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HYDRAZONES IN HETEROCYCLIC SYNTHESIS; SYNTHESIS OF 1,3,4-THIADIAZOLE DERIVATIVES

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HYDRAZONES IN HETEROCYCLIC SYNTHESIS; SYNTHESIS OF 1,3,4-THIADIAZOLE DERIVATIVES

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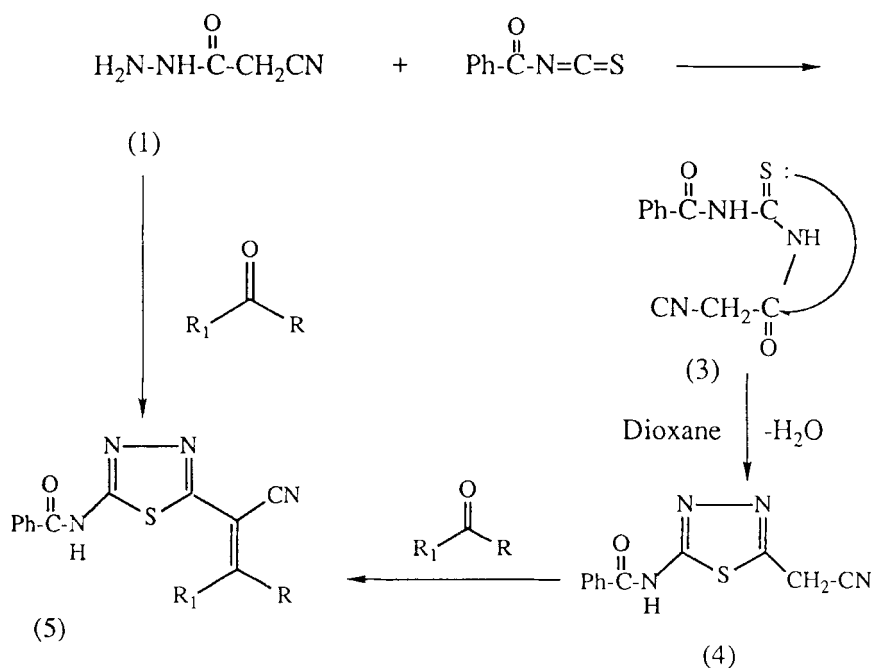
(Received 12 December, 1997; In final form 23 March, 1998)

A new synthesis of 1,3,4-thiadiazoles has been achieved. The reactivity of certain alkylheterocycles towards electrophilic reagents are reported.

Hydrazones and their derivatives¹⁻⁴ constitute an important class of compounds of considerable interest this is because of the diversity of chemical transformations and their uses as active ingredients of fungicidal, antimicrobial agents,^{5,6} and vasodilator agents.^{7,8} These compounds are precursors for the synthesis of inaccessible annelated heterocyclic systems.⁸ As part of our program to develop syntheses for functional heterocycles,⁷⁻⁹ we have recently reported the utility of 2-cyanoethanoic-hydrazide (**1**) for the synthesis of 1,3,4-thiadiazoles and their condensed systems. It has now been found that treatment of cyanoethanoic-hydrazide (**1**) with benzoyl isothiocyanate in acetone as a solvent afforded exclusively and in excellent yield the corresponding 1,3,4-thiadiazole derivative **5a**. The structure of **5a** was established via its elemental analysis and spectroscopic data. The mass spectrum of **5a** revealed a molecular formula C₁₄H₁₂N₄OS (m/z = 284). A ¹H NMR spectrum showed, in addition to the aromatic signals, two singlet signals at δ = 2.27 and 2.42 for two methyl groups. In addition, a signal at δ = 12.52 was assigned to the NH unit. This signal underwent a facile hydrogendeuterium exchange and disappeared upon addition of deuterium oxide

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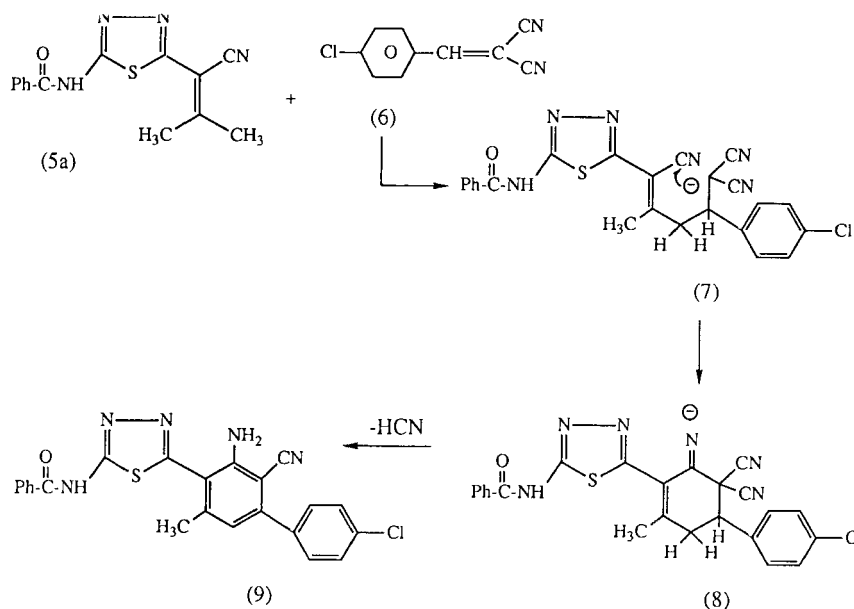
to the ^1H NMR sample. It is believed that **1** reacts initially with benzoyl isothiocyanate to yield the thiosemicarbazide derivative **3** which then cyclises under the reaction conditions to yield the thiadiazole **4**. The latter then condenses with acetone to yield **5a**. Isolation of **3** and **4** have been reported earlier from our laboratories.¹⁰ Compound **5a** could be prepared via an independent route involving the reaction of **1** with benzoyl isothiocyanate in dioxane as an inert solvent to give **4**. The latter was condensed with acetone in presence of piperidine to give **5a** via water elimination (Scheme 1). This synthetic methodology could be generalized using a variety of ketones in dioxane as inert solvent. Thus, compounds **5b-d** were obtained, in a one pot reaction on treatment of a boiling mixture of **1** and **2** with acetophenone, benzoylacetonitrile, and phenacyl thiocyanate, respectively.



- a, $\text{R} = \text{R}_1 = \text{CH}_3$
 b, $\text{R} = \text{CH}_3$; $\text{R}_1 = \text{Ph}$
 c, $\text{R} = \text{CH}_2\text{CN}$; $\text{R}_1 = \text{Ph}$
 d, $\text{R} = \text{CH}_2\text{SCN}$; $\text{R}_1 = \text{Ph}$

SCHEME 1

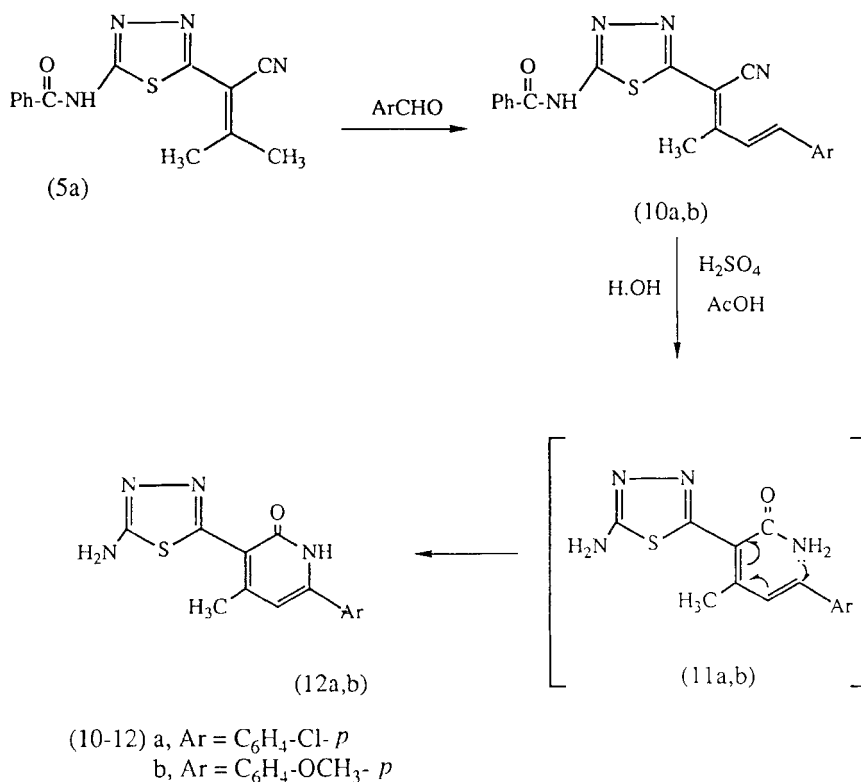
Compound **5a** exhibited high reactivity towards various reagents and underwent numerous chemical transformations which led to a wide range of certain polyfunctionally substituted heterocycles. The methyl group in compound **5a,b** proved to be highly active towards electrophilic reagents. Thus, **5a** reacted with *p*-chlorobenzylidenemalononitrile **6** to give polysubstituted benzene derivative **9**. Compound **9** is believed to be formed via Michael addition of the active methyl group in **5a** to the double bond in **6** followed by cyclization and aromatization by loss of hydrogen cyanide to give **9** (Scheme 2). Formation of benzonitriles from reaction of **6** with crotononitriles as well as alkylheteroaromatic carbonitrile have been reported earlier from our laboratories.^{9,10}



SCHEME 2

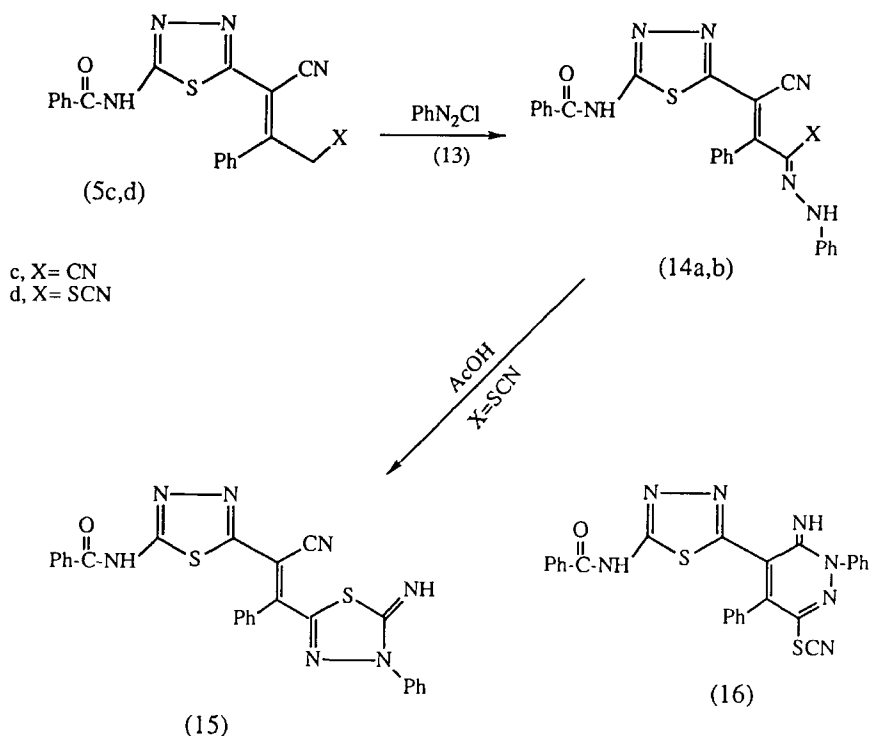
Compound **5a** also condensed readily with aromatic aldehydes to yield the isolable styryl derivatives **10a,b**. The latter were cyclised in the presence of concentrated sulphuric acid to yield **12a,b**. Compounds **12a,b** are assumed to be formed via the acyclic amide intermediate **11a,b** (Scheme 3).

At this point, we have tried to extend our synthetic methodology with active methylene ketones. Compounds **5c,d** were obtained in one pot reaction, on treatment of a boiled mixture of cyanoethanoichydrazide (**1**) and benzoyl isothiocy-



SCHEME 3

anate (2) with benzoylacetonitrile and with phenacyl thiocyanate, respectively. The structures of **5c,d** were inferred from the spectral and analytical data. Compound **5c** coupled readily with benzenediazonium chloride to yield the corresponding phenylhydrazone **14c**. Compound **5d** coupled with benzenediazonium chloride to give products that may be formulated as phenylhydrazone **14d** or **15**. Structure **14d** was preferred for the reaction product on the basis of IR spectrum which revealed cyano and thiocyanate bands at $\nu = 2220$ and sharp band at $\nu = 2210 \text{ cm}^{-1}$ for SCN group. If the reaction product is the cyclized isomer **15**, one would expect the disappearance of the SCN band. Product **15** could then be obtained by refluxing the hydrazone **14d** in acetic acid. The thiadiazole structure **15** was preferred over the pyridazine structure **16** on the basis of the IR spectral data which revealed the presence of CN group at $\delta = 2220 \text{ cm}^{-1}$ and the absence of the sharp band of SCN group (Scheme 4).



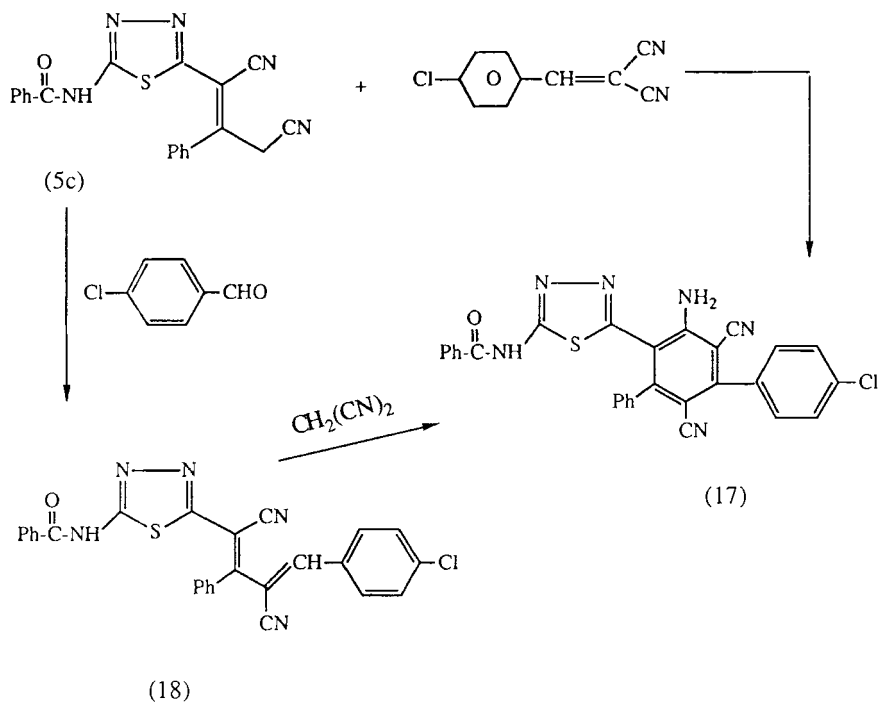
SCHEME 4

Compound **5c** reacted with *p*-chlorobenzylidenemalononitrile **6** to yield the benzene derivative **17**. Compound **17** was also obtained via condensing **5c** with *p*-chlorobenzaldehyde to yield the styryl derivative **18** and reacting the latter derivative with malononitrile.

The thiadiazole derivatives **22** could be prepared in good yield via reacting of the pyridazine **19** with hydrazine hydrate (Scheme 6) to give the hydrazide **20**.^{11,12} The hydrazide **20** reacted readily with benzoyl isothiocyanate in acetone to yield the thiosemicarbazide derivative **21**. The latter cyclized to yield thiadiazolyl pyridazine **22** on boiling in acetic acid.

EXPERIMENTAL

All melting points are uncorrected. IR spectra (KBr) were recorded on Shimatsu instrument 200-91506 spectrophotometer and the PERKIN ELMER 1650.



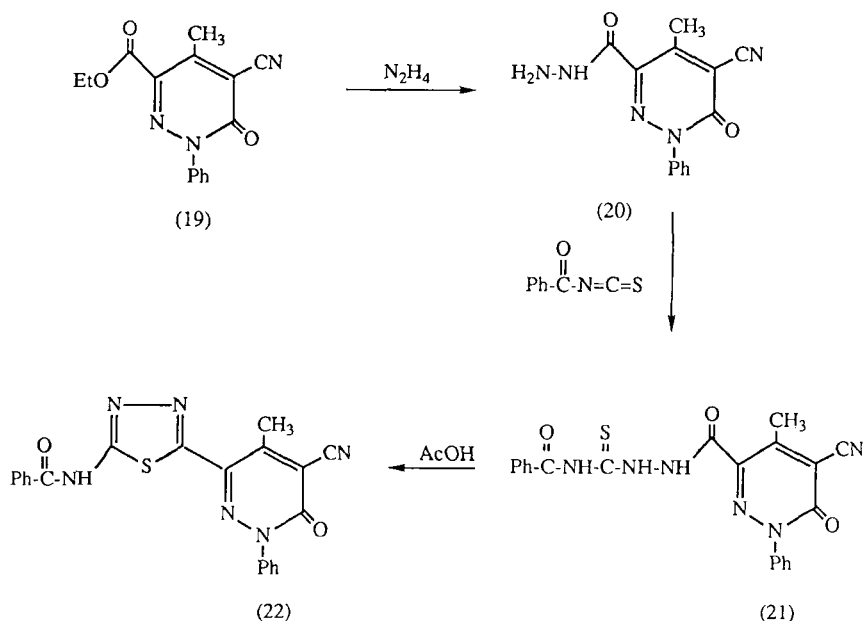
SCHEME 5

^1H NMR spectra were recorded on a varian EM 390–90 MHz using TMS as internal reference. The chemical shifts were expressed as δ ppm. Analytical data were obtained from the Microanalytical data Unit at Cairo University.

2-(5-Benzoylamino-1,3,4-thiadiazole-2-yl)acetonitrile (4)

A suspension of benzoyl chloride (2.8 g, 0.02 mol) and ammonium thiocyanate (1.5 g, 0.02 mol) in dioxane (20 ml) was refluxed for fifteen minutes and then was treated with cyanoethanoichydrazide **1** (2.0 g, 0.02 mol). The reaction mixture was refluxed for two hours, cooled, and then poured into water. The solid product so formed, was collected by filtration.

Compound **4** formed pale yellow crystals from dioxane, yield 2.0 g (81.9%), m.p. 220 °C, literature¹⁰ m.p. 220°C. IR: 3200 cm^{-1} (NH), 2220 cm^{-1} (CN) 1670 cm^{-1} (C=O). $\text{C}_{11}\text{H}_8\text{N}_4\text{SO}$ (244.283). Found: C, 54.2; H, 3.3; N, 23.0; S, 13.1%. Calcd for C, 54.08; H, 3.30; N, 22.93; S, 13.12%.



SCHEME 6

2-(2-Benzoylamino-1,3,4-thiadiazol-5-yl)-3-methylbut-2-enonitrile (5a)

Method A

A suspension of **4** (2.4 g, 0.01 mol) in ethanol (30 ml) was treated with acetone (0.6 ml, 0.01 mol) and a catalytic amount of piperidine. The reaction mixture was refluxed for two hours and then was evaporated and finally left to cool. The solid product was collected by filtration and crystallized from ethanol.

Method B

A suspension of benzoyl chloride (28 g, 0.2 mol) and ammonium thiocyanate (15 g, 0.2 mol) in acetone (50 ml) was refluxed for 15 minute and then was treated with cyanoethanoichydrazide (20 g, 0.2 mol). The mixture was refluxed for two hours, left to cool, and poured into cold water. The solid product, so formed, was collected by filtration.

Compound **5a**, formed white crystals from ethanol, yield 20.0 g (71.8%), m.p. 232 °C. IR: 3200 cm^{-1} (NH), 2220 cm^{-1} (CN); 1670 cm^{-1} (C=O). 1H NMR : δ 2.27 (s, 3 H, CH_3); 2.42 (s, 3 H, CH_3) ; 7.26–8.26 (m, 5 H, aromatic H); 12.55

(br, 1 H, NH). Mass (m/z): 284 (M^+). $C_{14}H_{12}N_4SO$ (284.384). Found: C, 59.3; H, 4.3; N, 19.6; S, 11.0%. Calcd. for C, 59.13; H, 4.25; N, 19.70; S, 11.27%.

3-Alkyl-3-phenyl-2-(2-benzoylamino-1,3,4-thiazol-5-yl)propionitrile (5b-d)

General procedure

A suspension of benzoyl chloride (7g, 0.05 mol) in dioxane (20 ml) was treated with ammonium thiocyanate (3.7 g, 0.05 mol), refluxed for fifteen minutes and then was treated with cyanoethanoichydrazide **1** (5 g, 0.05 mol). The reaction mixture was refluxed for half an hour and then was treated with an appropriate amount of acetophenone, benzoylacetonitrile, or phenacyl thiocyanate (0.05 mol), respectively. The mixture was refluxed for an additional one hour and then was poured into water. The solid products were collected by filtration and crystallized from the proper solvent.

Compound **5b** formed white crystals from ethanol, yield 2.6 g (76.4%), m.p. 182 °C. IR: 3212 cm^{-1} (NH); 2226 cm^{-1} (CN); 1680 cm^{-1} (C=O). 1H NMR: δ 3.81 (s, 3 H, CH_3); 7.51–7.99 (m, 10 H, aromatic-H); 12.55 (br, 1 H, NH), MS: m/z = 346 (M^+). $C_{19}H_{14}N_4OS$ (346.419). Found: C, 65.7; H, 4.0; N, 16.0; S, 9.2%. Calcd. for C, 65.87; H, 4.07; N, 16.17; S, 9.25%.

Compound **5c** formed pale yellow crystals from ethanol, yield 2.0 g (53.8%), m.p. 206 °C. IR: 3200 cm^{-1} (NH); 2220 cm^{-1} (CN); 1650 cm^{-1} (C=O). 1H NMR : δ 4.62 (s, 2 H, CH_2); 7.55–8.16 (m, 10 H-aromatic-H); 13.25 (br, 1 H, NH), MS: m/z = 371 (M^+). $C_{20}H_{13}N_5OS$ (371.430). Found: C, 64.7; H, 3.5; N, 18.7; S, 8.6%. Calcd. for C, 64.67; H, 3.52; N, 18.85; S, 8.63%.

Compound **5d** formed brown crystals from ethanol, yield 3.12 g (77.4%), m.p. 184 °C. IR: 3200 cm^{-1} (NH); 2941 cm^{-1} (CH_2); 2210–2220 cm^{-1} (CN); 1660 cm^{-1} (C=O). 1H NMR : δ 4.62 (s, 2 H, CH_2); 7.85–8.16 (m, 10 H-aromatic-H) ; 12.23 (br, 1 H, NH). $C_{20}H_{13}N_5OS_2$ (403.496). Found: C, 59.5; H, 3.1; N, 17.1; S, 15.6%. Calcd. for C, 59.53; H, 3.24; N, 17.3; S, 15.89%.

5-[4-Methyl-6-(p-chlorophenyl)anthranilonitrile-3-yl]1,3,4-thiadiazole-2-benzoylamine (9)

A suspension of **5a** (2.8 g; 0.01 mol) in ethanol (30 ml) was treated with p-chlorobenzylidenemalononitrile (1.8 g, 0.01 mol). The reaction mixture was refluxed for three hours then evaporated. The remaining product was triturated with water. The solid product was collected by filtration.

Compound **9** formed yellow crystals from ethanol, yield 2.8 g (63.6%), m.p. 140 °C IR : 3300–3200 cm^{-1} (NH, NH_2), 2220 cm^{-1} (CN); 1710 cm^{-1} (C=O)

^1H NMR: δ 2.51 (s, 3 H, CH_3); 3.36 (br, 2 H, NH_2); 7.55–7.99 (m, 9 H, aromatic-H) 8.14 (s, 1 H, H_4), 8.56 (s, 1 H, NH). $\text{C}_{23}\text{H}_{16}\text{N}_5\text{OSCl}$ (445.947). Found: C, 61.8; H, 3.5; N, 15.5; S, 7.0; Cl, 7.6%. Calcd. for C, 61.94; H, 3.61; N, 15.70; S, 7.19; Cl, 7.95%.

3-Methyl-5-aryl-2(thi adiazole-2-benzoylamine-5-el)penta-2,4-dienonitrile (10a,b)

General procedure

A suspension of **5a** (2.8 g; 0.01 mol) in dioxane (30 ml) containing few drops of piperidine was treated with appropriate amount of aromatic aldehydes (0.01 mol). The reaction mixtures were refluxed for three hours and then was evaporated and left to cool. The solid products were collected by filtration and crystallized from the proper solvent.

Compound **10a** formed light brown crystals from dioxane, yield 2.7 g (67.9%), m.p. 202 °C IR: 3200 cm^{-1} (NH) 2220 cm^{-1} (CN); 1680 cm^{-1} (C=O) ^1H NMR: δ 2.30 (s, 3 H, CH_3); 7.47–8.28 (m, 11 H, aromatic-H + ethylenic-H); 13.24 (br, 1 H, NH). $\text{C}_{21}\text{H}_{15}\text{N}_4\text{OSCl}$ (406.909). Found: C, 61.9; H, 3.7; N, 13.7; S, 7.8; Cl, 8.7%. Calcd. for C, 61.98; H, 3.71; N, 13.77; S, 7.88; Cl, 8.71%.

Compound **10b** formed yellow crystals from ethanol, yield 3.0 g (75%), m.p. 220 °C IR: 3210 cm^{-1} (NH) 2220 cm^{-1} (CN); 1680 cm^{-1} (C=O) ^1H NMR: δ 2.52 (s, 3 H, CH_3); 3.63 (s, 3 H, OCH_3); 7.55–8.17 (m, 11 H, aromatic-H + ethylenic-H); 13.22 (br, 1 H, NH). $\text{C}_{22}\text{H}_{18}\text{N}_4\text{O}_2\text{S}$ (402.484). Found: C, 65.5; H, 4.5; N, 13.7; S, 7.8%. Calcd. for C, 65.65; H, 4.50; N, 13.92; S, 7.96%.

3'-(5-Amino-1,3,4-thiadiazole-2-yl)-6'-aryl-1',2'-dihydro-4'-methyl-2-pyridin-2-one (12a,b)

General procedure

A suspension of **10a,b** (0.01 mol) in acetic acid (30 ml) was treated with sulphuric acid (3.0 mol). The reaction mixtures were refluxed for two hours then evaporated. The remaining products were triturated with water then left two hours at room temperature. The solid products, so formed, were collected by filtration.

Compound **12a** formed brown crystals from acetic acid, yield 1.9 g (60.1%), m.p. 172 °C. IR: 3300–3200 cm^{-1} (NH, NH_2); 1660 cm^{-1} (C=O). ^1H NMR: δ 2.44 (d, 3 H, CH_3); 4.49 (br, 2 H, NH_2); 7.52–8.13 (m, 5 H-aromatic-H + CH);

12.31 (br, 1 H, NH). $C_{14}H_{11}N_4OSCl$ (318.800). Found: C, 52.7; H, 3.2; N, 17.4; S, 9.9; Cl, 10.9%. Calcd. for C, 52.74; H, 3.47; N, 17.57; S, 10.05; Cl, 11.12%.

Compound **12b** formed brown crystals from ethanol, yield 2.0 g (64.1%), m.p. 165 °C. IR: 3300–3200 cm^{-1} (NH, NH₂); 1660 cm^{-1} (C=O). $C_{15}H_{14}N_4O_2S$ (314.375). Found: C, 57.7; H, 4.3; N, 17.8; S, 10.2%. Calcd. for C, 57.3; H, 4.48; N, 17.82; S, 10.19%.

Coupling of **5c,d** with diazonium salt (**14c,d**)

A cold solution of benzenediazonium chloride (0.01 mol) [prepared by adding sodium nitrite solution (0.69 g, 0.01 mol) to a cold solution of aniline (0.93 g, 0.01 mol) containing the appropriate amount of hydrochloric acid (6 ml) was added with stirring to a cold solution of **5c,d** (0.01 mol) in ethanol (30 ml) containing sodium acetate (2 g). The solid products, so formed, were collected by filtration.

Compound **14c** formed orange crystals from ethanol, yield 3.3 g (70%), m.p. 295 °C. IR: 3220–3100 cm^{-1} (NH, NH); 2225–2220 cm^{-1} (CN, CN) 1740 cm^{-1} (C=O). 1H NMR: δ 3.58 (s, 1 H, NH); 7.38–8.17 (m, 15 H-aromatic-H); 13.25 (br, 1 H, NH-CO). $C_{26}H_{17}N_7OS$ (475.544). Found: C, 65.4; H, 3.5; N, 20.7; S, 6.7%. Calcd. for C, 65.66; H, 3.60; N, 20.61; S, 6.74%.

Compound **14d** formed yellow crystals from ethanol, yield 3.2 g (63.1%), m.p. 206 °C. IR: 3200–3100 cm^{-1} (NH, NH); 2220 cm^{-1} (CN); 2210 cm^{-1} (SCN), 1740 cm^{-1} (C=O). 1H NMR: δ 2.51 (s, 1 H, NH); 7.56–8.16 (m, 15 H-aromatic-H); 13.38 (br, 1 H, NH-CO). $C_{26}H_{17}N_7OS_2$ (507.610). Found: C, 61.5; H, 3.3; N, 19.2; S, 12.7%. Calcd. for C, 61.52; H, 3.37; N, 19.31; S, 12.63%.

α -[5-Benzoylamino-1,3,4-thiadiazol-2-yl]- β -[2'-imino-3'-phenyl-1',3',4'-thiadiazol-5-yl]cinnamionitrile (**15**)

A suspension of **14d** (5.1 g, 0.01 mol) in acetic acid (30 ml) was refluxed for one hour and then evaporated. The remaining solid was then triturated with water. The solid product was collected by filtration.

Compound **15** formed brown crystals from acetic acid, yield 3 g (59%), m.p. 262 °C. IR: 3200–3100 cm^{-1} (NH, NH); 2220 cm^{-1} (CN); 1740 cm^{-1} (C=O); 1640 (C=S). $C_{26}H_{17}N_7OS_2$ (507.610). Found: C, 61.5; H, 3.3; N, 19.3; S, 12.6%. Calcd. for C, 61.52; H, 3.37; N, 19.31; S, 12.63%.

2-Benzoylamino-5-[2-amino-3',5'-dicyano-4'-(p-chlorophenyl)6'-phenyl]-1,3,4-thiadiazole (17)

Method (1)

A suspension of **5c** (3.7 g, 0.01 mol) in ethanol (30 ml) containing few drops of piperidine was treated with *p*-chlorobenzylidenemalononitrile (1.9 g, 0.01 mol). The reaction mixture was refluxed for three hours. The excess solvent was evaporated, then left to cool. The solid product was collected by filtration.

Method (2)

A suspension of **18** (4.9 g, 0.01 mol) in ethanol (30 ml) was treated with malononitrile (0.6 g, 0.01 mol) and few drops of piperidine. The reaction mixture was refluxed for three hours and then evaporated and allowed to cool. The solid product was collected by filtration.

Compound **17** formed yellow crystals from ethanol, yield 3 g (57%), m.p. 315°C. IR: 3200–3100 cm⁻¹ (NH, NH₂); 2220 cm⁻¹ (CN); 1680 cm⁻¹ (C=O). ¹H NMR: δ 3.48 (s, 2 H, NH₂); 7.49–8.23 (m, 14 H- aromatic-H); 13.21 (br, 1 H, NH). C₂₉H₁₇N₆OSCl (533.029). Found: C, 65.1; H, 3.2; N, 15.5; S, 5.9; Cl, 6.7%. Calcd. for C, 65.34; H, 3.21; N, 15.76; S, 6.01; Cl, 6.65%.

5-(p-Chlorophenyl)-3-phenyl-2-(2-benzoylamino-1,3,4-thiadiazol-5-yl)-penta-2,4-dieno-2,4-dicarbonitriles (18)

A suspension of **5c** (3.7 g, 0.01 mol) in dioxane (30 ml) containing few drops of piperidine was treated with *p*-chlorobenzaldehyde (1.4 g, 0.01 mol). The reaction mixture was refluxed for three hours. The solid product, so formed, after dilution was collected by filtration.

Compound **18** formed yellow crystals from dioxane, yield 3.7 g (75%), m.p. 212 °C. IR: 3200 cm⁻¹ (NH); 2225 cm⁻¹ (CN); 2221 cm⁻¹ (CN). ¹H NMR: δ 4.65 (s, 1 H, CH); 7.54–8.14 (m, 14 H, aromatic-H); 13.21 (br, 1 H, NH). C₂₇H₁₆N₅OSCl (493.991). Found: C, 65.5; H, 3.2; N, 13.9; S, 6.4; Cl, 7.0%. Calcd. for C, 65.64; H, 3.26; N, 14.17; S, 6.49; Cl, 7.17%.

Ethyl 5-cyano-1,6-dihydro-4-methyl-6-oxo-1-phenylpyridazine-3-carboxylate (19)

A mixture of equimolecular amount of diazonium salt of ethyl acetoacetate (2.2 g, 0.01 mol) and ethyl cyanoacetate (1.1 g, 0.01 mol) was treated with ammonium acetate (0.75 g, 0.01 mol). The mixture was heated in oil bath at

160 °C for half an hour and then left to cool. The resulting product was then triturated with ethanol and water. The solid product was collected by filtration.

Compound **19** formed yellow crystals from ethanol yield, 2.2 g, (80%), m.p. 165 °C, literature⁹ m.p. 165 °C.

5-Cyano-1,6-dihydro-4-methyl-6-oxo-1-phenylpyridazine-3-carboxylic acid hydrazide (20)

A suspension of **19** (2.8 g; 0.01 mol) in ethanol (50 ml) was treated with hydrazine hydrate (1.0 ml, 0.02 mol). The reaction mixture was refluxed for half an hour and then was left to cool at room temperature. The solid product was collected by filtration and crystallized.

Compound **20** formed pale yellow crystals from methanol, yield 1.8 g (70%), m.p. 230 °C. IR: 3400 cm⁻¹ (NH, NH₂); 2210 cm⁻¹ (CN); 1680 cm⁻¹ (C=O). C₁₃H₁₁N₅O₂ (269.271). Found: C, 57.8; H, 4.2; N, 26.2%. Calcd. for C, 57.98; H, 4.11; N, 26.01%.

4-Benzoyl-1-(4-cyano-5-methyl-3-oxo-2-phenylpyridazine-3-yl)-thiosemicarbazide (21)

A suspension of benzoyl chloride (1.4 g, 0.01 mol) and ammonium thiocyanate (0.75 g, 0.01 mol) in acetone (20 ml) was refluxed for fifteen minutes and then was treated with the hydrazide **20** (2.6 g, 0.01 mol). The reaction mixture was refluxed for three hours and then left to cool and finally was poured into water. The solid product was collected by filtration.

Compound **21** formed yellow crystals from dioxane, yield 2.8 g (65%), m.p. 180 °C. IR: 3500–3000 cm⁻¹ (3 NH); 2220 cm⁻¹ (CN); 1720 cm⁻¹ (C=O); 1670 cm⁻¹ (C=O); 1660 cm⁻¹ (C=O). C₂₁H₁₆N₆O₃S (432.473). Found: C, 58.4; H, 3.8; N, 19.5; S, 7.4%. Calcd. for C, 58.32; H, 3.72; N, 19.43; S, 7.41%.

3-(5'-Benzoylamino-1',3',4'-thiadiazol-2'-yl)-1-phenyl-4-methyl-5'-cyanopyridazin-6'-one (22)

A suspension of **21** (4.3 g, 0.01 mol) in acetic acid (30 ml) was refluxed for one hour, then left to cool at room temperature. The solid product was collected by filtration.

Compound **22** formed orange crystals from acetic acid and water, yield 2.1 g (50.7%), m.p. 190 °C. IR: 3200 cm⁻¹ (NH); 2220 cm⁻¹ (CN); 1740 cm⁻¹ (C=O); 1680 cm⁻¹ (C=O). ¹H NMR: δ 2.51 (s, 3 H, CH₃); 7.07–8.12 (m, 10 H-aro-

matic-H) ; 13.22 (br, 1 H, NH). $C_{21}H_{14}N_6O_2S$ (414.457). Found: C, 60.6; H, 3.1; N, 20.3; S, 7.9%. Calcd. for C, 60.85; H, 3.40; N, 20.27; S, 7.73%.

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