Indian Journal of Chemistry
Vol. 46B, May 2007, pp. 838-846

Chemical reactivity of 3-hydrazino-5,6-diphenyl-1,2,4-triazine towards π–acceptors activated carbonitriles

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Received 26 December 2005; accepted (revised) 29 August 2006

Behaviour of 3-hydrazino-5,6-diphenyl-1,2,4-triazine **1** as electron donor towards different electron acceptors activated carbonitriles has been investigated and a novel fused heterocyclic system and 2,3-disubstituted 1,2,4-triazines have been obtained. Compound **1** reacts with 1,2-dicyanobenzene as π–acceptor in DMF to form benzencarboximidamide **16**, while reaction of **1** with α-bromomalononitrile **17** in boiling DMF affords compound **18**. On the other hand, compound **1** reacts with tetracyanoethane **23** in DMF to yield compound **24**. The route of reaction in DMF indicates that charge–transfer complexation is the key intermediate to obtain new heterocyclic systems. Structures of the products are established by MS, IR, UV-Vis, CHN and ^{1}H NMR spectral data.

Keywords: Reactivity, 1,2,4-triazine derivatives, π–acceptors, carbonitriles

IPC: Int.Cl.[8] C07D

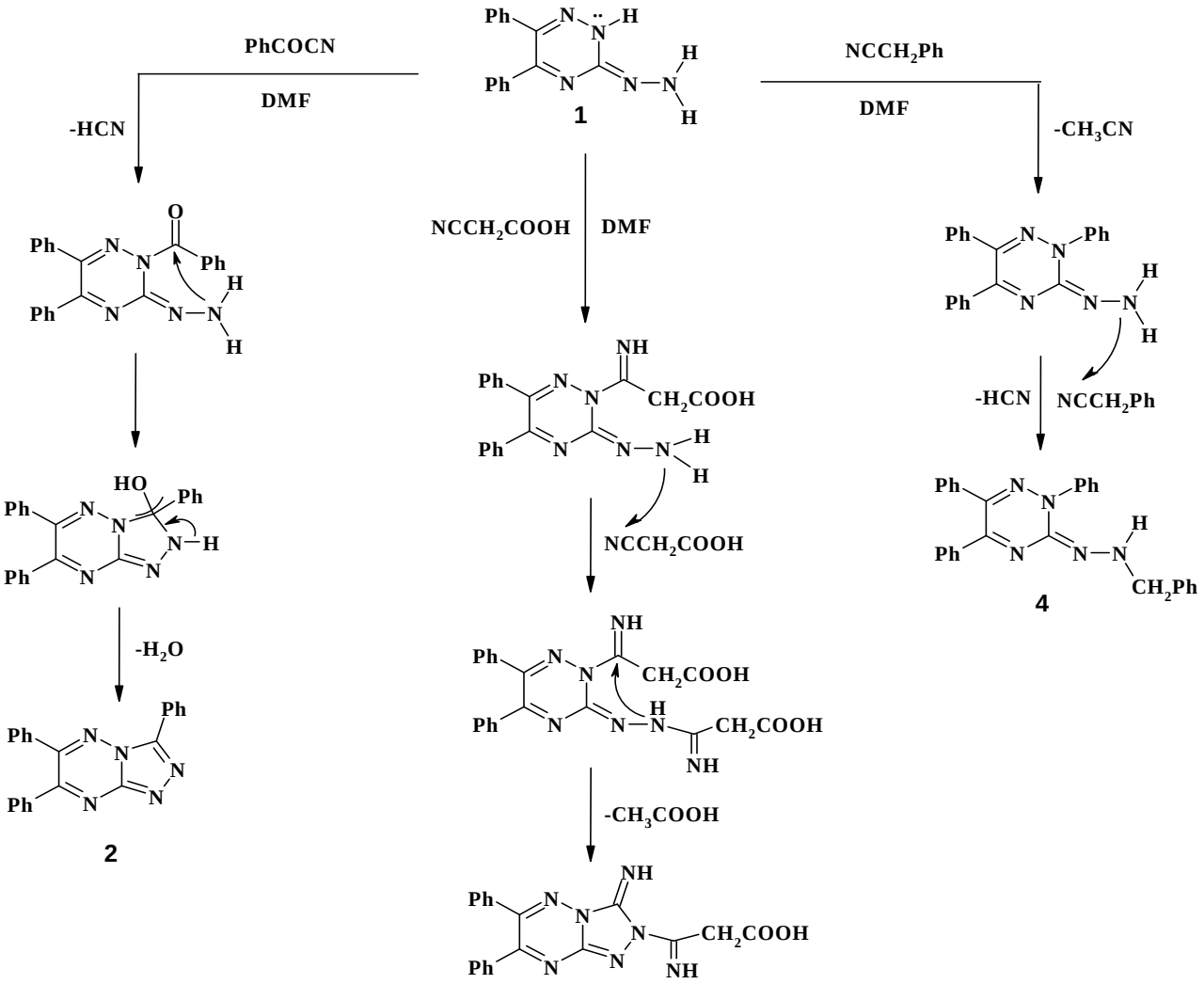
The chemistry of 1,2,4-triazines has proved to be very useful in the synthetic chemistry, as well as established in the field of pharmaceutical chemistry[1,2] and in the plant protection[3]. 5,6-Diphenyl-1,2,4-triazine containing functional groups at position 3 had been utilized for the synthesis of several fused and isolated heteropolycyclic systems[4]. Abdel-Rahman[5] reported the chemical reactivity of uncondensed functionally 1,2,4-triazines towards sulfur, oxygen, nitrogen and halogen compounds in different solvent media and various conditions. As a continuation of this work, attention has been turned to 3-hydrazino-5,6-diphenyl-1,2,4-triazine **1** as electron donors towards different electron acceptors activated carbonitriles. In boiling DMF solvent, DMF is a strongly polar aprotic solvent, therefore DMF accelerates the SN^2 reactions.

Recently, it was noted that most reactions of activated nitriles take place in basic medium leading to novel heterocyclic systems[6-10]. Hassan *et al.*[11-14] investigated the behavior of *N*-arylisoindolines, arylazo-aminopyrazoles, triazolethiones and amino-paracyclophanes towards π–acceptors. In addition, novel heterocyclic compounds have been obtained from treatment of 3-substituted-5*H*-1,2,4-triazino[5,6-*b*]indoles with π–acceptors carbonitriles[15].

Results and Discussion

Refluxing of 3-hydrazino-5,6-diphenyl-1,2,4-triazine **1** with 2-oxophenylacetonitrile[16] in DMF yielded 3,6,7-triphenyl-1,2,4-triazolo[4,3-*b*][1,2,4]triazine **2** *via* nucleophilic attack of compound **1** to 2-oxophenylacetonitrile to lose one mole of HCN followed by ring closure reaction by losing one mole of water (**Scheme I**). Structure of **2** was deduced from spectral data. IR spectrum showed the disappearance of OH, NH_2 and C=O functional groups. UV-Vis absorption spectrum of **2** recorded λ_{max} at 410 nm, 351 nm and 286 nm due to electronic transitions of 1,2,4-triazole and 1,2,4-triazine moieties. Mass spectrum of **2** exhibited a molecular ion peak at 351 (M+2, 3.88) with a base peak at *m/z* 178 due to diphenyl acetylene ion.

Behaviour of compound **1** towards aliphatic carbonitriles also was studied. Thus, boiling compound **1** with cyanoacetic acid in DMF yielded compound **3**, while reaction of **1** with phenylacetonitrile under the same condition afforded compound **4**. Formation of compounds **3** and **4** may occur *via* binucleophilic attack of compound **1** with two molecules of aliphatic nitriles through two steps (**Scheme I**). Chemical structures of **3** and **4** have been deduced from IR spectra which showed the disappearance of C≡N.

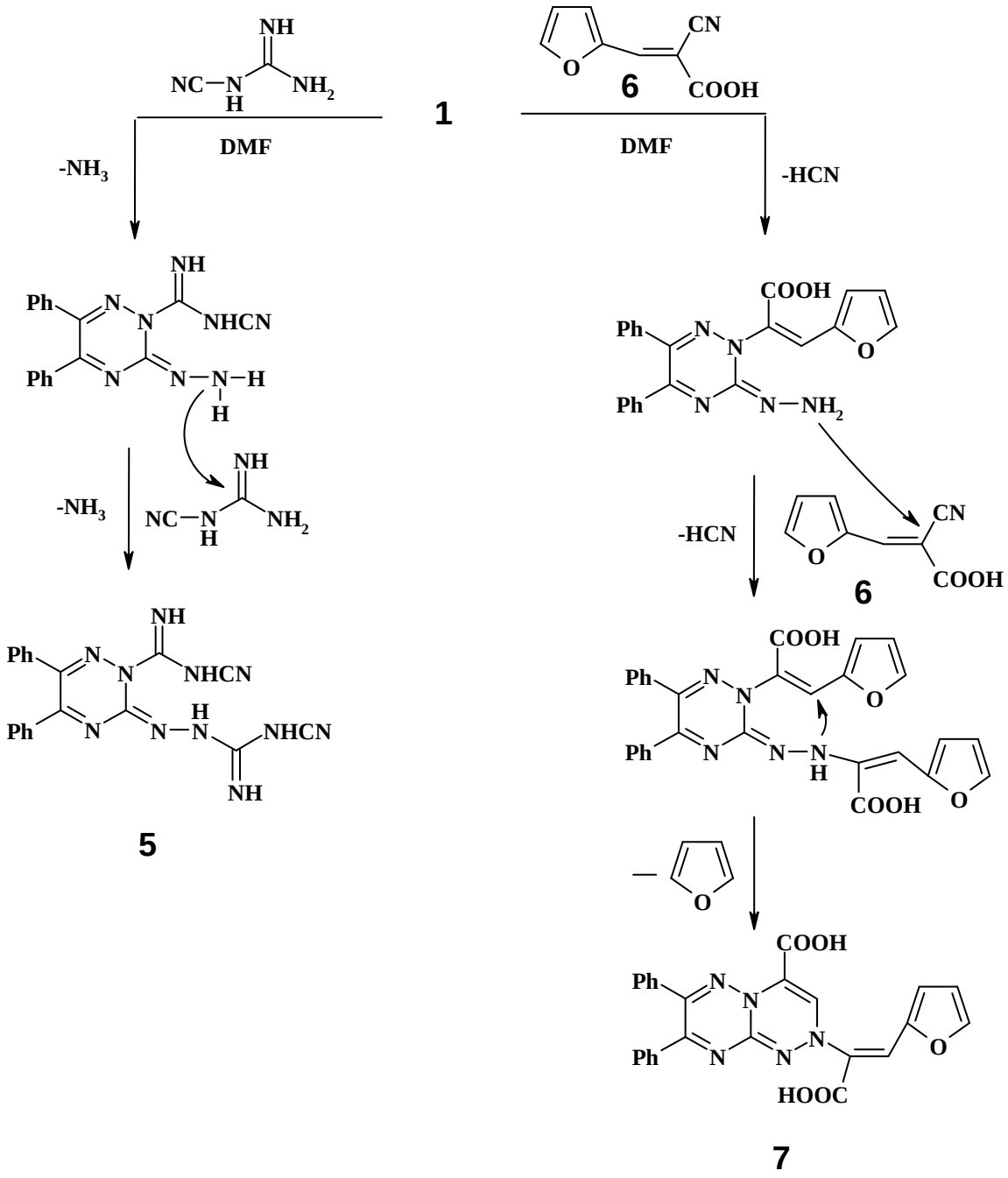


Scheme I

Mass spectrum of both **3** and **4** displayed molecular ion peak at 392 ($M^+ + H_2O$, 16.24) and 426 (0.53), respectively.

Treatment of compound **1** with 1-cyanoguanidine or arylidene cyanoacetic acid **6** in boiling DMF yielded 2-cyanoamidino-3-(4-cyanoaminoguanidino)-5,6-diphenyl-1,2,4-triazine **5** and 4-carboxy-2-arylidino-7,8-diphenyl-1,2,4-triazino[4,3-*b*][1,2,4]triazine **7** *via* bi-nucleophilic attack of 3-hydrazino-1,2,4-trazine **1** towards two molecules of π–acceptors reagents (**Scheme II**). In addition, IR spectra of **5** and **7** indicated the presence of both NH and C≡N **5** and COOH functional groups **7**. Mass spectrum of **5** exhibited a molecular ion peak at *m/z* 397, while that of **7** showed a molecular ion at *m/z* 467. ^{1}H NMR spectrum of **7** showed signals at δ 6.7 due to the presence of =CH (endo of 1,2,4-triazine); 6.9 (=CH exo of 1,2,4-triazine); 10.0 (OH of exo-COOH); 12.0 (OH of COOH) and 7.1–8.6 (m, 13H, aromatic and furyl).

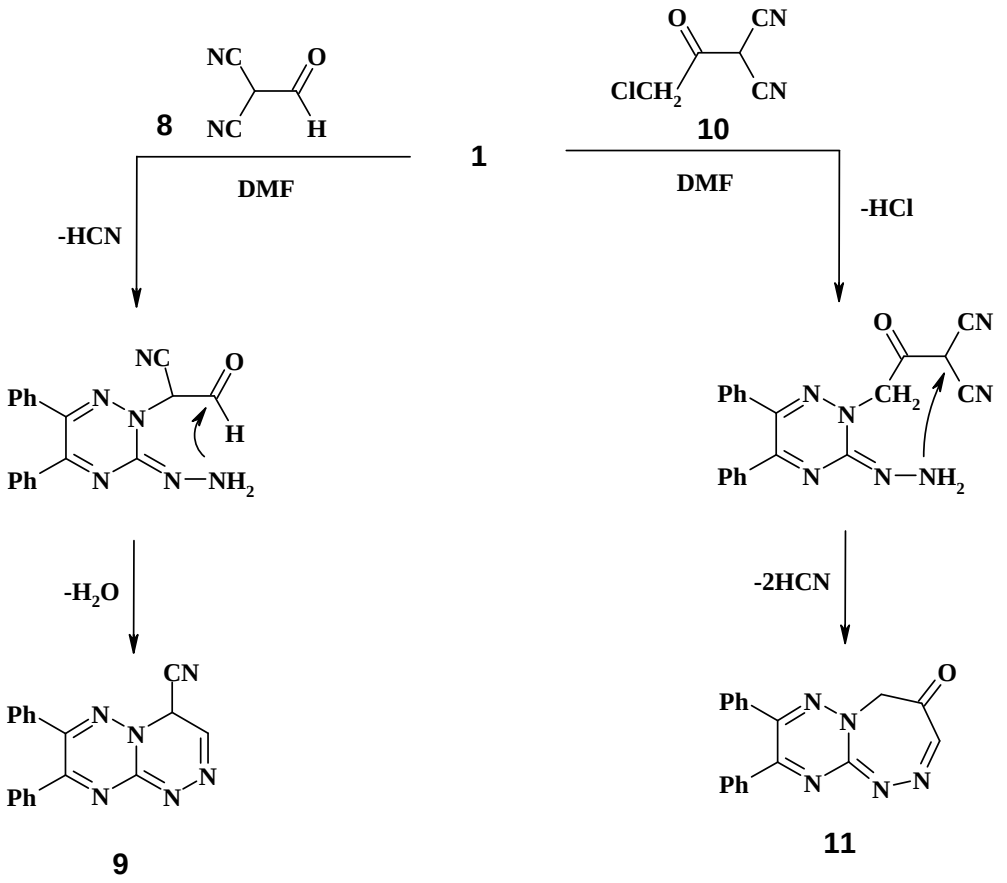
On the other hand, binucleophilic attacks of 3-hydrazino-5,6-diphenyl-1,2,4-triazine **1** with formyl-malononitrile **8** or chloroacetyl malononitrile **10** gave 4-cyano-3,4-dihydro-7,8-diphenyl-1,2,4-triazino[4,3-*b*][1,2,4]triazine **9** and 6,7-dihydro-2,3-diphenyl-7-oxo-1,2,4-triazino[3,2-*c*][1,2,4]triazepine **11**, respectively (**Scheme III**). Mass spectrum of **9** displayed a molecular peak ion at *m/z* 312 (1.87) while that of **11** exhibited the molecular ion peak at 315 (2.48) in addition to a base peak at *m/z* 178 due to a diphenylacetylene ion formed. UV-Vis absorption spectra of **9** and **11** showed λ_{max} 482 nm, 348 nm, 298 nm **9** and 492 nm, 395 nm, and 296 nm **11**, respectively. A degree of similarity of λ_{max} is due to the conjugation of the fused heterobicyclic systems[15].



Scheme II

When 3-hydrazino-5,6-diphenyl-1,2,4-triazine **1** reacted with α-unsaturated malononitrile derivatives such as **12** and **14** in boiling DMF leading to (4*E*)-1-(5,6-diphenyl-1,2,4-triazin-3-yl)-4-ethylidene-5-imino-4,5-dihydro-1*H*-pyrazol-3-amine **13** and (2*E*)-3-(2-furyl)-2-[(3*Z*)-3-[(2*E*)-(2-furylmethylene)-hydrazono]-5,6-diphenyl-1,2,4-triazin-2(3*H*)-yl]propenenitrile **15**, respectively[17] (**Scheme IV**). Mass spectrum of **13** exhibited a molecular ion peak at *m/z* 375 (2.01), while that of **15** at *m/z* 454 (1.14) and a base peak at *m/z* 178 due to a diphenylacetylene ion.

In case of using 1,2-dicyanobenzene as π–acceptor in DMF with compound **1** furnished 2-cyano-*N*-(1,3-diimino-1,3-dihydro-2*H*-isoindol-2-yl)-*N*-(5,6-diphenyl-1,2,4-triazin-3-yl) benzenecarboximidamide **16** (**Scheme V**). Formation of compound **16** can be attributed to the electrophilic addition of reagents than C=N. Formation of cyanohydrins is accelerated by



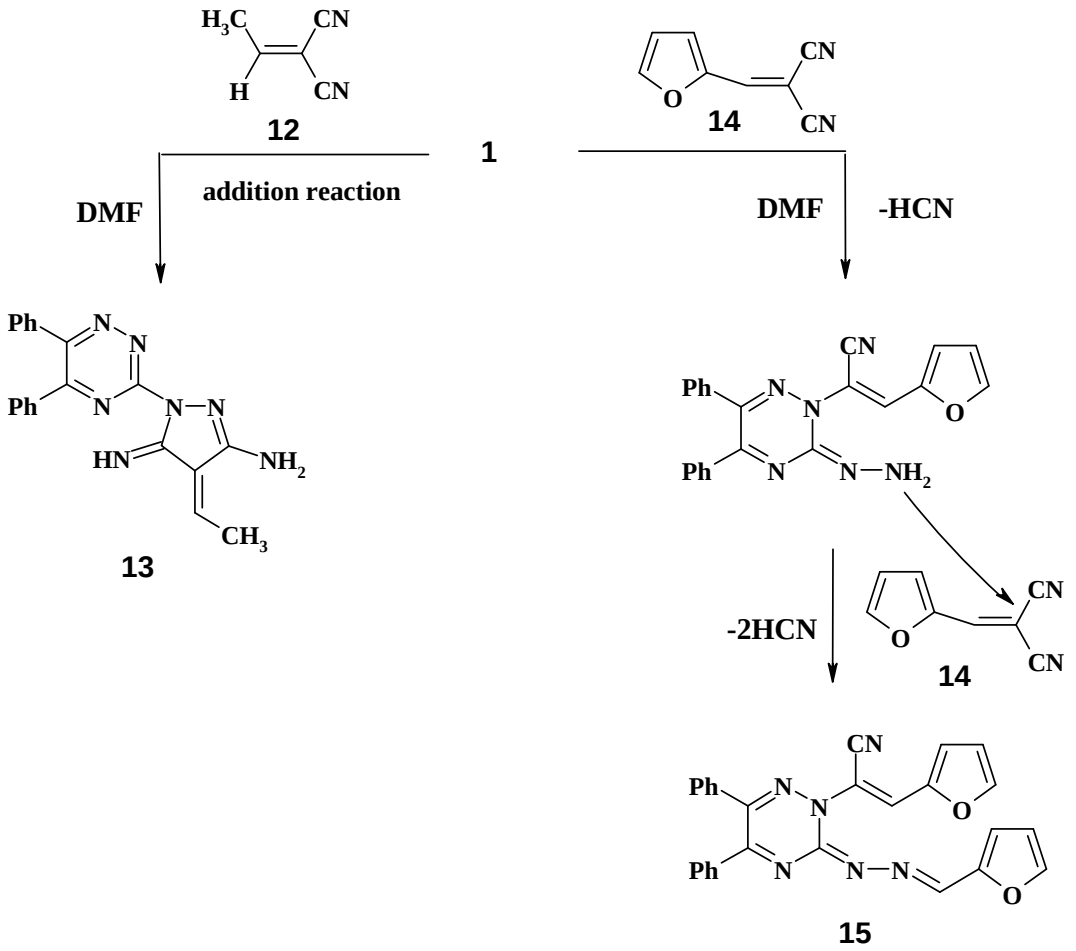
Scheme III

adding bases since the latter promotes the formation of strong nucleophilic reagents CN^-.

The type of halogen present as well as, degree of basicity of the medium used or the conditions of reactions affect on the type of heterocyclization[18-19]. Thus, when 3-hydrazino-5,6-diphenyl-1,2,4-triazine **1** treated with α-bromomalononitrile **17** in boiling DMF afforded 2-dicyanomethyl-3-cyano-1,2,4-triazolo[4,3-*b*][1,2,4]triazine **18** *via* bi-nucleophilic attack of compound **1** to two molecules of **17** through loss two moles of HBr followed by the elimination of HCN (**Scheme V**). Structure of **18** was elucidated by correct spectral and elemental analysis. Similarly, the reaction between compound **1** and α,α–dibromomalononitrile **19** under the same conditions yielded 2*H*-3-bromo-3-cyano-1,2,4-triazolo[4,3-*b*][1,2,4]triazine **20** (**Scheme VI**). The chemical structure of **20** was deduced from analysis and spectral data. Mass spectrum showed a molecular ion peak at *m/z* 397 (0.32), in addition to a base peak at *m/z* 178 due to diphenylacetylene ion formed.

It is interesting that, the behaviour of 3-hydrazino-5,6-diphenyl-1,2,4-triazine **1** towards tetracyanoethylene and tetracyanoethane is different in the route of attack and the ring closure reactions[20]. Thus, boiling compound **1** with tetracyanoethylene **21** in DMF furnished 1-(5,5-diphenyl-1,2,4-triazin-3-yl)-3,5-diamino-4-dicyano-methylpyrazoline **22** while the treatment of compound **1** with tetracyanoethane **23** under the same conditions yielded[15] 3-amino-8,9-diphenyl[1,2,4]triazino[3,2-*c*][1,2,4]triazepine-4,5-dicarbonitrile **24** (**Scheme VI**).

Structures of **22** and **24** were established from fit elemental analysis and spectral data. UV-Vis absorption spectrum of **22** recorded λ_{max} at 498 nm, 392 nm and 296 nm while those of **24** showed λ_{max} at 484 nm, 330 nm and 292 nm. The higher absorption bands of all tested compounds, are due to tautomeric hydrogen bonding formed (**Scheme VI**) which facilitates the e-transition *via* extension of C=NH through a fused heterocyclic nitrogen skeleton. Mass spectrum of **22** exhibited a molecular ion peak at *m/z* 411 (0.74) while that of **24** recorded a molecular ion peak at *m/z* 278 (3.81) [M^+ loss $C_5H_2N_3$]. ^{1}H NMR spectrum of **22** showed signals at δ 3.28–3.39 [$CH(CN)_2$], 5.22 (CH of pyrazole), 6.48, 6.67 (diaminopyrazole) and 7.23–



Scheme IV

7.42 (aromatic protons of 1,2,4-triazine), while that of compound **24** recorded signals at δ 3.37, 4.21(NH_2) and 7.25-7.56(10H, aromatic protons).

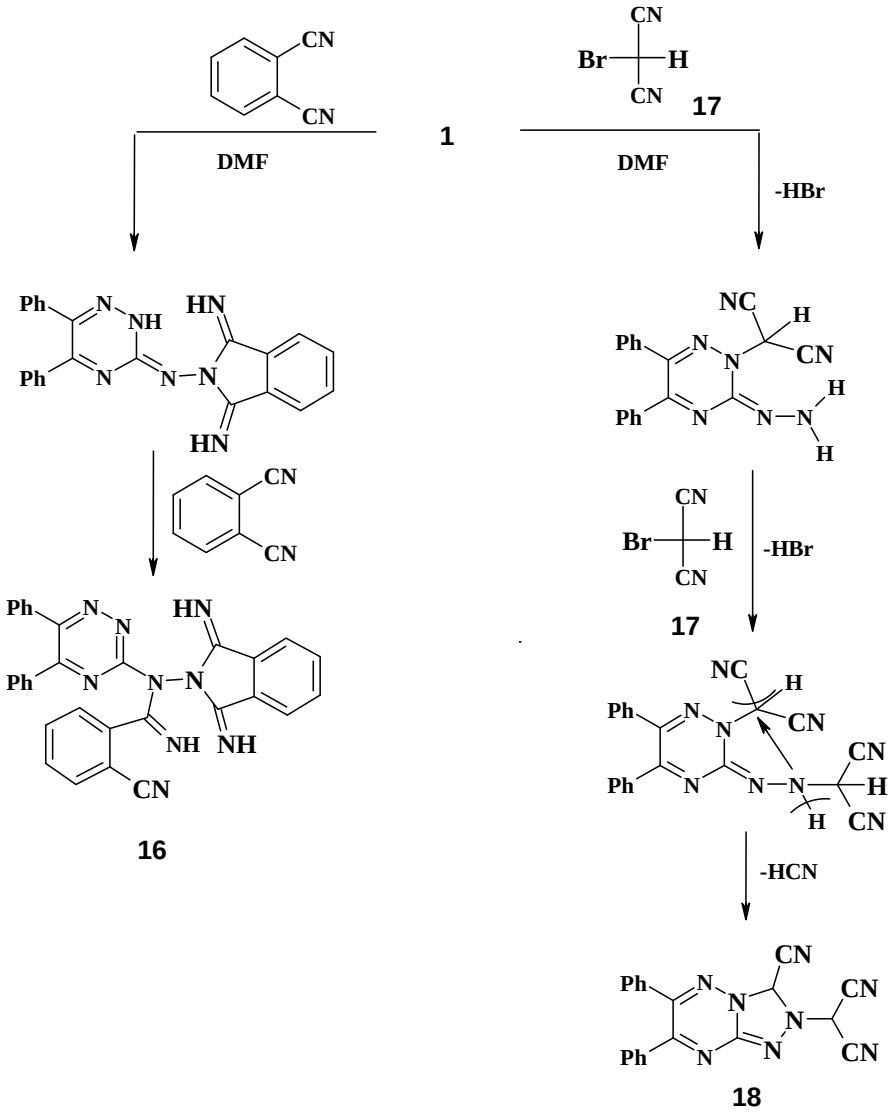
Experimental Section

All melting points are uncorrected. IR spectra (KBr) were recorded on Perkin-Elmer 293FT spectrophotometer. UV-Vis absorption spectra in DMF were recorded on a Perkin-Elmer Lambda 4B controller accessory interface UV-Vis spectrophotometer (λ_{max} in nm). ^{1}H NMR spectra were recorded on an EM NMR spectrometer (200 MHz) using DMSO-d_6 as solvent and TMS as internal reference (chemical shifts in ppm). The mass spectra were recorded on gas chromotographic GCMSQP 1000 ex Shimadzu instrument at 70 eV. 5,6-Diphenyl-3-hydrazino-5,6-diphenyl-1,2,4-triazine **1** was prepared according to literature method[21].

Arylidene carbonitriles **6** and **14** were freshly prepared from refluxing cyanoacetic acid or malononitrile with furfural in glacial acetic acid then crystallized from dry non-polar solvent. Formylmalononitrile **8** was prepared from refluxing equimolar formic acid with acetic anhydride then treated cold with ethanol solution of malononitrile. Chloroacetyl malononitrile **10** also was prepared from careful addition of chloroacetyl chloride to a solution of malononitrile in THF. Compound **12** was obtained from refluxing malononitrile with acetaldehyde in glacial acetic acid. On the other hand, α-bromo and α,α-dibromomalononitrile **17** and **19** were obtained from stirring Br_2 with malononitrile in CCl_4 (1:1 and 2:1 by moles). Compounds **21** and **23** were obtained by warming **17** and **19** with malononitrile (1:1 by moles) in CCl_4.

1,2,4-Triazolo[4,3-*b*][1,2,4]triazine derivatives 2, 3, 20

A mixture of **1** (0.01 mole) and 2-oxophenylacetonitrile, cyanoacetic acid or α,α-dibromonitrile **19** (0.02 mole) in DMF (50 mL) was refluxed for 2 hr, cooled and poured into ice. The solid that resulted was filtered off and crystallized

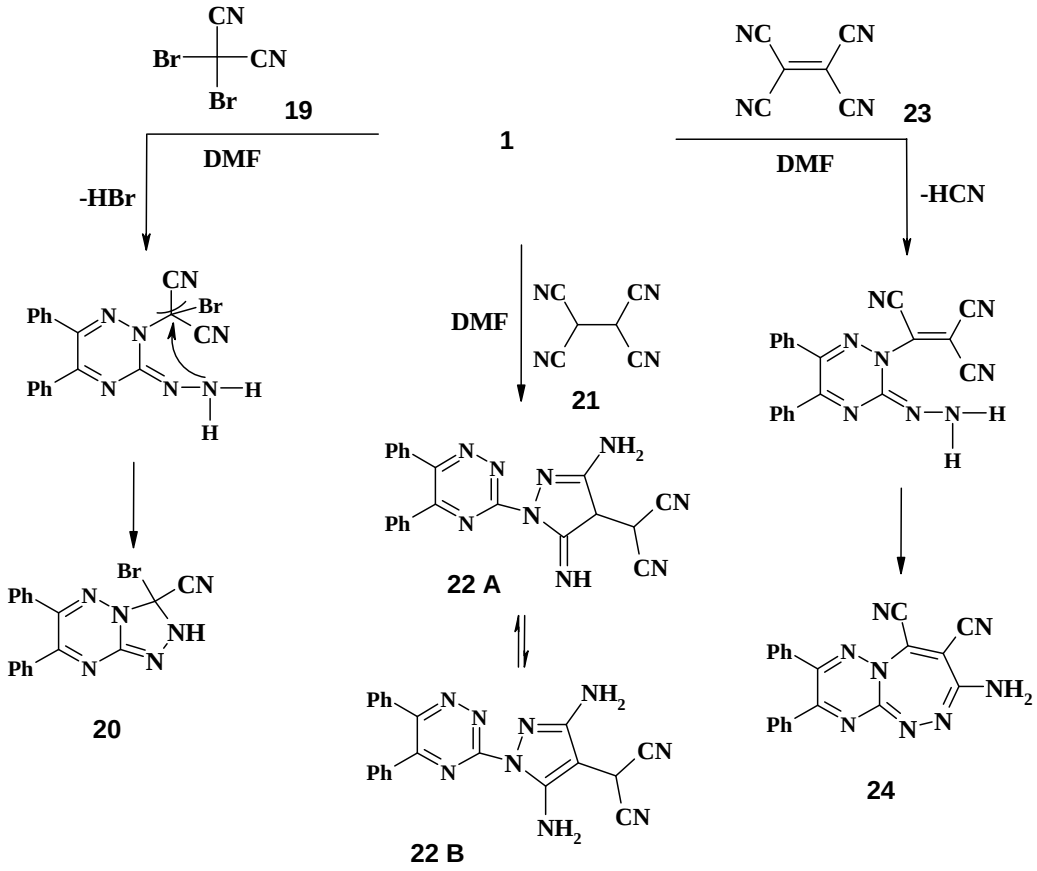


Scheme V

from methanol to give **2, 3** and **20**, respectively. The compound **2** was obtained as buff crystals (57%); m.p. 205ºC; UV-Vis $\lambda_{max/nm}$ (Log{ε}): 410(2.27), 351(4.19), 286(3.76); IR: 3050 (aromatic CH), 1610, 1590 (C=N), 810, 780 cm^{-1} (phenyls); MS: *m/z* (%) 351(M+2, 3.88), 271(6.88), 192(3.0), 178(100), 128(5.8), 97(12.4), 57(16.11); ^{1}H NMR: δ 7.17-8.18(m, 15H aromatic protons). Anal. Calcd for $C_{22}H_{15}N_5$: C, 75.64; H, 4.29; N, 20.05. Found: C, 75.39; H, 4.05; N, 19.76%. Compound **3**, was obtained as yellow crystals (69%); m.p. 150ºC; UV-Vis $\lambda_{max/nm}$ (Log{ε}): 418(0.8), 357(4.0), 292(3.43); IR: 3450(OH), 3186(NH), 1708 (C=O), 1579 (C=N), 1359 cm^{-1} (NCN); MS: *m/z* (%) 392(M+H_2O, 16.24), 354(74.10), 288(28.01), 250(15.57), 185(28.91), 178(100), 165(19.91), 152(15.370, 103 (16.31), 76(10.0); ^{1}H NMR: δ 2.70-3.15 (m, 2H, CH_2), 3.95, 4.25 (2H, C=NH), 7.20-7.50 (10H, aromatic protons) and 10.0 (s, H, OH); Anal. Calcd for $C_{19}H_{15}N_7O_2$: C, 61.12; H, 4.02; N, 26.27. Found: C, 60.84; H, 3.78; N, 25.99%. Compound **20**, was obtained as brown crystals (52%) m.p. 240ºC; UV-Vis $\lambda_{max/nm}$ (Log{ε}): 476(1.0), 329(2.41), 294(3.13); IR: 3323(NH), 2221 cm^{-1} (CN); MS: *m/z* (%) 397(M+H_2O, 0.32), 290(1.74), 248(1.37), 178(100), 150(4.37), 88 (4.07), 77 (3.5), 69(2.32), 51(1.58); ^{1}H NMR: δ 3.49 (NH-N=), 7.21-7.51 (10H, aromatic protons); Anal. Calcd for $C_{17}H_{11}N_6Br$: C, 53.82; H, 2.90; N, 22.16. Found: C, 53.58; H, 2.65; N, 21.92%.

N^1-Substituted hydrazino-5, 6-diphenyl-1, 2, 4-triazine derivatives 4, 5, 15 and 16

A mixture of **1** (0.01 mole) and phenylacetonitrile, 1-cyanoguanidine, furoethylenedicarbonitrile **14**, or



Scheme VI

benzene-1, 2-dicarbonitrile (0.02 mole) in DMF (50 mL) was refluxed for 2 hr, cooled and poured into ice. The solid that resulted was filtered off and purified by recrystallization from ethanol to give **4, 5, 15** and **16**, respectively. Compound **4** was obtained as orange crystals (68%); m.p. 160ºC; UV-Vis $\lambda_{max/nm}$ (Log{ε}): 453(3.4), 342(3.24), 297(3.83)**;** IR: 3164(NH), 3052 (aromatic CH), 2942 (CH_2), 1597 cm^{-1} (C=N); MS: *m/z* (%) 426(0.53), 248(11.84), 178(100), 128(3.29), 103(15.97), 85(4.04), 77(5.55), 69(5.09), 50(3.28); ^{1}H NMR: δ 2.65-2.80 (m, 2H, CH_2), 3.34 (NH-N=), 7.50-8.60 (20H, aromatic protons); Anal. Calcd for $C_{28}H_{23}N_5$: C, 78.32; H, 5.36; N, 16.31. Found: C, 78.09; H, 5.13; N, 16.05%. Compound **5** was obtained as pale yellow crystals (59%); m.p. 170ºC; UV-Vis $\lambda_{max/nm}$ (Log{ε}): 434(0.7), 365(3.6), 292(3.32); IR: 3429, 3382, 3335 (NH_2), 3186, 3152 (NH), 2206, 2162 (2CN), 1638 cm^{-1} (def.NH_2); MS: *m/z* (%) 397(0.52), 293(47.55), 281(94.58), 264(4.3), 212(24.70), 210(25.67), 178(18.84), 132(51.33), 85(55.22), 884(100), 81 (88.48), 55(42.20); ^{1}H NMR: δ 3.38(NH-N=); 3.95, 4.18 (2H, C=NH) 5.24, 6.24 (2NHCN), 7.36-8.7 (10H aromatic protons); Anal. Calcd for $C_{19}H_{15}N_{11}$: C, 57.43; H, 3.77; N, 38.79. Found: C, 57.17; H, 3.50; N, 38.43%. Compound **15** was obtained as yellow crystals (62%); m.p. 220ºC; UV-Vis $\lambda_{max/nm}$ (Log{ε}): 486(0.41), 408(0.86), 335(3.30), 296(3.4); IR: 2213(CN), 1623 cm^{-1} (C=C); MS: *m/z* (%) 458(1.14), 411(1.0), 286(12.1), 255(16.43), 178(100), 165(17.85), 152(43.24), 128 (20.95), 75(20.87), 62(9.88), 50(7.78); ^{1}H NMR: δ 3.38 (b, 2H, =CH), 7.36-8.45 (aromatic and furyl protons); Anal. Calcd for $C_{27}H_{18}N_6O_2$: C, 70.74; H, 3.93; N, 18.34. Found: C, 70.48; H, 3.68; N, 18.07%. Compound **16**, was obtained as deep yellow coloured crystals (56%); m.p. 190ºC; UV-Vis $\lambda_{max/nm}$ (Log{ε}) : 408(3.2), 354(4.1), 289(3.5); IR: 3426(NH_2), 3102(NH), 2232(CN), 1622(C=N), 1593 cm^{-1} (C=N); MS: *m/z* (%) 519(0.10), 368(1.55), 255(19.24), 178(100), 152(7.35), 114(1.37), 98 (2.37), 76 (3.78), 59(1.74), 55(3.06); ^{1}H NMR: δ 4.16 (CH-CN), 5.0-5.26 (3H, C=NH), 7.42-7.83 (18H, aromatic protons); Anal. Calcd for $C_{31}H_{21}N_9$: C, 71.67; H, 4.04; N, 24.27. Found: C, 71.38; H, 3.78; N, 23.99%.

3-(3, 4, 5-Trisubstitutedpyrazol-1-yl)-5, 6-diphenyl-1, 2, 4-triazine derivatives (13 and 22)

A mixture of **1** (0.01 mole) and α-unsaturated malononitrile **12** or tetracyanoethane **21**) (0.02 mole) in DMF (50 mL) was refluxed for 2 hr, cooled and poured into ice. The solid that resulted was filtered off and crystallized from ethanol to give **13** and **22**, respectively. Compound **13** was obtained as reddish brown crystals (55%); m.p. 197ºC; UV-Vis $\lambda_{max/nm}$ (Log {ε}): 423(0.47), 342(3.66), 292 (3.01); IR: 3425(NH_2), 3100(NH), 2926(CH_3), 1599 cm^{-1} (C=N); MS: *m/z* (%) 375(M+H_2O, 2.01), 374(5.58), 265(3.55), 252 (4.05), 218(3.42), 178(100), 155 (10.30), 129 (5.75), 84 (3.23), 77 (10.33), 57(4.17); ^{1}H NMR: δ 1.64-1.66(CH_3), 3.02-3.05, 3.07 (3H, NH, NH, NH_2), 4.15-4.6(2H, CH=, NH=), 7.3-7.40 (10H aromatic); Anal. Calcd for $C_{20}H_{17}N_7$: C, 67.60; H, 4.78; N, 27.60. Found: C, 67.31; H, 4.51; N, 27.40. Compound **22** was obtained as pale brown crystals (59%); m.p. 189ºC; UV-Vis $\lambda_{max/nm}$ (Log{ε}): 498(1.4), 392(4.2), 296(3.3); IR: 3307(NH_2), 3169(NH), 2193(CN), 2049 cm^{-1} (CN); MS: *m/z* (%) 393(0.74), 338(M^+–2CN, 1.22), 285 (2.4), 265(7.3), 252(3.83), 178(100), 129 (2.46), 104(5.45), 83(5.01), 77(7.38), 51(3.13); ^{1}H NMR: δ 3.28-3.39[$CH(CN)_2$], 5.22(CH of pyrazole), 6.48 and 6.67 (=NH), 8.37(NH), 7.23-7.42(10H aromatic); Anal. Calcd for $C_{21}H_{15}N_9$: C, 64.12; H, 3.81; N, 32.06. Found: C, 63.83; H, 3.53; N, 31.77%.

1, 2, 4-Triazino[4, 3-*b*][1, 2, 4]triazine derivatives 7, 9 and 18

A mixture of **1** (0.01 mole) and arylidene-cyanoacetic acid **6**, formylmalononitrile **8** or α-bromomalononitrile **17** (0.02 mole) in DMF (50 mL) was refluxed for 2 hr, cooled and poured into ice. The solid that resulted was filtered off and crystallized from acetic acid or ethanol to give **7, 9** and **18**, respectively. Compound **7** was obtained as deep orange crystals (59%); m.p. 110ºC; UV-Vis $\lambda_{max/nm}$ (Log{ε}): 423(0.3), 41(3.6), 296(3.38); IR: 3418(OH), 1757, 1679 cm^{-1} (C=O); MS: *m/z* (%) 467(0.25), 411(3.08), 364(32.78), 288(15.32), 258(7.82), 192(2.44), 178(100), 165(12.77), 131(3.15), 118(4.72), 89(3.38), 76(5.85), 50 (3.42); ^{1}H NMR: δ 6.7 and 6.9 (s, 2H, CH=), 7.1-8.6 (13H, aromatic and furyl protons), 10 and 12.1 (s, 2H, OH); Anal. Calcd for $C_{25}H_{17}N_5O_5$: C, 64.23; H, 3.64; N, 14.98. Found: C, 63.98; H, 3.40; N, 14.71%. Compound **9** was obtained as yellow crystals (62%); m.p. 213ºC; UV-Vis $\lambda_{max/nm}$ (Log{ε}): 482(0.32), 348(4.0), 298(3.98); IR: 3055 (aromatic CH), 2203 (CN), 1610 cm^{-1} (C=N); MS: *m/z* (%) 312(1.87), 178(30.54), 152(2.71), 111(2.17), 97(41.00), 85(54.04), 84(100), 76 (1.58), 56 (31.30), 55(55.47); ^{1}H NMR: δ 4.13(CH-CN), 6.35(CH= of 1, 2, 4-triazine), 7.22-7.92 (10H aromatic protons); Anal. Calcd for $C_{18}H_{12}N_6$: C, 69.23; H, 3.84; N, 26.92. Found: C, 68.98; H, 3.58; N, 26.63%. Compound **18** was obtained as buff crystals (73%); m.p. 230ºC; UV-Vis $\lambda_{max/nm}$ (Log{ε}): 472(1.3), 360(2.27), 295(3.13); IR: 3250(NH), 2220, 2140 cm^{-1} (2CN); MS: *m/z* (%) 364(0.34), 287(1.02), 255(45.92), 191 (13.3), 159(22.51), 128(25.38), 995(10.48), 85(55.83), 84(100), 56(3(0.58); ^{1}H NMR: δ 3.27 [CH(CN)], 3.45- 3.66[$CH(CN)_2$], 7.50-8.20 (10H, aromatic protons); Anal. Calcd for $C_{20}H_{13}N_8$: C, 65.93; H, 3.56; N, 30.76. Found: C, 65.66; H, 3.26; N, 30.47%.

1, 2, 4-Triazino[4, 2-*c*][1, 2, 4]triazepine derivatives (11 and 24)

A mixture of **1** (0.01 mole) and chloroacetyl malononitrile **10** or tetracyanoethene **23**, (0.02 mole) in DMF (50 mL) was refluxed for 2 hr, cooled and poured into ice. The solid that resulted was filtered off and crystallized from ethanol to give **11** and **24,** respectively. Compound **11** was obtained as brown crystals (56%); m.p. 176ºC; UV-Vis $\lambda_{max/nm}$ (Log {ε}): 492(0.42), 395(1.25), 296(3.4); IR: 3132(b, OH), 1756 cm^{-1} (C=O); MS: *m/z* (%) 315(2.48), 248(3.88), 179(17.18), 178(100), 123(5.32), 99(5.96), 84(13.90), 55(14.74); ^{1}H NMR: δ 4.0, 4.50 (m, 2H, CH_2), 6.50 (s, 2H, CH=), 7.23-7.67 (10H, aromatic protons); Anal. Calcd for $C_{18}H_{13}N_5O$: C, 68.57; H, 4.12; N, 22.22. Found: C, 68.31; H, 3.84; N, 21.97%. Compound **24** was obtained as buff crystals (54%): m.p. 199ºC; UV-Vis $\lambda_{max/nm}$ (Log{ε}): 484(0.6), 330(3.32), 292(3.45); IR: 3415(NH_2), 3312(NH), 2210(CN), 1628 cm^{-1} (def.NH_2); MS: *m/z* (%) 260(M^+–$C_5H_2N_3$, 3.81), 258(21.02), 213(14.64), 178(74.0), 149(41.05), 137(23.18), 129(32.88), 100(20.14), 83(48.51), 69(100), 68(46.11); ^{1}H NMR: δ 3.37, 4.21(NH_2), 7.25-7.56(10H, aromatic protons); Anal. Calcd for $C_{20}H_{13}N_8$: C, 65.93; H, 3.56; N, 30.76. Found: C, 65.68; H, 3.36; N, 30.48%.

Conclusion

From the results of the present study, it can be concluded that the binucleophilic of 3-hydrazino-5,6-diphenyl-1,2,4-triazine **1** attack one molecule of the reagents in the type of aromatic carbonitriles and two

molecules of the reagents in the type of aliphatic carbonitriles. Also, in case of utilizing DMF as solvent, the reactions proceeded in an interesting manner, caused by the participation of DMF, which may be explained on the basis of complex formation between DMF and halogenated carbonitriles which gradually split off a molecule of hydrogen halide and/or DMF give stability for CT–complex was formed which dissociates into components which explained the color of the reaction mixture changed gradually from green to blue and finally brown by warming[15].

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