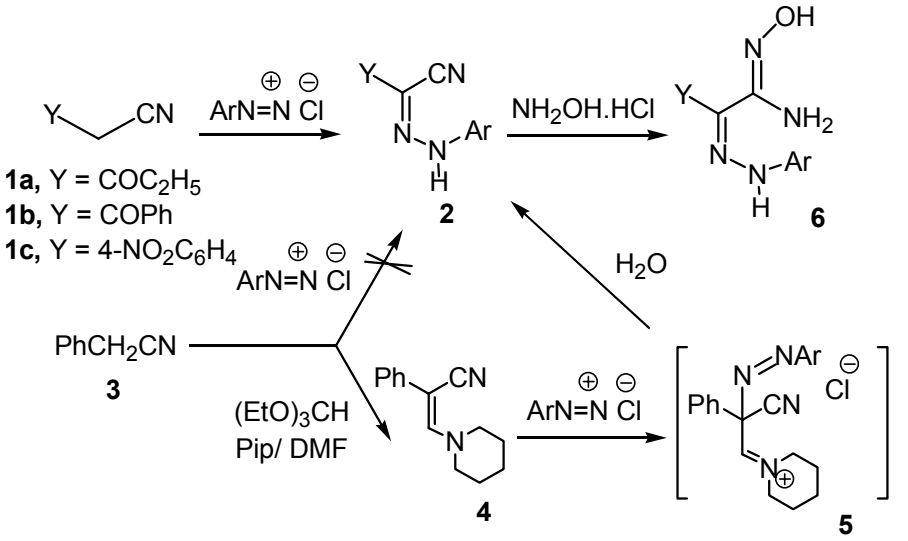
Keywords: Enaminonitriles; X-ray crystal structure determination, acetylamino-1,2,3-triazol-5-amines; NOE difference, Boulton-Katritzky rearrangement

Introduction

The chemistry of 2-arylhydrazono-3-substituted nitriles has been extensively investigated in our laboratories in the past.[1-3] Our interest in the chemistry of these compounds has recently been revived and we could show that these compounds are excellent precursors to 4-aminopyrazole-5-carboxylic acid derivatives,[4,5] interesting precursors to phosphodiesterase inhibitors such as sildenafil citrate (viagra)[4,5] as well as 4-acyl-2-substituted-1,2,3-triazolamines, potential precursors to pharmaceutically active triazoloazines; e.g. 1,4-dihydro-5-(2-propoxyphenyl)-7*H*-1,2,3-triazolo[4,5-d]pyrimidine-7-one (Zaprinast).[5,6] In conjunction to our interest in the chemistry of these compounds we report here the results of our work that enabled developing simple, efficient, novel routes to both 1,2,4-triazol-5-amines and 2,4-disubstituted-1,2,3-triazol-5-amines. Derivatives of both ring systems are important both in the dye industry[7] and as potential intermediates in pharmaceutical industry.[8,9]

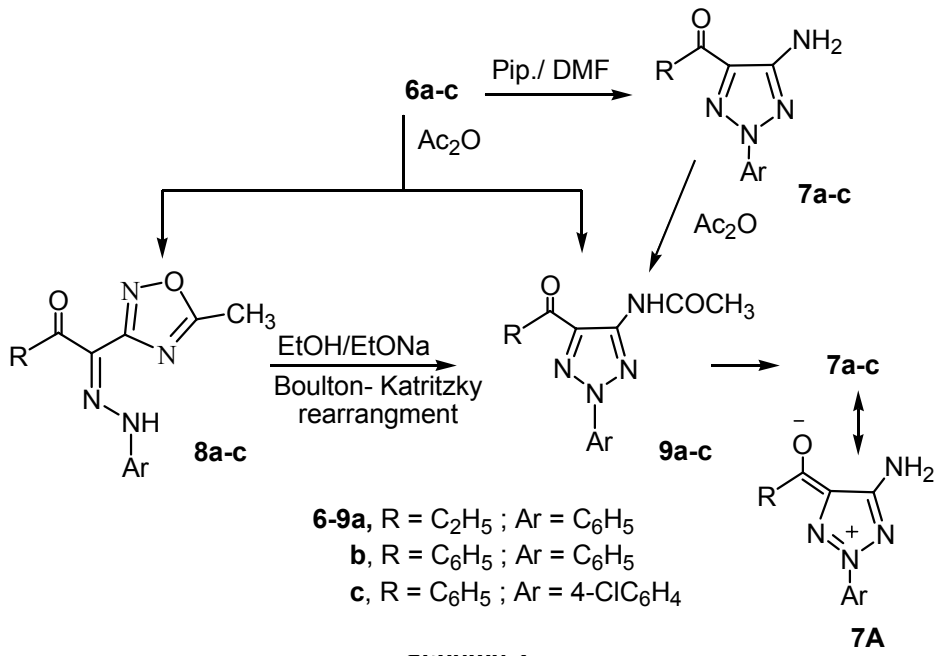
Results and Discussion

2-Arylhydrazononitriles are readily obtainable *via* variety of procedures;[10-13] the simplest is coupling of active methylene nitriles with aromatic diazonium salts.[11] In this work we could successfully couple active methylene nitriles **1a-c** with aromatic diazonium salts producing the 2-arylhydrazolononitriles **2a-d**. Benzyl cyanide (**3**) failed to couple with aromatic diazonium salts under these conditions. As the *β*-carbon in enaminonitriles has recently been shown by us to be sufficiently electrophilic to couple readily with aromatic diazonium salts,[14] benzyl cyanide (**3**) was condensed with triethyl orthoformate and piperidine following a recently published procedure.[5] The so formed 2-phenyl-3-piperidinoacrylonitrile (**4**) coupled smoothly with aromatic diazonium salts yielding 2-arylhydrazononitriles **2e-h**. It is believed that **5** is a non-isolable intermediate as it undergoes ready Japp-Klingemann cleavage[15] yielding **2e-h** (Scheme 1).



Scheme 1

Similar to the reported[16] formation of amidoximes **6a-c** on reacting **2a-c** with hydroxylamine hydrochloride, the arylhydrazononitriles **2d-h** afforded amidoximes **6d-h** upon treatment with hydroxylamine hydrochloride under similar conditions. Amidoximes **6a-c** have been previously cyclized into 1,2,3-triazol-5-amines **7a-c**, whose structure was supported by X-ray for **7c**, upon reflux in dimethyl formamide in presence of sodium acetate.[16] However, in our hands, much better yields of 1,2,3-triazol-5-amines were obtained upon replacing sodium acetate by piperidine (Scheme 2).



Scheme 2

In an attempt to accelerate cyclization, amidoximes **6a-c** were refluxed in acetic anhydride. The obtained products could be assigned the oxadiazolylarylhydrazone structure **8a-c** or acetylamino-1,2,3-triazoles **9a-c**. Structure **9** could be confirmed for these products based on their identity with acetylamino-1,2,3-triazole **9**, prepared *via* acylating **7a-c** with acetic anhydride. Interestingly **9a-c**, could be converted into **7a-c** upon reflux in ethanolic sodium ethoxide. To verify whether or not an oxadiazole **8** is formed initially, amidoximes **6** were acylated with acetyl chloride at room temperature, and even under such conditions the only products formed were acetylamino-1,2,3-triazoles **9** (cf. Scheme 2). Thus the intermediacy of oxadiazoles and subsequent Boulton-Katritzky[17,18] rearrangement, as has recently been assumed, seems least likely. In contrast to the behavior of **6a-c** amidoxime **6d** cyclized upon reflux in DMF in presence of piperidine to yield the 1,2,4-triazol-5-amine **11d** as was established by X-ray crystal structure (cf. Fig. 1).

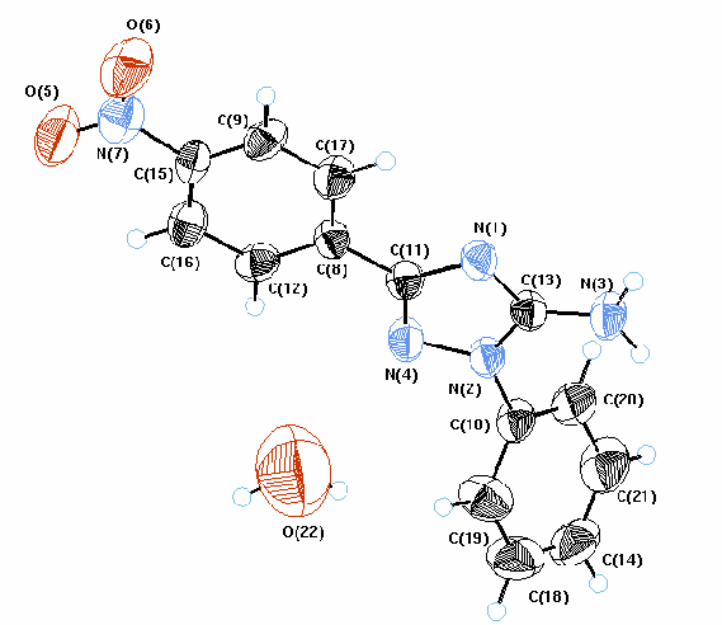


Figure 1. Crystal structure of 3-(4-nitrophenyl)-1-phenyl-1H-1,2,4-triazol-5-amine (11d).

It is believed that amidoxime **6d** in this case has initially undergone a Tiemann rearrangment[19-24] to yield intermediate **10d** that then further cyclized into **11d**. It became now clear that we have two competing modes of cyclization that may lead either to 1,2,4-triazole or 1,2,3-triazole amines. It seemed thus mandatory to develop a way to establish, spectroscopically, structure for product of cyclization. An easy way could be achieved through NOE difference experiments. Thus irradiating NH_2 protons in **11d** at δ 6.64 ppm enhanced *ortho*-aromatic protons at δ 7.65 ppm while in the 1,2,3-triazole irradiating amino protons did not effect such enhancement.

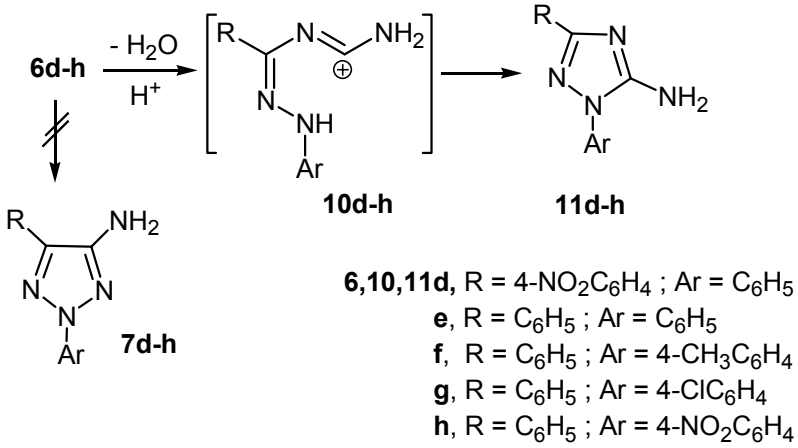
Compounds **6e-h** also cyclized in refluxing DMF, piperidine yielding the 1,2,4-triazol-5-amines **11e-h** as indicated from NOE difference experiments (cf. Scheme 3). Conversion of **6** into a 1,2,3-triazole necessitates formation of N-N bond which is an energy demanding process. Aromaticity of the formed 2-substituted-1,2,3-triazole is thus a driving force especially if the substituent can contribute an extra resonance form as in **7a-c** (cf. form **7A**).

Conclusions

Arylhydrazonoamidoximes are readily obtainable compounds that can be easily cyclized to afford in good yields either 1,2,3-triazolamines or 1,2,4-triazolamines depending on the nature of substituent on the hydrazone carbon. A simple spectroscopic method that allows a reliable structure determination of the cyclization product is also suggested.

Acknowledgements

The support of this work was received from University of Kuwait through research grant (SC04/06) and the facilities of Analab/SAF (GS01/01) and (GS03/01) are gratefully acknowledged.



Scheme 3

Experimental Section

General Procedures. Melting points were recorded on Gallenkamp apparatus and are uncorrected. Infrared spectra (KBr) were determined on a Perkin-Elmer 2000 FT-IR system. ^{1}H NMR was determined on a Bruker DPX 400 MHz superconducting spectrometer in $CDCl_3$ and DMSO-d_6 as solvents and using TMS as internal standard. Mass spectra were measured on MS 30 and MS 9 (AEI) spectrometers, with EI 70 eV. Elemental analyses were measured by means of LECO CHNS-932 Elemental Analyzer. Compounds **2a-c**, **6a-c** and **7a-c** were prepared as described in literature.[16]

Crystallographic analysis

The crystals were mounted on a glass fiber. All measurements were performed on an ENRAF NONIUS FR 590. The data were collected at a temperature of 25 ^{o}C using the ω scanning technique to a maximum of a 2θ of 24.108 ^{o}. The structure was solved by direct method using SIR 92 and refined by full-matrix least squares. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located geometrically and were refined isotropically.

Crystal data

$C_{14}H_{11}N_5O_2$, M = 281.275, monoclinic, a = 7.9303 (7), b = 7.3875 (7), c = 23.421 (3) Å, v = 1357.1 (2) (Å)^3, α = γ = 90.00 ^{o}, β = 98.483 (3)^o, space group: $P2_1/c$, D_x = 1.377 Mg m^{-3}

reflection 690 measured, θ_{max} = 24.09 °, ωR factor = 0.278. Figure 1 illustrates the structure as determined. Full data can be obtained on request from the CCDC.[25]

Synthesis of 2-substituted-2-(2-arylhydrazono) acetonitriles (2d-h)

A cold solution of aryldiazonium salts (10 mmol) was prepared by adding a solution of sodium nitrite (1.4 g dissolved in 10 mL water) to cold solution of arylamine hydrochloride (10 mmol of arylamine in 6 mL, 6M HCl) with stirring. The resulting solution of aryldiazonium salts were then added to a cold solution of either enaminonitrile (**4**) or acetonitrile derivatives (**1**) in ethanol (50 mL) in the presence of sodium acetate trihydrate (2.8 g, 20 mmol). The mixture was stirred at room temperature for 1 h and the solid product was collected by filtration, washed with water and recrystallized from the appropriate solvent.

2-(4-Nitrophenyl)-2-(2-phenylhydrazono)acetonitrile (2d). 1.99g (75%) (green), mp 198 °C [EtOH]; IR (KBr) υ = 3240 (NH), 2208 (CN), 1599 (C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 7.15-7.46 (m, 5H, Ar-H), 7.95 (d, 2H, *J* = 8 *Hz*), 8.33 (d, 2H, *J* = 8 *Hz*), 9.10 (s, 1H, NH); MS, *m/z* (%) 266 (M^+, 80), 239 (10), 91 (100), 77 (40). *Anal*. Calcd. for $C_{14}H_{10}N_4O_2$: C, 63.15; H, 3.79; N, 21.04. Found: C, 62.99; H, 4.10; N, 20.92.

2-Phenyl-2-(2-phenylhydrazono)acetonitrile (2e). 1.55g (70%) (pale yellow), mp 140 °C [MeOH]; IR (KBr) υ = 3235 (NH), 2215 (CN), 1601 (C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 7.06-7.84 (m, 10H, Ar-H), 8.84 (s, 1H, NH); MS, *m/z* (%) 221 (M^+, 100), 194 (80), 91 (90), 77 (60). *Anal*. Calcd. for $C_{14}H_{11}N_3$: C, 76.00; H, 5.01; N, 18.99. Found: C, 75.88; H, 5.12; N, 18.77.

2-Phenyl-2-[2-(4-methylphenyl)hydrazono]acetonitrile (2f). 1.69g (72%) (yellow), mp 120 °C [MeOH]; IR (KBr) υ = 3252 (NH), 2207 (CN), 1612 (C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 2.36 (s, 3H, Ar-CH_3), 7.16-7.83 (m, 9H, Ar-H), 8.78 (s, 1H, NH); MS, *m/z* (%) 235 (M^+, 90), 105 (100), 91 (25), 77 (50). *Anal*. Calcd. for $C_{15}H_{13}N_3$: C, 76.57; H, 5.57; N, 17.86. Found: C, 76.64; H, 5.72; N, 17.93.

2-[2-(4-Chlorophenyl)hydrazono]-2-phenyl acetonitrile (2g). 1.99g (78%) (pale orange), mp 168 °C [EtOH]; IR (KBr) υ = 3258 (NH), 2209 (CN), 1601 (C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 7.21-7.48 (m, 5H, Ar-H), 7.69 (d, 2H, *J* = 8 *Hz*), 7.81 (d, 2H, *J* = 8 *Hz*), 8.79 (s, 1H, NH); MS, *m/z* (%) 257 (M^++2, 40), 256 (M^++1, 50), 255 (M^+, 100), 125 (90), 111 (20), 77 (15). *Anal*. Calcd. for $C_{14}H_{10}ClN_3$: C, 65.76; H, 3.94; N, 16.43. Found: C, 65.57; H, 3.83; N, 16.43.

2-[2-(4-Nitrophenyl)hydrazono]-2-phenylacetonitrile (2h). 2.13g (80%) (pale yellow), mp 214 °C [EtOH]; IR (KBr) υ = 3250 (NH), 2216 (CN), 1598 (C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 7.46-7.64 (m, 5H, Ar-H), 7.83 (d, 2H, *J* = 8 *Hz*), 8.23 (d, 2H, *J* = 8 *Hz*), 11.90 (s, 1H, NH); MS, *m/z* (%) 266 (M^+, 100), 239 (40), 105 (20), 77 (10). *Anal*. Calcd. for $C_{14}H_{10}N_4O_2$: C, 63.15; H, 3.79; N, 21.04. Found: C, 63.12; H, 3.80; N, 21.11.

Synthesis of *N*-hydroxy-2,2-disubstituted-acetamidines (6c-h)

A mixture of 2-arylhydrazonoacetonitrile (**2**) (10 mmol), hydroxylamine hydrochloride (0.69 g, 10 mmol) and sodium acetate anhydrous (3 g) in ethanol (20 mL) was heated under reflux for 3 h. The reaction mixture was poured on water, collected by filtration and recrystallized from the appropriate solvent.

2-[(4-Chlorophenyl)hydrazono]-*N*-hydroxy-3-oxo-3-phenyl-propionamidine (6c). 2.37g (75%) (yellow), mp 226 ^{o}C [H_2O/ EtOH]; IR (KBr) υ = 3488 (OH), 3436, 3276, 3175 (NH_2, NH), 1625 (CO), 1599 (C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 6.50 (s, 2H, NH_2), 7.01-7.54 (m, 5H, Ar-H), 7.61 (d, 2H, *J* = 9 *Hz*), 7.75 (d, 2H, *J* = 9 *Hz*), 8.11 (s, 1H, NH), 13.49 (s, 1H, OH); MS, *m/z* (%) 316 (M^+, 20), 299 (40), 105 (100), 77 (80).

***N*-Hydroxy-2-(4-nitrophenyl)-2-(phenylhydrazono)-acetamidine (6d).** 1.79g (61%) (red), mp 215 ^{o}C [H_2O/ MeOH]; IR (KBr) υ = 3499 (OH), 3437, 3314, 3180 (NH_2, NH), 1650, 1598 (2C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 5.70 (s, 2H, NH_2), 7.18-8.41 (m, 9H, Ar-H), 10.98 (s, 1H, NH), 12.92 (s, 1H, OH); MS, *m/z* (%) 299 (M^+, 100), 284 (20), 239 (30), 91 (90), 77 (55). *Anal*. Calcd. for $C_{14}H_{13}N_5O_3$: C, 56.18; H, 4.38; N, 23.40. Found: C, 56.02; H, 4.26; N, 23.62.

***N*-Hydroxy-2-phenylhydrazono-2-phenyl-acetamidine (6e).** 1.77g (70%) (yellow), mp 160 ^{o}C [MeOH]; IR (KBr) υ = 3497 (OH), 3381, 3329, 3215 (NH_2, NH), 1651, 1609 (2C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 4.48 (s, 2H, NH_2), 7.01-7.81 (m, 10H, Ar-H), 8.21 (s, 1H, NH), 11.01 (s, 1H, OH); MS, *m/z* (%) 254 (M^+, 100), 221 (40), 91 (40), 77 (45). *Anal*. Calcd. for $C_{14}H_{14}N_4O$: C, 66.13; H, 5.55; N, 22.03. Found: C, 66.08; H, 5.61; N, 22.12.

***N*-Hydroxy-2-[(4-methylphenyl)hydrazono]-2-phenyl-acetamidine (6f).** 1.88g (70%) (yellow), mp 152 ^{o}C [MeOH]; IR (KBr) υ = 3498 (OH), 3392, 3337, 3226 (NH_2, NH), 1650, 1613 (2C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 2.34 (s, 3H, Ar-CH_3), 4.50 (s, 2H, NH_2), 6.91-7.58 (m, 9H, Ar-H), 7.66 (s, 1H, NH), 10.68 (s, 1H, OH); MS, *m/z* (%) 268 (M^+, 100), 234 (35), 106 (45), 91 (30), 77 (30). *Anal*. Calcd. for $C_{15}H_{16}N_4O$: C, 67.15; H, 6.01; N, 20.88. Found: C, 67.08; H, 6.08; N, 20.62.

***N*-Hydroxy-2-[(4-chlorophenyl)hydrazono]-2-phenyl-acetamidine (6g).** 1.87g (60%) (yellow), mp 148 ^{o}C [H_2O/ MeOH]; IR (KBr) υ = 3499 (OH), 3399, 3274, 3185 (NH_2, NH), 1641, 1599 (2C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 5.75 (s, 2H, NH_2), 7.16-7.59 (m, 9H, Ar-H), 7.68 (s, 1H, NH), 12.89 (s, 1H, OH); MS, *m/z* (%) 288 (M^+, 60), 253 (80), 125 (100), 91 (30), 77 (50). *Anal*. Calcd. for $C_{14}H_{13}ClN_4O$: C, 58.24; H, 4.54; N, 19.40. Found: C, 58.27; H, 4.63; N, 19.35.

***N*-Hydroxy-2-[(4-nitrophenyl)hydrazono]-2-phenyl-acetamidine (6h).** 1.79g (60%) (pale yellow), mp 204 ^{o}C [H_2O/ MeOH]; IR (KBr) υ = 3495 (OH), 3383, 3270, 3180 (NH_2, NH), 1638, 1601 (2C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 6.07 (s, 2H, NH_2), 7.38-8.16 (m, 9H, Ar-H), 9.92 (s, 1H, NH), 10.76 (s, 1H, OH); MS, *m/z* (%) 299 (M^+, 30), 284 (65), 239 (100), 91 (30), 77 (50). *Anal*. Calcd. for $C_{14}H_{13}N_5O_3$: C, 56.18; H, 4.38; N, 23.40. Found: C, 56.12; H, 4.31; N, 23.55.

Synthesis of *N*-[2,5-disubstituted-2*H*-1,2,3-triazol-4-yl]acetamide (9a-c)

Method A. Compound (**6**) (1 mmol) was dissolved in 20 mL acetic acid in the presence of few drops of acetic anhydride. The reaction mixture was refluxed for 4 h and poured into ice-water mixture, extracted with chloroform (3X10 ml). The organic extracts were dried over anhydrous magnesium sulfate, and evaporated under reduced pressure. The residue was purified through preparative thin layer chromatography [eluent: hexane / AcOEt (3:1)]

Method B. Compound (**6**) (1 mmol) was treated with acetyl chloride (0.079 g, 1 mmol) in piperidin (10 mL) and the reaction mixture was stirred for 4 h at room temperature and triturated as in method A.

***N*-[2-Phenyl-5-propionyl-2*H*-1,2,3-triazol-4-yl]acetamide (9a).** 0.18g (72%) (yellow), mp 176 ^{o}C; IR (KBr) υ = 3268 (NH), 1712, 1675 (2CO), 1599 (C=N) cm^{-1}; ^{1}H NMR (DMSO-d$_6$) δ = 1.2 (t, 3H, *J* = 7.5 Hz), 2.35 (s, 3H, CH$_3$), 2.41 (q, 2H, *J* = 7.5 Hz), 7.21-7.62 (m, 5H, Ar-H), 10.51 (s, 1H, NH); MS, *m/z* (%) 258 (M$^+$, 100), 229 (60), 201 (50), 77 (35). *Anal*. Calcd. for $C_{13}H_{14}N_4O_2$: C, 60.45; H, 5.46; N, 21.69. Found: C, 60.22; H, 5.61; N, 21.72.

***N*-[5-Benzoyl-2-phenyl-2*H*-1,2,3-triazol-4-yl] acetamide (9b).** 0.21g (70%) (yellow), mp 196 ^{o}C; IR (KBr) υ = 3271 (NH), 1675, 1663 (2CO), 1599 (C=N) cm^{-1}; ^{1}H NMR (DMSO-d$_6$) δ = 2.15 (s, 3H, CH$_3$), 7.21-7.82 (m, 10H, Ar-H), 10.71 (s, 1H, NH); MS, *m/z* (%) 306 (M+, 40), 291 (80), 105 (50), 77 (100). *Anal*. Calcd. for $C_{17}H_{14}N_4O_2$: C, 66.66; H, 4.61; N, 18.29. Found: C, 66.52; H, 4.82; N, 18.36.

***N*-[5-Benzoyl-2-(4-chlorophenyl)-2*H*-1,2,3-triazol-4-yl]acetamide (9c).** 0.255g (75%) (yellow), mp 226 ^{o}C; IR (KBr) υ = 3280 (NH), 1689, 1671 (2CO), 1596 (C=N) cm^{-1}; ^{1}H NMR (DMSO-d$_6$) δ = 2.05 (s, 3H, CH$_3$), 7.56-7.73 (m, 5H, Ar-H), 8.00 (d, 2H, *J* = 9 *Hz*), 8.04 (d, 2H, *J* = 9 *Hz*), 10.83 (s, 1H, NH); ^{13}C NMR (DMSO-d$_6$) δ = 23.81 (CH$_3$), 121.39, 129.68, 130.73, 130.92, 133.67, 134.68, 137.28, 138.44, 138.81, 145.83 (Ar-Cs), 169.15, 187.04 (2C=O); MS, *m/z* (%) 340 (M$^+$, 50), 325 (100), 105 (80), 77 (40). *Anal*. Calcd. for $C_{17}H_{13}ClN_4O_2$: C, 59.92; H, 3.85; N, 16.44. Found: C, 59.62; H, 3.82; N, 16.46.

Synthesis of 1,3-disubstituted-1*H*-[1,2,4]triazol-5-amines (11d-h)

A solution of **6** (1 mmol) in DMF (20 mL) in presence of piperidin (2 mL) was refluxed for 4 h. acidified with HCl/ ice mixture. The solid product was collected by filtration and recrystallized from appropriate solvent.

3-(4-Nitrophenyl)-1-phenyl-1*H*-[1,2,4]triazol-5-amine (11d). 0.195g (68%) (pale brown), mp 204 ^{o}C [EtOH]; IR (KBr) υ = 3465, 3332 (NH$_2$), 1597 (C=N) cm^{-1}; ^{1}H NMR (DMSO-d$_6$) δ = 6.74 (s, 2H, NH$_2$), 7.42-7.65 (m, 5H, Ar-H), 8.17 (d, 2H, *J* = 8 *Hz*), 8.31 (d, 2H, *J* = 8 *Hz*); ^{13}C NMR (DMSO-d$_6$) δ = 125.11, 127.51, 128.64, 129.90, 130.57, 137.95, 138.46, 148.42, 156.86, 157.59; MS, *m/z* (%) 281 (M$^+$, 100), 239 (50), 91 (90), 77 (25). *Anal*. Calcd. for $C_{14}H_{11}N_5O_2$: C, 59.78; H, 3.94; N, 24.90. Found: C, 59.61; H, 3.88; N, 24.85.

1,3-Diphenyl-1*H*-[1,2,4]triazol-5-amine (11e). 0.165 g (70%) (dark yellow), mp 175 ^{o}C [EtOH]; IR (KBr) υ = 3430, 3307 (NH$_2$), 1608 (C=N) cm^{-1}; ^{1}H NMR (DMSO-d$_6$) δ = 5.71 (s, 2H, NH$_2$), 7.61-8.31 (m, 10H, Ar-H); ^{13}C NMR (DMSO-d$_6$) δ = 124.81, 125.11, 125.64, 126.42, 127.07, 129.45, 130.16, 141.22, 150.46, 152.51; MS, *m/z* (%) 236 (M$^+$, 100), 194 (40), 77 (55). *Anal*. Calcd. for $C_{14}H_{12}N_4$: C, 71.17; H, 5.12; N, 23.71. Found: C, 71.09; H, 5.01; N, 23.60.

1-(4-Methylphenyl)-3-phenyl-1*H*-[1,2,4]triazol-5-amine (11f). 0.175g (70%) (yellow), mp 160 ^{o}C [MeOH]; IR (KBr) υ = 3455, 3317 (NH$_2$), 1599 (C=N) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 2.3 (s, 3H, Ar-CH$_3$), 5.81 (s, 2H, NH$_2$), 7.11-7.93 (m, 9H, Ar-H); ^{13}C NMR (CDCl$_3$) δ = 26.61, 123.81, 124.15, 124.54, 124.92, 125.51, 125.92, 131.27, 133.82, 143.16, 151.53; MS, *m/z* (%) 250 (M$^+$,

100), 208 (60), 91 (40), 77 (25). *Anal*. Calcd. for $C_{15}H_{14}N_4$: C, 71.98; H, 5.64; N, 22.38. Found: C, 71.90; H, 5.41; N, 22.50.

1-(4-Chlorophenyl)-3-phenyl-1*H*-[1,2,4]triazol-5-amine (11g). 0.19g (70%) (orange), mp 148 ^{o}C; IR (KBr) υ = 3446, 3327 (NH_2), 1599 (C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 5.84 (s, 2H, NH_2), 7.16 (d, 2H, *J* = 8 *Hz*), 7.21-7.53 (m, 5H, Ar-H), 7.59 (d, 2H, *J* = 8 *Hz*); ^{13}C NMR ($CDCl_3$) δ = 124.18, 125.82, 127.14, 127.95, 130.18, 135.45, 136.28, 145.11, 154.22, 156.12; MS, *m/z* (%) 272 (M^++2, 50), 270 (M^+, 20), 228 (60), 125 (100), 77 (25). *Anal*. Calcd. for $C_{14}H_{11}ClN_4$: C, 62.11; H, 4.10; N, 20.70. Found: C, 61.99; H, 4.01; N, 20.60.

1-(4-Nitrophenyl)-3-phenyl-1*H*-[1,2,4]triazol-5-amine (11h). 0.20g (70%) (dark yellow), mp 182 ^{o}C; IR (KBr) υ = 3447, 3387 (NH_2), 1598 (C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 5.75 (s, 2H, NH_2), 7.45-8.05 (m, 5H, Ar-H), 8.07 (d, 2H, *J* = 8 *Hz*), 8.47 (d, 2H, *J* = 8 *Hz*); ^{13}C NMR ($CDCl_3$) δ = 126.45, 126.70, 127.64, 129.56, 129.93, 130.54, 138.05, 144.21, 145.16, 153.50; MS, *m/z* (%) 281 (M^+, 30), 239 (40), 77 (100). *Anal*. Calcd. for $C_{14}H_{11}N_5O_2$: C, 59.78; H, 3.94; N, 24.90. Found: C, 59.90; H, 4.01; N, 24.71.

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