The Reaction of 1-Phenylpyrazolidine-3,5-dione with Active Nitriles Using Phase Transfer Catalysis Conditions Technique

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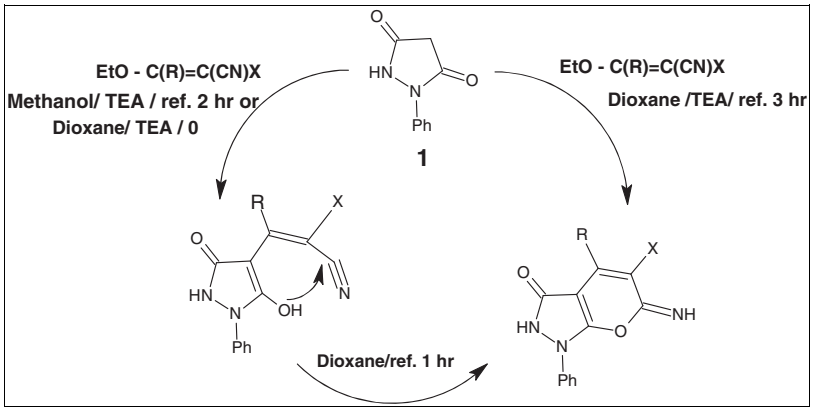

Heterocyclization reaction of 1-phenylpyrazolidine-3,5-dione with some active nitriles and acrylonitriles is described. These cyclization reactions afforded novel heterocyclic derivatives such as pyrano[2,3-c]pyrazoles, pyrazolyl-thiazole, pyrazolyl-1,3-thiazines, and pyrazolyl-1,3-oxathiino[6,5-c]pyrazoles. Heating 1-phenylpyrazolidine-3,5-dione alone under phase transfer catalysis conditions afforded the tricyclic dipyrazolofurandione. The structure of the new products has been characterized by IR, NMR, mass spectra, and their elemental analyses.

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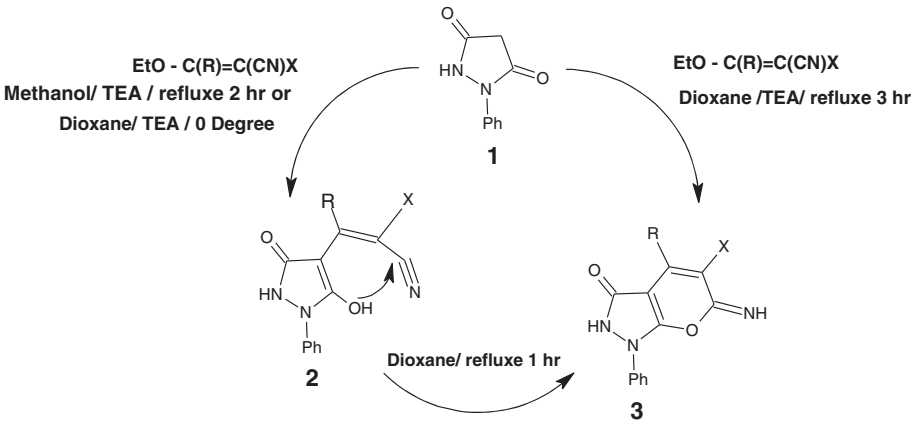
INTRODUCTION

3,5-Pyrazolidendiones[1–4] were reported to possess antibacterial, anti-inflammatory[5], antiviral[6], antimicrobial[7] and uricosuria properties[8]. Pyranopyrazoles[9], 1,3-thiazines[10], thiazoles [11], thienopyrazoles [12], and furopyrazole [13] represent important classes of heterocycles, which have been developed for different purposes in the pharmaceutical field. In continuation of our previous works, which had dealt with using active nitriles in synthesis of polyfused- and spiropyrazoles [14–21], herein, we report the synthesis of pyrano[2,3-*c*] pyrazole, thiazole, 1,3-thiazine, 1,3-oxothiinopyrazole, and furo[2,3-*c*]pyrazole derivatives starting with 1-phenylpyrazolidine-3,5-dione[1–4,10,14].

RESULTS AND DISCUSSION

The reaction of 1-phenylpyrazolidine-3,5-dione[10] (**1**) with ethoxymethylenemalononitrile, 1-ethoxyethylidenemalononitrile or ethyl 2-cyano-3-ethoxyacrylate in refluxing methanol or at 0°C in dioxane, afforded [(3,5-dioxo-1-phenylpyrazolidin-4-yl)methylene]-malononitrile (**2a**), 1-[(3,5-dioxo-1-phenylpyrazolidin-4-yl)ethylidene] malononitrile **(2b)** and ethyl [(3,5-dioxo-1-phenylpyrazolidin-4-yl)methylene]cyanoacetate (**2c**), respectively. These compounds were cyclized in refluxing dioxane to give pyrano[2,3-*c*]pyrazole-5-carbonitriles **3a,b** and ethyl pyrano[2,3-*c*]pyrazole-5-carboxylate **3c**, respectively, in good yield. Compounds **3a–c** were obtained directly via the reaction of compound **1** with the same reagents in refluxing dioxane, containing triethylamine as a catalyst (cf. Scheme 1). IR spectra of compounds **2a–c** showed appearance of new absorption bands corresponding to CN groups and C═O_{ester} at ν2220–2208 cm^{-1} and 1705 cm^{-1}, respectively, whereas IR spectra of compounds **3a–c** revealed the absence of one of the absorption bands corresponding to C═O group at position-5 of compound **1** and showed absorption bands corresponding to NH groups at ν 3282–3230 cm^{-1}. ^{1}H NMR spectrum of compounds **3a–c** showed new signals corresponding to NH groups at δ 10.30 and 8.20 ppm, ═CH at δ 6.10 ppm, methyl group at δ 2.20 ppm and ester group at δ 4.40–4.00 and 1.30–1.00 ppm, respectively. MS spectra of compounds **2b**, **3a**, **3b**, and **3c** showed the molecular peak ions at 266 (23%), 252 (34%), 266(7.4%), and 299(65.5%), respectively. The reaction pathway was assumed to proceed through the nucleophilic addition of the formed carbanion at position-4 of compound **1** on the C═C group of the nitrile reagent with elimination of ethanol molecule to give **2a–c**. The subsequent step is the addition of the tautomeric OH [14,16–18] to the CN group in all cases forming the corresponding pyranopyrazoles **3a–c**.

Scheme 1



2a, 3a; R = H, X = CN

2 $_b$,3 $_a$; R = CH_3, X = CN

2c, 3c ; R = H, X = COOEt

The resulting mixture of compound **1** and phenylisothiocyanate was treated with phenacyl bromide, (1-ethoxyethylidene)malononitrile or ethyl 2-cyano-3-ethoxyacrylate in 1: 1: 1 M ratio under phase transfer catalysis conditions (PTC) [K_2CO_3/tetrabutylammonium bromide (TBAB)/ dioxane] to afford the corresponding thiazole **4** and 1, 3-thiazines **5a,b** derivatives, respectively (cf. Scheme 2). ^{1}H NMR spectrum of compound **5a** showed new signals corresponding to NH group at δ 8.50 ppm, methyl group at δ 2.23 ppm in addition to aromatic protons and NH group at δ 7.80–6.70 ppm. MS spectra of compounds **4** and **5a** gave the molecular ion peaks at 397 (7%) and 401 (2%), respectively. Khodairy[14] reported that the reaction of compound **1** with a mixture of phenylisothiocyanate and benzylidenemalononitrile in refluxing pyridine gave 1,4-dioxo-2,8-diphenyl-6-(phenylimino)-10-imino-7-thia-2,3-diazaspiro[4.5]dec-8-ene-9-carbonitrile in 60% yield. But we report here the reaction of compound **1** with the same reagents under PTC conditions, gave the corresponding 4-imino-1,3-thiazine-5-carbonitrile derivative **6a** in 90% yield. Mass spectrum of compound **6a** showed the molecular ion peak at 463 (2%). In analogy, treatment of compound **1** with phenyl isothiocyanate and ethyl benzylidenecyanoacetate under PTC conditions afforded ethyl 4-imino-1,3-thiazine-5-carboxylate **6b** (cf. Scheme 2). ^{1}H NMR spectrum of compound **6b** showed ethyl ester protons at δ 4.40–4.10 and 1.30–1.00 ppm and NH proton at δ 8.80–8.60 ppm as a broad signal (D_2O exchangeable).

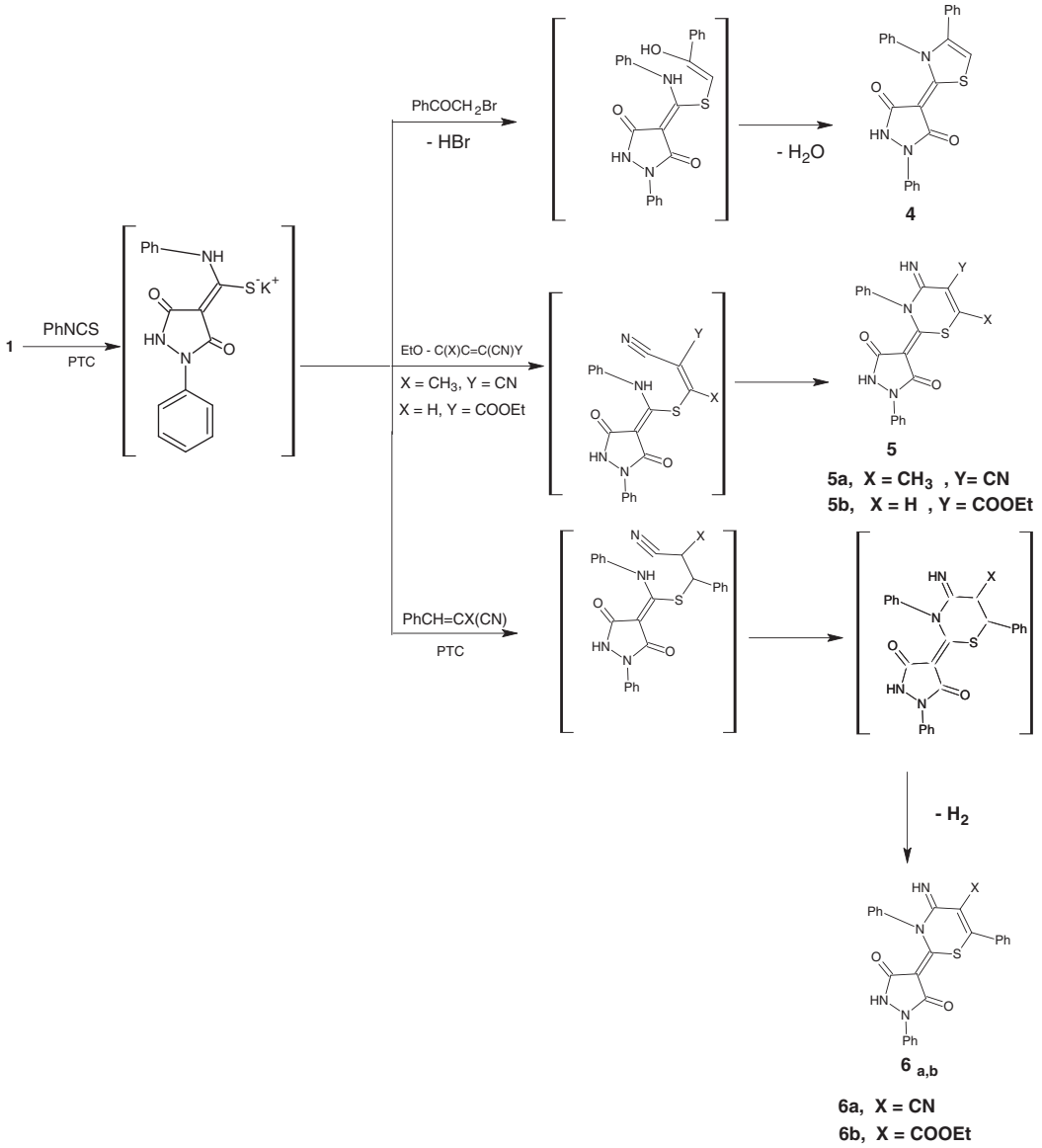
Also, compound **1** was allowed to react with a mixture of carbon disulfide and ethoxymethylenemalononitrile or ethyl 2-cyano-3-ethoxyacrylate under PTC conditions [K_2CO_3/(TBAB)/dioxane] where, 2(3-oxo-1-phenyl-4-thioxo-1,2,3,4-tetrahydro[1,3]oxa-thiino[6,5-c]-pyrazol-6-yl) malononitrile **(7a)** or ethyl 2-cyano-2(3-oxo-1-phenyl-4-thioxo-2,3,4,6-tetrahydro-[1,3]oxathiino[6,5-c]pyrazol-6-yl) carboxylate **(7b)** were obtained, respectively (cf. Scheme 3). The IR spectra of compounds **7a,b** revealed the absence of the absorption band corresponding to C═O group at position-5 of compound **1** and appearance of new absorption bands corresponding to CN, C═O_{ester} and C═S groups at ν 2203, 1710, and 1150 cm^{-1}, respectively. Their ^{1}H NMR spectra showed the absence of the signal corresponding to CH_2 group of compound **1** and appearance of new signals corresponding to CH and ester groups.

Unexpectedly, stirring of compound **1** alone under PTC conditions [K_2CO_3/TBAB/dioxane] afforded pyrazolo [3′,4′:4,5]furo[2,3-c]pyrazol-3,7-dione **8** (Scheme 4) in 83% yield. Its ^{1}H NMR spectrum showed new signals corresponding to two methane groups at 3.30–3.10 ppm. as dd, J = 7.20 Hz., whereas the ^{13}C NMR spectrum showed signals at 72 and 50 ppm characteristics for C4 and C8, respectively. Its mass spectrum showed the molecular ion peak at 334(6%).

EXPERIMENTAL

All reagents and solvents were of commercial quality; solvents were dried according to standard procedures when deemed necessary. All melting points are uncorrected and were recorded on Melt-Temp II melting point apparatus. IR spectra were measured as KBr pellets on a Shimadzu DR-8001 spectrometer. ^{1}H-NMR spectra were recorded on a Varian Gemini at 200 MHz using TMS as an internal reference and DMSO-d6 as a solvent. Mass spectra were performed on a Shimadzu GCMS-QP 1000 mass spectrometer at 70 ev. The elemental analyses were carried out on a Perkin-Elmer 240oC Microanalyzer. All compounds were checked for their purity on TLC plates.

Scheme 2

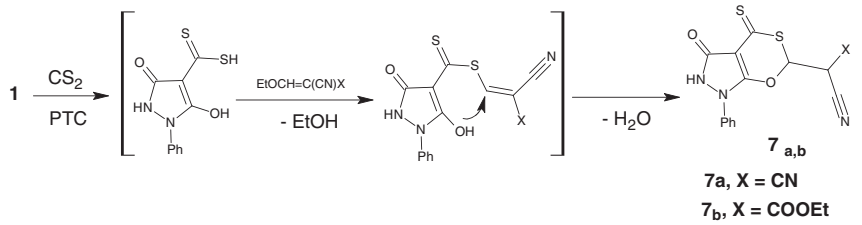


Synthesis of compounds 2a–c

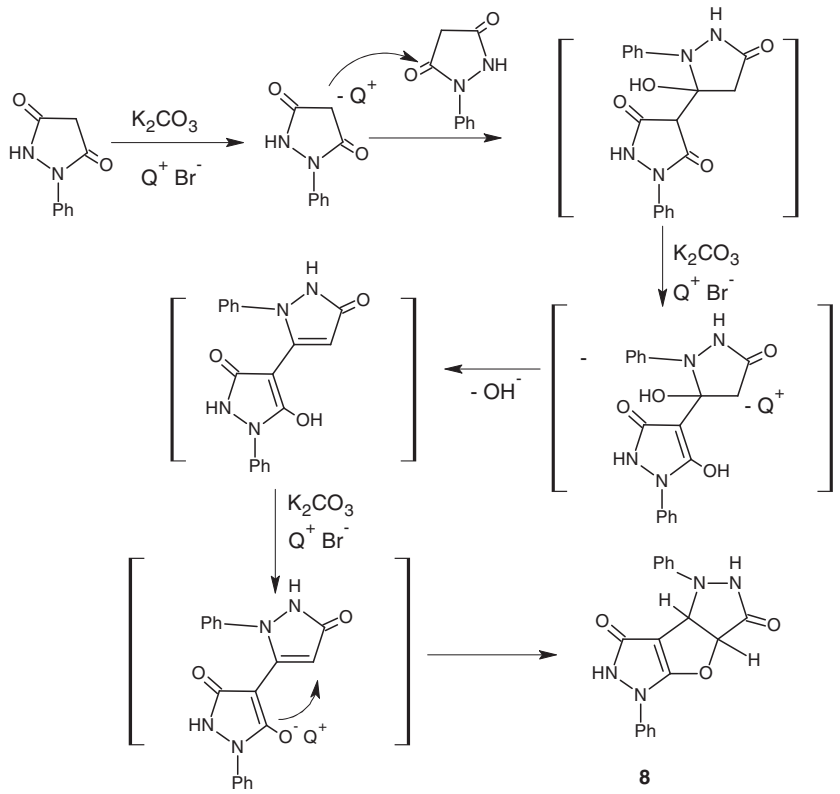
Procedure A. A mixture of 1-phenylpyrazolidine-3,5-dione **1** (0.01 mol, 1.76 g) and ethoxymethylenemalononitrile (0.01 mol, 1.22 g), (1-ethoxyethylidene)malononitrile (0.01 mol, 1.36 g) or ethyl 2-cyano-3-ethoxyacrylate (0.01 mol, 1.69 g) and TEA (0.2 mL) was refluxed in methanol (20 mL) for 2 h. The solid product so formed on hot was filtered off, dried, and crystallized from the appropriate solvent.

Procedure B. A mixture of 1-phenylpyrazolidine-3,5-dione **1** (0.01 mol, 1.76 g) and ethoxymethylenemalononitrile (0.01 mol, 1.22 g), (1-ethoxyethylidene)malononitrile (0.01 mol, 1.36 g) or ethyl 2-cyano-3-ethoxyacrylate (0.01 mol, 1.69 g) and TEA

Scheme 3



Scheme 4



(0.2 mL) was stirred in dioxane (15 mL) at 0°C for 2 h. The solid product so formed was filtered off, dried, and crystallized from the appropriate solvent.

[(3,5-Dioxo-1-phenylpyrazolidin-4-yl)methylene]malononitrile (2a). Yellow crystals from ethanol, yield (59%); mp 270–2°C; IR (KBr) ν cm^{-1} : 3240 (NH), 2220 (CN), 1672, 1636 (2C═O). ^{1}H NMR (DMSO-d_6) δ ppm: 9.00 (s, 1H, exchangeable with D_2O, NH); 8.30–8.00 (br, 1H, CH═); 7.97–6.90 (m, 5H, $H_{arom.}$); 4.20–4.00 (d, J = 11.2 Hz, 1H, $CH_{pyrazole}$). Found, %: C, 61.76; H, 3.32; N, 22.40. $C_{13}H_8N_4O_2$ (252.22). Calcd. %: C, 61.90; H, 3.20; N, 22.21.

[1(3,5-Dioxo-1-phenylpyrazolidin-4-yl)ethylidene]malononitrile (2b). Yellow crystals from ethanol, yield (79%); mp 278°C; IR (KBr) ν cm^{-1} : 3154 (NH), 2208 (CN), 1678, 1634 (2C═O). ^{1}H NMR(DMSO-d_6) δ ppm:9.40–9.20 (br, 1H, exchangeable with D_2O, NH); 7.80–6.70 (m, 5H, $H_{arom.}$); 4.00 (s, 1H, $CH_{pyrazole}$); 2.30 (s, 3H, CH_3). MS (EI, 70 eV), *m/z* (I_{rel}, %): 266 (23), 265 (100), 241 (2), 220 (3), 201 (4.6), 175 (19), 103 (14), 83 (34). Found, %: C 63.30; H 3.50; N 21.23. $C_{14}H_{10}N_4O_2$ (266.25). Calcd. %: C, 63.15; H, 3.79; N, 21.04.

Ethyl [(3,5-dioxo-1-phenylpyrazolidin-4-yl)methylene] cyanoacetate (2c). Green crystals from ethanol, yield (85%); mp 223–5°C; IR (KBr) ν 3240(NH), 2211(CN), 1705 (C═O_{ester}), 1672, 1636 (2C═O). ^{1}H NMR (DMSO-d_6) δ ppm:8.70 (s, 1H, exchangeable with D_2O, NH); 8.20–8.00 (d, J = 10.6 Hz, 1H, ═CH); 7.90–6.80 (m, 5H, $H_{arom.}$); 4.40–4.00 (m, 3H, CH_{2ester} + $CH_{pyrazole}$); 1.30–1.00(t, J = 5.1 Hz, 3H, CH_3). Found, %: C, 60.33; H, 4.54; N, 14.21. $C_{15}H_{13}N_3O_4$ (299.28). Calcd. %: C, 60.20; H, 4.38; N, 14.04.

Synthesis of compounds 3a–c

Procedure A. A suspension of compound **2a** (0.01 mol, 2.52 g), compound **2b** (0.01 mol, 2.66 g), or compound **2c** (0.01 mol, 2.99 g) in dioxine (20 mL) containing TEA (0.2 mL) was refluxed for 1 h. The reaction mixture was left to cool and poured into crushed ice; the separated solid was filtered off, dried, and crystallized.

Procedure B. A mixture of 1-phenyl-3,5-pyrazolidindione (0.01 mol, 1.76 g) and ethoxymethylenemalononitrile (0.01 mol, 1.22 g), (1-ethoxyethylidene) malononitrile (0.01 mol, 1.36 g), or 2-cyano-3-ethoxyacrylate (0.01 mol, 1.69) in dioxane (20 mL) containing TEA (0.2 mL) was refluxed for 2 h and then left to cool. The solid product so formed was filtered off, dried, and crystallized from the appropriate solvent.

6-Imino-3-oxo-1-phenyl-1,2,3,6-tetrahydropyrano[2,3-c]-pyrazole-5-carbonitrile (3a). White crystals from ethanol, yield (69%); mp 300–2°C; IR (KBr) ν: 3282, 3220 (2NH), 2215 (CN), 1634 (C═O). ^{1}H NMR (DMSO-d_6) δ ppm: 8.70 (s, 1H, exchangeable with D_2O, $NH_{pyrazole}$); 8.50 (s, 1H, exchangeable with D_2O, NH); 7.80–6.70 (m, 5H, $H_{arom.}$); 6.00 (s, 1H, ═CH). ^{13}C NMR (d_6-DMSO) δ ppm: 150(C═O), 148(C═NH), 142, 134(CH═), 125, 122, 114(–CN), 111(C_4), 100, 92(C–CN). MS (EI, 70 eV), *m/z* (I_{rel}, %): 252 (34), 251 (10), 181 (3), 146 (13), 133 (6), 119 (4), 91 (100), 77 (31), 64 (21), 51 (15). Found, %: 61.76; H, 3.32; N, 22.40 $C_{13}H_8N_4O_2$ (252.22). Calcd. %: C, 61.90; H, 3.20; N, 22.21.

6-Imino-4-methyl-3-oxo-1-phenyl-1,2,3,6-tetrahydropyrano [2,3-c]pyrazole-5-carbonitrile (3b). Brown crystals from ethanol, yield (79%); mp 245–7; IR (KBr) ν, 3230, 3150(2NH), 2218(CN), 1624 (C═O). ^{1}H NMR (DMSO-d_6), δ ppm: 8.50 (s, 1H, exchangeable with D_2O, $NH_{pyrazole}$); 7.80–6.60 (m, 6H, $H_{arom.}$ + NH); 2.20 (s, 3H, CH_3). MS (EI, 70 eV), *m/z* (I_{rel}, %): 266 (7.4), 262 (18), 242 (14), 224 (21), 196 (30), 193 (70), 186 (100), 178 (17), 135 (24), 85 (45), 60 (80). Found, %: C, 63.30;

H, 3.50; N, 21.23 $C_{14}H_{10}N_4O_2$ (266.25). Calcd. %: C, 63.15; H, 3.79; N, 21.04.

Ethyl 6-imino-3-oxo-1-phenyl-1,2,3,6-tetrahydropyrano[2,3-c] pyrazole-5-carboxylate (3c). Yellow crystals from ethanol, yield (80%); mp 320–2°C; IR (KBr) cm^{-1}, ν: 3301, 3150 (2NH), 1710 (CO_{ester}), 1630 (C═O). ^{1}H NMR (DMSO-d_6) δ ppm: 8.70 (s, 1H, exchangeable with D_2O, $NH_{pyrazole}$); 8.10 (s, 1H, exchangeable with D_2O, NH); 7.90–6.90 (m, 5H, $H_{arom.}$); 6.00 (s, 1H, ═CH); 4.40–4.00 (q, J = 4.1 Hz 2H, CH_2); 1.30–1.00 (t, J = 4.9 Hz, 3H, CH_3). MS (EI, 70 eV), *m/z* (I_{rel}, %): 299 (65.5), 298 (38.6), 253 (59.3), 252 (62.6), 187 (8.5), 186 (9.3), 182 (2.4), 164 (8.9), 154 (2.4), 137 (6.5), 128 (5.3), 119 (5.7), 105 (14.6), 91 (100), 77 (89). Found, %: C, 60.43; H, 4.50; N, 14.33. $C_{15}H_{13}N_3O_4$ (299.28). Calcd. %: C, 60.20; H, 4.38; N, 14.04.

Synthesis of compounds 4–6

General procedure. A mixture of compound **1** (0.01 mol, 1.76 g), phenylisothiocyanate (0.01 mol, 1.3 mL), anhydrous potassium carbonate (3 g), TBAB (0.003 g), and dioxane (20 mL) was stirred for 2 h. at 60°C. To the reaction mixture, phenacyl bromide (0.01 mol, 1.99 g), (1-ethoxyethylidene) malononitrile (0.01 mol, 1.36 g), 2-cyano-3-ethoxyacrylate (0.01 mol, 1.69), benzylidenemalononitrile (0.01 mol, 1.54 g) or ethyl benzylidenecyanoacetate (0.01 mol, 2.01 g) was added, then the reaction mixture was stirred for 3 h at 60°C until the completion of the reaction (TLC). The reaction mixture was filtered off and the filtrate was evaporated in vacuo. The residue was triturated with pet. ether (40–60°C), the separated solid was crystallized from the appropriate solvent to give compounds **4–6**.

2-(3,5-Dioxo-1-phenylpyrazolidin-4-ylidene)-3,4-diphenyl-1,3-thiazole (4). Amber yellow crystals from acetic acid, yield (60%); mp 138–140°C IR (KBr) ν, cm^{-1}: 3240 (NH), 1675, 1641 (2C═O). ^{1}H NMR (DMSO-d_6) δ ppm: 7.90–6.70 (m, 16H, $H_{arom.}$ + $NH_{pyrazole}$); 5.50 (s, 1H, ═CH). ^{13}C NMR (d_6-DMSO) δ ppm: 163 (C═O position-5), 160 (C═O position-3), 142, 140 (C-Ph), 133, 130, 125, 123(=CH), 120, 97. MS (EI, 70 eV), *m/z* (I_{rel}, %): 397 (7), 387 (5), 228 (5), 210 (4), 197 (7), 194 (17), 180 (19), 135 (100), 105 (88), 93 (68), 77(76). Found: C, 70.24; H, 4.30; N, 10.31; S, 7.90. $C_{24}H_{17}N_3O_2S$ (411.47). Calcd. %: C, 70.05; H, 4.16; N, 10.21; S, 7.79.

2-(3,5-Dioxo-1-phenylpyrazolidin-4-yliden)-4-imino-6-methyl-3-phenyl-3,4-dihydro-2H-1,3-thiazine-5-carbonitrile (5a). Yellow crystals from benzene, yield (85%); mp 300°C. IR (KBr) ν cm^{-1}: 3282, 3220 (2NH), 2215 (CN), 1670, 1630 (2C═O). ^{1}H NMR (DMSO-d_6) δ ppm: 8.50 (s, 1H, exchangeable with D_2O, NH); 8.00–6.90 (m, 6H, $H_{arom.}$ + $NH_{pyrazole}$); 2.20 (s, 3H, CH_3). MS (EI, 70 eV), *m/z* (I_{rel}, %): 401 (2), 396 (1), 389 (2), 306 (4), 279 (9), 256 (14), 193 (28), 186 (42), 169 (7), 105 (6), 85 (41), 71(100). Found, %: C, 62.66; H, 3.40; N, 17.70; S, 7.75. $C_{21}H_{15}N_5O_2S$ (401.44). Calcd. %: C, 62.83; H, 3.77; N, 17.45; S, 7.99.

Ethyl l2-(3,5-Dioxo-1-phenylpyrazolidin-4-yliden)-4-imino-3-phenyl-3,4-dihydro-2H-1,3-thiazine-5-carboxylate (5b). Amber yellow crystals from DMF, yield (90%); mp 217–9°C. IR (KBr) ν cm^{-1}: 3272, 3210 (2NH), 1710 (CO_{ester}), 1673, 1636 (2C═O). ^{1}H NMR (DMSO-d_6) δ, ppm: 8.60 (s, 1H, exchangeable with D_2O, NH); 8.10–6.60 (m, 11H, $H_{arom.}$ + $NH_{pyrazole}$); 5.30 (s, 1H, ═CH); 4.40–4.10 (q, J = 4.1 Hz, 2H, CH_2); 1.30–1.00 (t, J = 5 Hz, 3H, CH_3). Found, %: C, 60.61; H, 4.30; N, 12.70; S, 7.50. $C_{22}H_{18}N_4O_4S$ (434.46). Calcd. %: C, 60.82; H, 4.18; N, 12.90; S, 7.38.

2-(3,5-Dioxo-1-phenylpyrazolidin-4-yliden)-4-imino-3,6-diphenyl-3,4-dihydro-2H-1,3-thiazine-5-carbonitrile (6a). Colorless crystals from acetic acid, yield (90%); mp 240–2°C. IR (KBr) ν cm^{-1}: 3330, 3220 (2NH), 2100 (CN) 1670, 1640 (2C═O). ^{1}H NMR (DMSO-d_6) δ, ppm: 8.70–8.50 (br, exchangeable with D_2O, 1H, NH); 8.40–8.20 (br, 1H, exchangeable with D_2O, $NH_{pyrazole}$); 7.90–6.80 (m, 15H, $H_{arom.}$). MS (EI, 70 eV), *m/z* (I_{rel}, %): 463 (2), 428 (1), 392 (5), 367 (6), 308 (64), 292 (31), 276 (15), 262 (25), 216 (32), 174 (20), 158 (3), 118 (13), 85 (100). Found, %: C, 67.10; H, 3.54; N, 15.32; S, 6.80. $C_{26}H_{17}N_5O_2S$ (463.51). Calcd. %: C, 67.37; H, 3.70; N, 15.11; S, 6.92.

Ethyl 2-(3,5-dioxo-1-phenylpyrazolidin-4-yliden)-4-imino-3,6-diphenyl-3,4-dihydro-2H- 1,3-thiazine-5-carboxzlate (6b). White crystals from ethanol, yield (83%); mp 200–2°C. IR (KBr) ν cm^{-1}: 3229, 3220 (2NH), 1710(CO_{ester}), 1670, 1642 (2C═O). ^{1}H NMR (DMSO-d_6) δ ppm: 8.70–8.40 (br, 1H, exchangeable with D_2O, NH); 8.20–8.60 (br, 1H, exchangeable with D_2O, $NH_{pyrazole}$); 7.90–6.80 (m, 15H, $H_{arom.}$); 4.40–4.10 (q, J = 4.6 Hz, 2H, CH_2); 1.30–1.00 (t, J = 4.9 Hz, 3H, CH_3). ^{13}C NMR (d_6-DMSO) δ ppm 164 (C═O position-5), 161(C═O position-3), 148 (C═NH), 145(C–Ph), 142, 139, 131, 130, 126, 124, 120(C–COOEt), 102(C4), 60(CH_2), 14(CH_3). Found, %: C, 65.60; H, 4.50; N, 10.70; S, 6.28. $C_{28}H_{22}N_4O_4S$ (510.56). Calcd. %: C, 65.86; H, 4.34; N, 10.97; S, 6.28.

Synthesis of compounds 7a,b

General procedure. A mixture of compound **1** (0.01 mol, 1.76 g), carbon disulfide (0.01 mol, 0.76 ml), anhydrous potassium carbonate (3 g), TBAB (0.003 g), and dioxane (20 mL) was stirred for 2 h. at 60°C. To the reaction mixture, ethoxymethylenemalononitrile (0.01 mol, 1.22 g) or ethyl 2-cyano-3-ethoxyacrylate (0.01 mol, 1.61 g) was added, then the reaction mixture was stirred for 3 h at 60°C until the completion of the reaction (TLC). The reaction mixture was filtered off and the filtrate was evaporated in vacuo. The residue was triturated with pet. ether (40–60°C), the separated solid was crystallized from the appropriate solvent to give compounds **7a,b**.

2(3-Oxo-1-phenyl-4-thioxo-1,2,3,4-tetrahydro[1,3]oxathiino [6,5-c]pyrazol-6-yl)-malononitrile (7a). Light brown crystals from dioxane, yield (60%); mp 234–6°C. IR (KBr) ν, cm^{-1}: 3222 (NH), 2203 (CN), 1638 (C═O). ^{1}H NMR ($CDCl_3$) δ ppm: 8.30 (s, 1H, exchangeable with D_2O, $NH_{pyrazole}$); 7.40–6.80 (m, 5H, $H_{arom.}$); 5.30 (d, J = 9.1 Hz, 1H, CH oxathiine); 3.50 (d, J = 9.7 Hz, 1H, CH). Found, %: C, 51.45; H, 2.65; N, 17.30; S, 19.78. $C_{14}H_8N_4O_2S_2$ (328.36). Calcd. %: C, 51.21; H, 2.46; N, 17.06; S, 19.53.

Ethyl 2-cyano-2(3-oxo-1-phenyl-4-thioxo-2,3,4,6-tetrahydro [1,3]oxathiino-[6,5-c]-pyrazol-6-yl)carboxylate (7b). Brown crystals from benzene, yield (85%); mp 177–8°C. IR (KBr) ν, cm^{-1}: 3220 (NH), 2211 (CN), 1710, 1638 (2C═O). ^{1}H NMR (DMSO-d_6) δ ppm: 8.30–8.00 (br, 1H, exchangeable with D_2O, $NH_{pyrazole}$); 7.40–6.80 (m, 5H, $H_{arom.}$); 5.40 (d, J = 10 Hz, 1H, CH oxathiine); 3.50 (d, J = 9.4 Hz, 1H, CH), 4.40–4.10 (q, J = 3.90 Hz, 2H, CH_2); 3.60 (s, 1H, CH); 1.30–1.00 (t, J = 4.00 Hz 3H, CH_3). Found, %: C, 51.38; H, 3.65; N, 11.35; S, 17.22. $C_{16}H_{13}N_3O_4S_2$ (375.42). Calcd. %: C, 51.19; H, 3.49; N, 11.19; S, 17.08.

1,5-Diphenyl-1,2,3a,5,6,7b-hexahydropyrazolo[3',4':4,5]furo [2,3-c]pyrazol-3,7-dione 8. To a solution of compound **1** (0.01 mol, 1.76 g) in dioxane (20 mL), anhydrous potassium carbonate (3 g), and TBAB (0.003 g) were added. The reaction mixture was stirred for 3 h at 60°C until the completion of the reaction (TLC) and worked up as before. Yellow crystals from DMF, yield (83%); mp 265–7°C. IR (KBr) ν, cm^{-1}: 3220 (NH), 1646 (C═O). ^{1}H NMR (DMSO-d_6) δ ppm: 8.30–8.10 (br, 2H, exchangeable with D_2O, $2NH_{pyrazole}$); 7.30–6.70 (m, 10H, $H_{arom.}$); 3.30–3.10 (dd, J = 7.20 Hz, 2H, 2CH). ^{13}C NMR (d_6-DMSO) δ, ppm: 170 (C═O), 166 (═C–O), 160 (C═O), 138,

132, 128, 125, 124, 123, 120, 118, 110, 89, 72 (C_4), 50 (C_8). MS (EI, 70 eV), *m/z* (I_{rel}, %): 334 (6), 313 (4), 279 (10), 256 (36), 236 (13), 205 (18), 167 (35), 149 (100), 129 (20), 112 (25), 97 (63), 83 (48). Found, %: C, 64.40; H, 4.41; N, 16.55. $C_{18}H_{14}N_4O_3$ (334.32). Calcd. %: C, 64.66; H, 4.22; N, 16.76.

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