Studies with 2-Arylhydrazononitriles: Further Investigations on Reactivity of 2-Arylhydrazononitriles Towards Hydroxylamine

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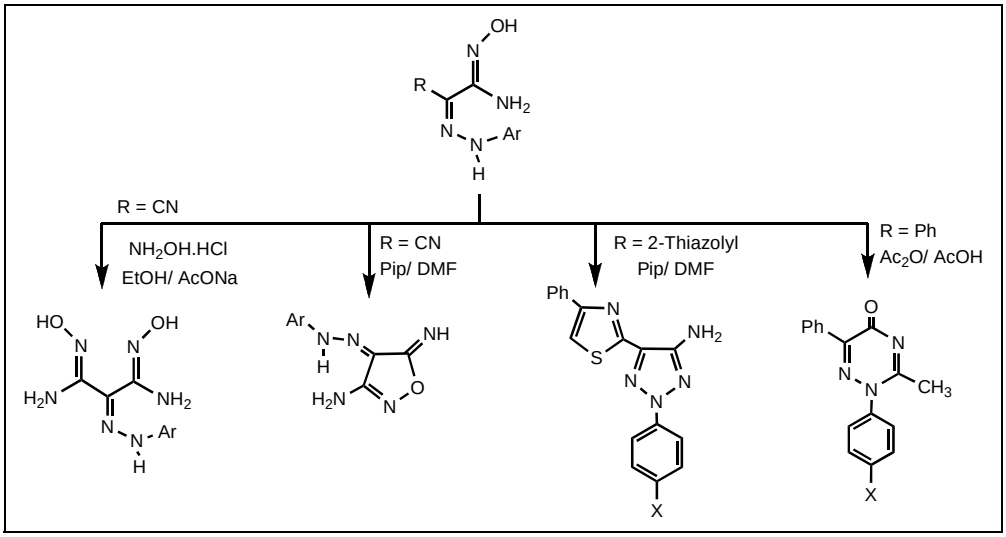

The utilization of arylhydrazononitriles (**6-9**) for synthesis of azoles is demonstrated. Thus, arylazomalononitriles (**6**) reacted with hydroxylamine hydrochloride to afford isoxazol-5-imine (**10**), amidoxime (**12**) and *bis*-amidoxime (**13**) derivatives depending upon both the reaction conditions and molar ratio employed. 2-Thiazolyl-2-arylhydrazononitriles (**7**) and cyanoformazans (**8**) gave 1,2,3-triazole derivatives (**15**) and (**17**) respectively upon treatment with hydroxylamine hydrochloride and concomitant loss of water molecule. Formation of novel 1,2,4-triazin-5(4*H*)-one derivatives (**21**) has efficiently been carried out by treatment of amidoximes (**18**) with acetic anhydride in acetic acid.

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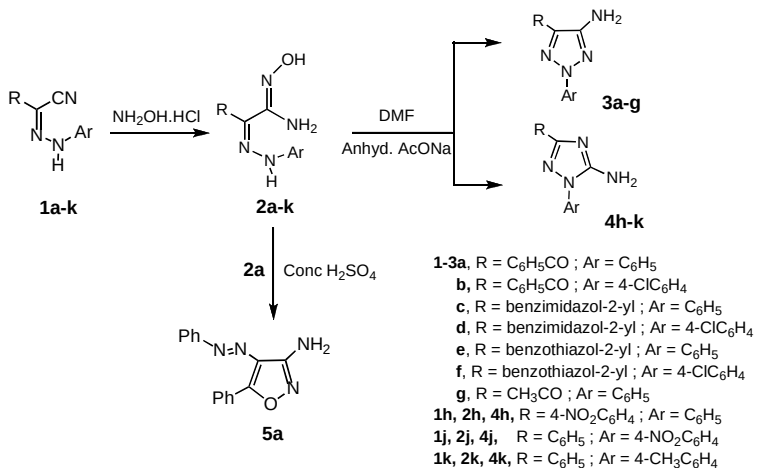
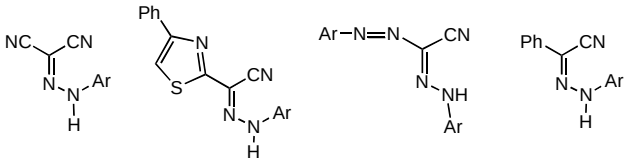
RESULTS AND DISCUSSION

Arylhydrazononitriles are versatile reagents that have already been extensively utilized as precursors to polyfunctional substituted heteroaromatics [1-4]. Recently it has been found that whereas the arylhydrazononitriles **(1a-g)** [5,6] reacted with hydroxylamine hydrochloride in refluxing DMF in presence of sodium acetate to yield 1,2,3-triazoles **3a-g** (Scheme 1), treatment of **(1h-k)** [7] under the same conditions afforded 1,2,4-triazol-5-amine **4h-k**. Amidoximes are isolable intermediates in these reactions. Amidoxime **2a** has been reported earlier [8] to be cyclized into aminoisoxazole **5a** when treated with concentrated sulphuric acid (*cf.* Scheme 1).

Scheme 1



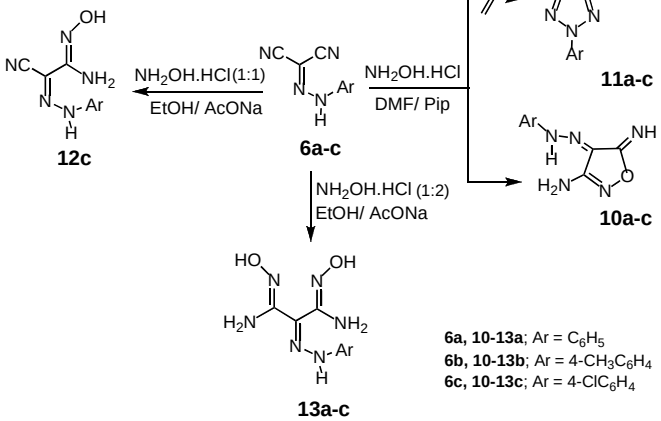
It became quite clear that, the nature of end products of these simple reactions is dependant on both nature of substituent (R) in **1** as well as the pH of the cyclization reaction. It occurred to us of value to investigate further these reactions with the hope of arriving at firm conclusions concerning anticipated reaction products. In the present article we report on the behavior of the arylhydrazononitriles **6-9** towards hydroxylamine hydrochloride and then rationalize for previous discrepancies.



6 **7** **8** **9**

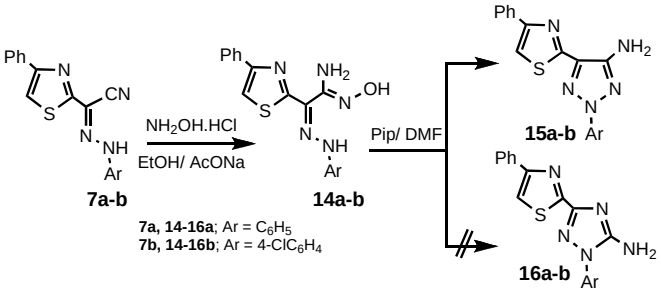
Thus, reacting **6a-c** with hydroxylamine hydrochloride under reflux for 8 hours in DMF solution afforded the corresponding 3-aminoisoxazol-5-imines **10a-c**. We could not trace any formation of the 1,2,3-triazoles **11a-c**; clearly deviating from behavior of **1a-g** (Scheme 2). On the other hand, refluxing of hydrazononitrile **6c** with hydroxylamine hydrochloride (1:1) in ethanolic sodium acetate afforded the amidoxime **12c**. Reaction of **6a-c** with excess hydroxylamine (1:2) furnished the corresponding *bis*-amidoximes **13a-c** (*cf.* Scheme 2).

Scheme 2



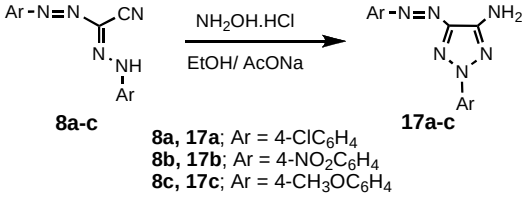
The reactions of **7a-b** with hydroxylamine hydrochloride in ethanolic sodium acetate have afforded as recently reported [5] amidoximes **14a-b**. Cyclization of the latter in DMF and piperidine gave 1,2,3-triazoles **15a-b** (Scheme 3). Possible rearrangement into isomeric 1,2,4-triazoles **16a-b** was excluded based on NOE difference experiments. Thus, irradiation of NH_2 at δ 5.37 ppm did not enhance aryl protons and *vice versa* irradiation *o*-aryl protons at δ 7.91 ppm did not enhance amino protons (*cf.* Scheme 3). Moreover, HMBC-^{15}N NMR revealed that aromatic protons at δ 8.02 ppm have two cross peaks with nitrogen atoms resonating δ 245 and 305 ppm for sp^2 (N1, N3), while compound **16** should show only one cross peak at higher field for sp^2 (N1).

Scheme 3



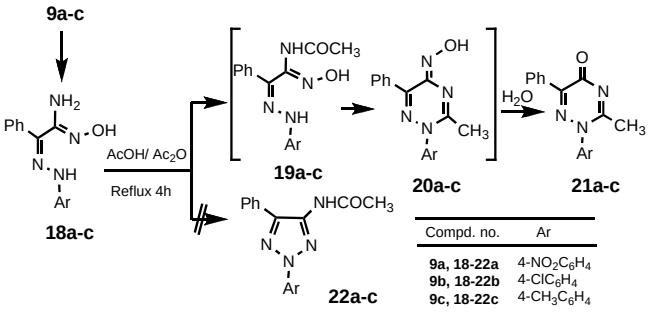
Analogously, cyanoformazans **8a-c** reacted with hydroxylamine hydrochloride in ethanolic sodium acetate to afford directly 1,2,3-triazoles **17a-c** (Scheme 4).

Scheme 4



In an attempt to affect cyclization of amidoxime **18a** by action of acetic anhydride in the presence of acetic acid a product of molecular formula $C_{16}H_{12}N_4O_3$ was obtained. This was formulated as **21a** and is assumed to be formed *via* initial acylation of **18a** into **19a** that then cyclized to **20a**. Hydrolysis of the oxime moiety in the latter afforded a novel 1,2,4-triazinone derivative **21a**. Absence of NH proton in ^{1}H NMR enabled ruling out structure **22** (*cf.* Scheme 5). Similar treatment of **18b-c** under the same conditions gave **21b-c**. Although oximes are not readily hydrolysable, the situation with compound **20** is different. As initially compound **20** tautomerizes into nitroso

Scheme 5



Compd. no.	Ar
9a, 18-22a	4-$NO_2C_6H_4$
9b, 18-22b	4-ClC_6H_4
9c, 18-22c	4-$CH_3C_6H_4$

tautomer it will undergo *ipso*-substitution with acetoxy group. The formed acetoxy compound is hydrolysed readily upon water treatment. *Ipso* substitution is well known [9].

In conclusion of this work and previous one [5-7] it may be suggested that amidoximes are prime products of reacting functionally substituted arylhydrazononitriles with hydroxylamine hydrochloride. Cyclization of the products can afford either 1,2,3-triazoles, 1,2,4-triazoles or isoxazoles depending on the nature of substituents and applied cyclization conditions. The acyl, aroyl, azolyl and other substituents that can stabilize a 1,2,3-triazole ring by effective delocalization of nitrogen lone pair would cyclize into 1,2,3-triazoles, in the absence of this effect or if the reactivity of substituents is sufficient to allow for isoxazole formation, the latter would be formed. In absence of both effects a rare Beckmann like rearrangement leading to 1,2,4-triazoles would occur.

EXPERIMENTAL

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. Arylhydrazononitriles (**6**) [10], (**7**) [11], (**8**) [4] and (**9**) [7] were prepared as previously described.

Synthesis of 5-imino-4-arylhydrazono-4,5-dihydroisoxazol-3-ylamine (10a-c). To a stirred solution of arylazomalononitrile (10 mmol) in DMF (50 mL) containing anhydrous piperidine (2 mL) was added hydroxylamine hydrochloride (0.7 g, 10 mmol). The mixture was refluxed for 8 hours and poured into water. The solid precipitate was collected by filtration and purified by long column chromatography [eluent: hexane/AcOEt (3:1)]

5-Imino-4-phenylhydrazono-4,5-dihydro-isoxazol-3-ylamine (10a). This compound was obtained in 1.42 g (70%), mp 145 °C; IR (KBr) ν = 3434, 3271 (NH_2), 3317 (NH), 3166 (NH), 1601 (C=N) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ = 5.94 (s, 2H, NH_2), 7.34 (s, 1H, NH), 7.34-7.55 (m, 3H, Ar-H), 7.78 (s, 1H, NH), 7.91 (d, 2H, Ar-H); ^{13}C NMR δ = 118.67, 127.89, 128.05, 130.59, 139.98, 155.41, 164.50; MS, *m/z* (%) 203 (M^+, 100), 160 (80), 92 (40), 77 (10). *Anal.* Calcd. for $C_9H_9N_5O$: C, 53.20; H, 4.46; N, 34.47. Found: C, 53.40; H, 4.51; N, 34.26.

5-Imino-4-(4-methylphenylhydrazono)-4,5-dihydroisoxazol-3-ylamine (10b). This compound was obtained in 1.56 g (72%), mp 195 °C; IR (KBr) ν = 3455, 3224 (NH_2), 3357 (NH), 3166 (NH), 1617 (C=N) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ = 2.34 (s, 3H, Ar-CH_3), 5.90 (s, 2H, NH_2), 7.32 (d, 2H, *J* = 8 Hz), 7.45 (s, 1H, NH), 7.73 (s, 1H, NH), 7.81 (d, 2H, *J* = 8 Hz); ^{13}C NMR δ = 21.58 (Ar-CH_3), 118.79, 127.14, 131.00, 137.62, 138.02, 155.14, 164.78; MS, *m/z* (%) 217 (M^+, 100), 174 (55), 106 (25), 91 (40). *Anal.* Calcd. for $C_{10}H_{11}N_5O$: C, 55.29; H, 5.10; N, 32.24. Found: C, 55.21; H, 4.90; N, 32.01.

5-Imino-4-(4-chlorophenylhydrazono)-4,5-dihydroisoxazol-3-ylamine (10c). This compound was obtained in 1.85 g (78%), mp 210 °C; IR (KBr) ν = 3474, 3201 (NH_2), 3301 (NH), 3148 (NH), 1617 (C=N) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ = 6.00 (s, 2H, NH_2), 7.61 (s, 1H, NH), 7.62 (d, 2H, *J* = 8 Hz), 7.89 (s, 1H, NH), 7.92 (d, 2H, *J* = 8 Hz); ^{13}C NMR δ = 120.45, 127.96, 130.57, 132.45, 138.54, 155.37, 164.57; MS, *m/z* (%) 238 (M^++1, 40), 237 (M^+, 100), 195 (45), 126 (40), 111 (20). *Anal.* Calcd. for $C_9H_8ClN_5O$: C, 45.49; H, 3.39; N, 29.47. Found: C, 45.28; H, 3.38; N, 29.17.

Synthesis of acetamidines (12), (14) and propanediimidamides (13). To a solution of arylazomalononitrile (10 mmol) in ethanol (95%, 40 mL) were added hydroxylamine hydrochloride (0.7 g, 10 mmol) (or 1.4 g, 20 mmol) and anhydrous sodium acetate (1 g). The mixture was refluxed for 3 hours and the solvent was removed under vacuum. The residue was diluted with water. The solid precipitate was collected by filtration and recrystallized from appropriate solvent.

2-Cyano-2-(4-chlorophenylhydrazono)-*N*-hydroxyacetamidine (12c). This compound was obtained in 1.89 g (80%), mp 271 °C [MeOH]; IR (KBr) ν = 3498 (OH), 3441, 3175 (NH_2), 3336 (NH), 2214 (CN), 1603 (C=N) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ = 5.67 (s, 2H, NH_2), 7.38 (d, 2H, *J* = 8 Hz), 7.50 (s, 1H, NH), 7.68 (d, 2H, *J* = 8 Hz), 11.79 (s, 1H, OH); MS, *m/z* (%) 239 (M^++2, 40), 238 (M^++1, 20), 237 (M^+, 100), 125 (80), 111 (50). *Anal.* Calcd. for $C_9H_8ClN_5O$: C, 45.49; H, 3.39; N, 29.47. Found: C, 45.23; H, 3.49; N, 29.29.

***N*,*N*`-Dihydroxy-2-phenylhydrazonopropanediimidamide (13a).** This compound was obtained in 1.42 g (60%), mp 160 °C [EtOH/H_2O]; IR (KBr) ν = 3462 (OH), 3344, 3230 (NH_2), 3171 (NH), 1599 (C=N) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ = 5.65 (s, 2H, NH_2), 6.90 (s, 2H, NH_2), 7.21-7.36 (m, 5H, Ar-H), 9.95 (s, 1H, OH), 10.19 (s, 1H, NH), 12.90 (s, 1H, OH); ^{13}C NMR δ = 120.37, 126.38, 128.15, 143.18, 144.75, 164.31, 164.56; MS, *m/z* (%) 236 (M^+, 100), 219 (20), 177 (40), 77 (50). *Anal.* Calcd. for $C_9H_{12}N_6O_2$: C, 45.76; H, 5.12; N, 35.58. Found: C, 45.57; H, 5.04; N, 35.77.

***N*,*N*'-Dihydroxy-2-(4-methylphenylhydrazono)-propanediimidamide (13b).** This compound was obtained in 1.50 g (62%), mp 140 °C [MeOH/H_2O]; IR (KBr) ν = 3463 (OH), 3342, 3228 (NH_2), 3161 (NH), 1609 (C=N) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ = 2.24 (s, 3H, Ar-CH_3), 5.62 (s, 2H, NH_2), 6.65 (s, 2H, NH_2), 7.11-7.22 (m, 4H, Ar-H), 9.91 (s, 1H, OH), 10.14 (s, 1H, NH), 12.90 (s, 1H, OH); ^{13}C NMR δ = 23.55 (Ar-CH_3), 118.45, 124.18, 125.31, 142.88, 143.57, 164.08, 164.29; MS, *m/z* (%) 250 (M^+, 100), 233 (40), 191 (25), 91 (20). *Anal.* Calcd. for $C_{10}H_{14}N_6O_2$: C, 47.99; H, 5.64; N, 33.58. Found: C, 47.83; H, 5.42; N, 33.39.

***N*,*N*'-Dihydroxy-2-(4-chlorophenylhydrazono)-propanediimidamide (13c).** This compound was obtained in 1.62 g (60%), mp 188 °C [MeOH]; IR (KBr) ν = 3471 (OH), 3348, 3241 (NH_2), 3183 (NH), 1611 (C=N) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ = 5.68 (s, 2H, NH_2), 6.81 (s, 2H, NH_2), 7.23-7.68 (m, 4H, Ar-H), 9.98 (s, 1H, OH), 10.33 (s, 1H, NH), 13.21 (s, 1H, OH); ^{13}C NMR δ = 121.18, 126.91, 128.88, 144.16, 146.23, 164.98, 165.36; MS, *m/z* (%) 272 (M^++2, 30), 271 (M^++1, 10), 270 (M^+, 100), 253 (20), 211 (35), 111 (40). *Anal.* Calcd. for $C_9H_{11}ClN_6O_2$: C, 39.94; H, 4.10; N, 31.05. Found: C, 39.83; H, 4.13; N, 31.23.

***N*-Hydroxy-2-(phenylhydrazono)-2-(4-phenylthiazol-2-yl)-acetamidine (14a).** This compound was obtained in 2.02 g (60%), mp 193 °C [MeOH]; IR (KBr) ν = 3434 (OH), 3394, 3241 (NH_2), 3104 (NH), 1600 (C=N) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ = 5.81 (s, 2H, NH_2), 7.01-8.08 (m, 10H, Ar-H), 8.31 (s, 1H,

thiazole-H), 10.11 (s, 1H, NH), 14.28 (s, 1H, OH); MS, *m/z* (%) 337 (M^+, 100), 319 (50), 187 (25), 134 (20), 77 (20). *Anal.* Calcd. for $C_{17}H_{15}N_5OS$: C, 60.52; H, 4.48; N, 20.76; S, 9.50. Found: C, 60.64; H, 4.57; N, 20.66; S, 9.63.

***N*-Hydroxy-2-(4-chlorophenylhydrazono)-2-(4-phenylthiazol-2-yl)-acetamidine (14b).** This compound was obtained in 2.22 g (60%), mp 216 °C [MeOH]; IR (KBr) υ = 3438 (OH), 3370, 3252 (NH_2), 3116 (NH), 1602 (C=N) cm^{-1}; ^1H NMR (DMSO-d_6) δ = 5.86 (s, 2H, NH_2), 7.31-7.88 (m, 5H, Ar-H), 7.91 (d, 2H, *J* = 8 Hz), 8.41 (s, 1H, thiazole-H), 8.61 (d, 2H, *J* = 8 Hz), 10.31 (s, 1H, NH), 13.88 (s, 1H, OH); MS, *m/z* (%) 373 (M^++2, 10), 372 (M^++1, 30), 371 (M^+, 100), 353 (40), 126 (20), 111 (50). *Anal.* Calcd. for $C_{17}H_{14}ClN_5OS$: C, 54.91; H, 3.79; N, 18.83; S, 8.62. Found: C, 54.77; H, 3.59; N, 18.76; S, 8.53.

Synthesis of 1,2,3-triazol-4-amines (15a-b). A solution of acetamidine **14** (1 mmol) in dry DMF (40 mL) and piperidine (2 mL) was refluxed for 4 hours, until the reaction was completed (TLC). The mixture was treated with water and extracted by chloroform. The organic layer was dried and concentrated. The residue was purified by column chromatography [eluent: hexane/AcOEt (3:1)].

2-Phenyl-5-(4-phenylthiazol-2-yl)-2*H*-1,2,3-triazol-4-amine (15a). This compound was obtained in 0.21 g (65%), mp 164 °C; IR (KBr) ν = 3407, 3271 (NH_2), 1603 (C=N) cm^{-1}; ^1H NMR (DMSO-d_6) δ = 5.33 (s, 2H, NH_2), 7.35-8.12 (m, 10H, Ar-H), 8.21 (s, 1H, thiazole-H); ^{13}C NMR δ = 114.61, 118.43, 127.28, 127.87, 129.38, 129.72, 129.89, 130.72, 134.52, 139.87, 152.45, 155.79, 159.44; MS, *m/z* (%) 319 (M^+, 100), 277 (50), 187 (25), 134 (20), 77 (50). *Anal.* Calcd. for $C_{17}H_{13}N_5S$: C, 63.93; H, 4.10; N, 21.93; S, 10.04. Found: C, 63.84; H, 4.21; N, 21.81; S, 9.93.

2-(4-Chlorophenyl)-5-(4-phenylthiazol-2-yl)-2*H*-1,2,3-triazol-4-amine (15b). This compound was obtained in 0.23 g (68%), mp 181 °C; IR (KBr) ν = 3410, 3288 (NH_2), 1600 (C=N) cm^{-1}; ^1H NMR (DMSO-d_6) δ = 5.36 (s, 2H, NH_2), 7.35-7.92 (m, 5H, Ar-H), 8.02 (d, 2H, *J* = 8 Hz), 8.31 (s, 1H, thiazole-H), 8.51 (d, 2H, *J* = 8 Hz); ^{13}C NMR δ = 115.11, 118.13, 127.48, 128.17, 129.83, 130.33, 130.89, 131.52, 135.62, 139.21, 151.23, 145.85, 158.65; MS, *m/z* (%) 355 (M^++2, 10), 354 (M^++1, 30), 353 (M^+, 100), 126 (20), 111 (50). *Anal.* Calcd. for $C_{17}H_{12}ClN_5S$: C, 57.71; H, 3.42; N, 19.79; S, 9.06. Found: C, 57.64; H, 3.51; N, 19.66; S, 8.93.

2-(4-Chlorophenyl)-5-(4-chlorophenylazo)-2*H*-1,2,3-triazol-4-amine (17a). This compound was obtained in 0.20 g (61%), mp 192 °C; IR (KBr) ν = 3448, 3281 (NH_2), 1635 (C=N) cm^{-1}; ^1H NMR (DMSO-d_6) δ = 5.72 (s, 2H, NH_2), 7.51 (d, 2H, *J* = 8 Hz), 7.62 (d, 2H, *J* = 8 Hz), 7.79 (d, 2H, *J* = 8 Hz), 7.91 (d, 2H, *J* = 8 Hz); ^{13}C NMR δ = 127.15, 127.67, 129.23, 129.84, 130.51, 131.12, 134.62, 135.21, 139.11, 141.51; MS, *m/z* (%) 335 (M^++2, 30), 334 (M^++1, 50), 333 (M^+, 80), 139 (40), 111 (100). *Anal.* Calcd. for $C_{14}H_{10}Cl_2N_6$: C, 50.47; H, 3.03; N, 25.22. Found: C, 50.64; H, 3.11; N, 25.33.

2-(4-Nitrophenyl)-5-(4-nitrophenylazo)-2*H*-1,2,3-triazol-4-amine (17b). This compound was obtained in 0.22 g (60%), mp 205 °C; IR (KBr) ν = 3451, 3292 (NH_2), 1625 (C=N) cm^{-1}; ^1H NMR (DMSO-d_6) δ = 5.82 (s, 2H, NH_2), 7.68 (d, 2H, *J* = 8 Hz), 7.82 (d, 2H, *J* = 8 Hz), 8.82 (d, 2H, *J* = 8 Hz), 8.31 (d, 2H, *J* = 8 Hz); ^{13}C NMR δ = 127.25, 127.88, 129.11, 129.94, 139.43, 141.47, 142.23, 143.16, 147.11, 147.93; MS, *m/z* (%) 354 (M^+, 20), 176 (40), 122 (100). *Anal.* Calcd. for $C_{14}H_{10}N_8O_4$: C, 47.46; H, 2.85; N, 31.63. Found: C, 47.64; H, 3.01; N, 31.53.

2-(4-Methoxyphenyl)-5-(4-methoxyphenylazo)-2*H*-1,2,3-triazol-4-amine (17c). This compound was obtained in 0.20 g (62%), mp 184 °C; IR (KBr) ν = 3453, 3281 (NH_2), 1601 (C=N) cm^{-1}; ^1H NMR (DMSO-d_6) δ = 3.50 (s, 3H, Ar-CH_3), 3.52 (s, 3H, Ar-CH_3), 5.62 (s, 2H, NH_2), 7.03 (d, 2H, *J* = 8 Hz), 7.05 (d, 2H, *J* = 8 Hz), 7.75 (d, 2H, *J* = 8 Hz), 7.77 (d, 2H, *J* = 8 Hz); ^{13}C NMR δ = 55.52, 56.21, 118.62, 119.13, 121.55, 122.18, 128.51, 129.21, 139.77, 141.56, 152.56, 153.13; MS, *m/z* (%) 324 (M^+, 100), 135 (20), 107 (60). *Anal.* Calcd. for $C_{16}H_{16}N_6O_2$: C, 59.25; H, 4.97; N, 25.91. Found: C, 59.44; H, 5.01; N, 25.83.

Synthesis of 1,2,4-triazinones (21a-c). To a solution of acetamidine **18** (1 mmol) in acetic acid (15 mL) was added acetic anhydride (1 mmol). The reaction mixture was heated under reflux for 4 hours, cooled to room temperature, quenched by the addition of H_2O (20 mL), and extracted with chloroform (3 x 25 mL). The combined organic extracts were dried over $MgSO_4$, and evaporated under reduced pressure. The residue was purified by column chromatography [eluent: hexane/AcOEt (3:1)].

3-Methyl-2-(4-nitrophenyl)-6-phenyl-1,2,4-triazin-5(2*H*)-one (21a). This compound was obtained in 0.22 g (70%), mp 180 °C; IR (KBr) ν = 1656 (CO), 1596 (C=N) cm^{-1}; ^1H NMR (DMSO-d_6) δ = 2.29 (s, 3H, CH_3), 7.45-7.53 (m, 3H, Ar-H), 8.04 (d, 2H, *J* = 8 Hz), 8.07 (m, 2H, Ar-H), 8.47 (d, 2H, *J* = 8 Hz); ^{13}C NMR δ = 23.99 (CH_3), 126.03, 129.20, 129.26, 129.68, 131.51, 132.99, 147.46, 147.80, 148.73, 161.29 (Ar-C), 161.78 (CO); MS, *m/z* (%) 308 (M^+, 20), 205 (100), 163 (60), 77 (15). *Anal.* Calcd. for $C_{16}H_{12}N_4O_3$: C, 62.33; H, 3.92; N, 18.17. Found: C, 62.41; H, 3.81; N, 18.26.

3-Methyl-2-(4-chlorophenyl)-6-phenyl-1,2,4-triazin-5(2*H*)-one (21b). This compound was obtained in 0.19 g (65%), mp 190 °C; IR (KBr) ν = 1662 (CO), 1601 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.39 (s, 3H, CH_3), 7.45-7.52 (m, 3H, Ar-H), 7.71 (d, 2H, *J* = 8 Hz), 7.72 (m, 2H, Ar-H), 8.09 (d, 2H, *J* = 8 Hz); ^{13}C NMR δ = 23.15 (CH_3), 125.53, 128.58, 128.96, 129.88, 130.41, 133.09, 144.51, 145.71, 148.43, 161.89 (Ar-C), 162.57 (CO); MS, *m/z* (%) 297 (M^+, 30), 194 (100), 151 (40), 77 (25). *Anal.* Calcd. for $C_{16}H_{12}ClN_3O$: C, 64.54; H, 4.06; N, 14.11. Found: C, 64.71; H, 3.81; N, 14.28.

3-Methyl-2-(4-methylphenyl)-6-phenyl-1,2,4-triazin-5(2*H*)-one (21c). This compound was obtained in 0.17 g (60%), mp 235 °C; IR (KBr) ν = 1660 (CO), 1598 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.29 (s, 3H, CH_3), 2.53 (s, 3H, Ar-CH_3), 7.04 (d, 2H, *J* = 8 Hz), 7.42-7.52 (m, 5H, Ar-H), 8.21 (d, 2H, *J* = 8 Hz); ^{13}C NMR δ = 22.59 (Ar-CH_3), 23.68 (CH_3), 121.83, 125.11, 128.21, 128.71, 130.67, 131.65, 143.79, 144.80, 147.70, 161.74 (Ar-C), 163.13 (CO); MS, *m/z* (%) 277 (M^+, 30), 174 (100), 133 (80), 77 (30). *Anal.* Calcd. for $C_{17}H_{15}N_3O$: C, 73.63; H, 5.45; N, 15.15. Found: C, 73.41; H, 5.61; N, 15.28.

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