Synthesis of Some Novel 3,7-Dimethyl-4*H*-pyrazolo[5,1-*c*][1,2,4]triazin-4-ones

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Some novel 3,7-dimethyl-6*H*-pyrazolo[5,1-*c*][1,2,4]triazin-4-ones were prepared (**3a-g**). Compounds **3a,b** were treated with hydrazines to afford various products **7a,b, 8a,b, 9 and 11a,b** depending on the type of hydrazine derivative and reaction conditions. The benzoyloxyimino-pyrazolo[5,1-*c*][1,2,4]triazines (**13a,b**) were synthesized by refluxing of compounds **3a,b** with hydroxylamine hydrochloride to afford the corresponding oxime derivatives followed by treatment with benzoyl chloride.

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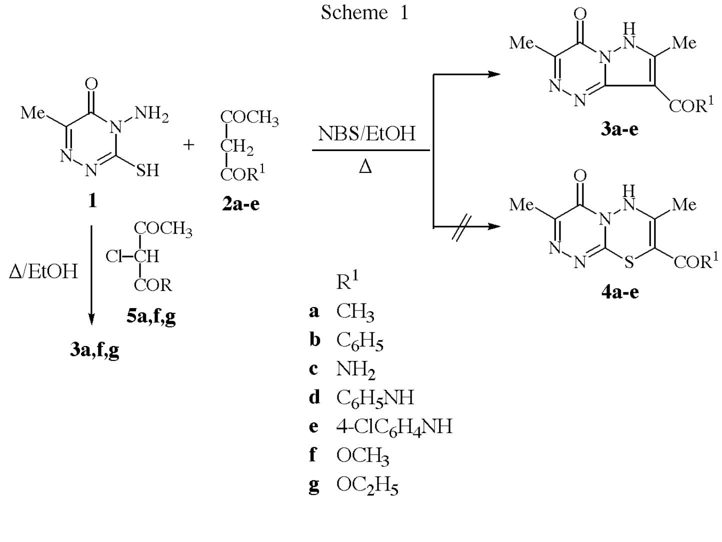
For few years, we have been occupied with the chemistry of 1,2,4-triazines[1-3] due to their importance and wide application in biological fields. A number of this class of compounds were found to act as antimicrobial [4], antiviral [5], anti-inflammatory [6-8] and antimalarial [9] agents. 4-Amino-1,2,4-triazin-5(4*H*)-one derivatives have attracted considerable interest, because of their herbicidal activities and important intermediates for the preparation of the fused 1,2,4-triazinone heterocycles [10].

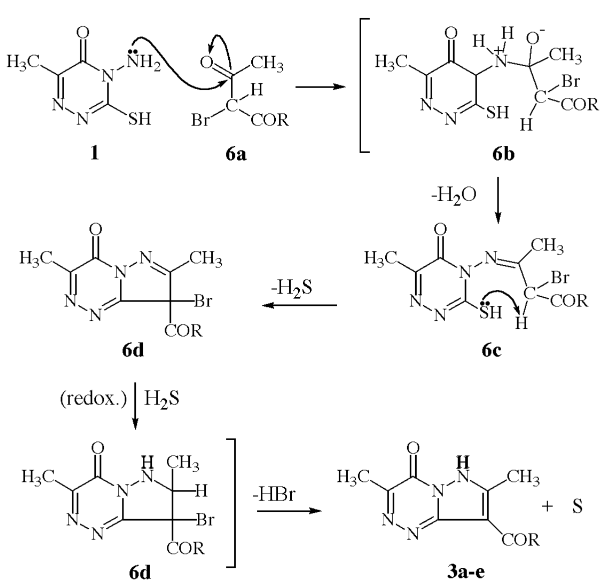
In an attempt to synthesize fused 1,2,4-thiadiazine ring with 1,2,4-triazines, we studied the reaction of 4-amino-6-methyl-5-oxo-3-thioxo-2,3,4,5-tetrahydro-1,2,4-triazine (**1**) with brominated 1,3-dicarbonyl active methylene compounds. The reaction was carried out by stirring of 1,3-dicarbonyl active methylene compounds (**2a-e**) with *N*-bromosuccinimide (NBS) in the presence of benzoyl peroxide in ethanol at room temperature for $^1/_2$ hour followed by addition of compound **1** and refluxing for 2 hours. The products from this reaction were shown to be 3,7-dimethyl-6*H*-pyrazolo[5,1-*c*][1,2,4]triazin-4-ones (**3a-e**) rather than the expected 3,7-dimethyl-6*H*-[1,2,4]thiadiazino[2,3-*c*][1,2,4]triazin-4-ones (**4a-e**) (*cf*. Scheme 1). In the ir, ^{1}H nmr and ^{13}C nmr spectra no observable differences are found capable of differentiating between compounds **3a-e** and **4a-e**. The only differences capable of differentiating between them were observed in their mass spectra and elemental analyses. Mass spectra showed the existence of the molecular ion peaks M^+ at m/z 206, 268 and 207 corresponding to **3a, 3b,** and **3c** respectively and the elemental microanalysis of these compounds for S gave zero %. The proof for formation of elemental sulfur came from its mass spectrum corresponding to $M^+ = 256$ (S_8). The above results confirm that pyrazolo[5,1-*c*][1,2,4]triazine structures (**3a-e**) were formed, and not the expected [1,2,4]thiadiazino[2,3-*c*]-[1,2,4]triazine structures (**4a-e**).

The mechanism for the formation of compounds **3a-e** is postulated as shown in scheme 2. It proceeds by nucleophilic attack of the amino group of **1** on the carbonyl group of **6a** to give **6b**, followed by elimination of water from **6b** to gave **6c** which subsequently undergoes internal nucleophilic attack accompanied by the elimination of hydrogen sulfide to give the 8-bromopyrazolo[5,1-*c*]-[1,2,4]triazines derivative (**6d**). Compound **6d** undgoes a redox reaction with the eliminated hydrogen sulfide to afford the 8-bromo-6,7,8-trihydropyrazolo[5,1-*c*]-[1,2,4]triazines (**6e**) and elemental sulfur. Elimination of hydrogen bromide from **6e** afforded the 6,7-dimethyl-6*H*-

Scheme 1



Scheme 2

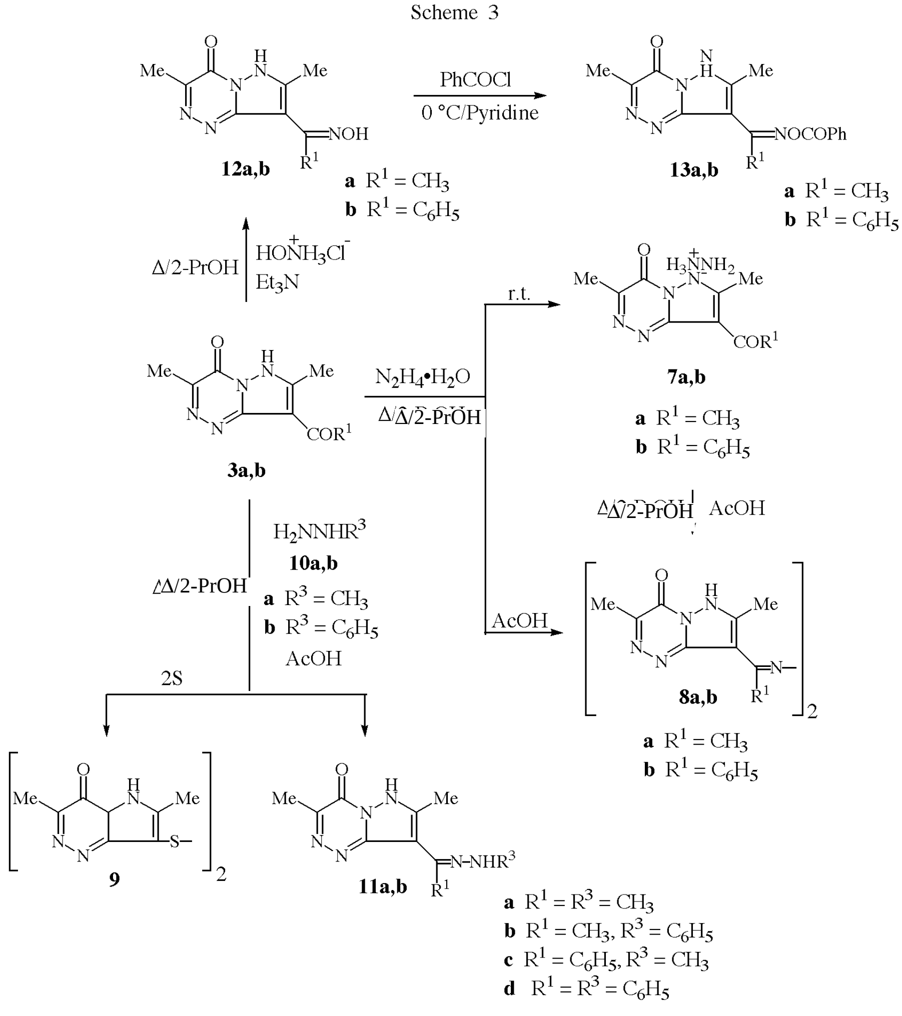


pyrazolo[5,1-*c*][1,2,4]triazin-4-ones (**3a-e**). The isolation of elemental sulfur, the observation of a pale red color resulting from elimination of hydrogen bromide and the effervescence of the mother liquor upon treatment with aqueous sodium bicarbonate solution are all consistent with the proposed mechanism.

Compounds **3a,f,g** were prepared directly in good yields by the reaction of **1** with 3-chloro-2,4-pentandione **5a** and/or methyl(ethyl)-2-chloroacetoacetate **5f,g** in refluxing ethanol (*cf.* Scheme 1).

Treatment of **3a,b** with hydrazine hydrate in 2-propanol at room temperature afforded the hydrazinium salts **7a,b** which by refluxing in 2-propanol in the presence of few drops of acetic acid furnished *N*,*N'*-bis[(3,7-dimethyl-4-oxo-4,6-dihydro-pyrazolo[5,1-*c*][1,2,4]triazin-8-yl)-ethylidene(and/or benzylidene)]-hydrazine (**8a,b**). Compounds **8a,b** were prepared directly by the reaction of **3a,b** with hydrazine hydrate in refluxing 2-propanol in the presence of few drops of acetic acid (*cf.* Scheme 3). The ^{1}H nmr spectrum of compounds **7a** showed the presence of a broad singlet signal (five protons) at 6.8 ppm corresponding to the hydrazinium ion ($N_2H_5^+$). The ^{13}C nmr spectrum of

Scheme 3



compound **7a** showed a resonance at 191.6 ppm corresponding to the 8-CO carbon. A signal corresponding to this carbon was not observed in the spectra of **8a,b** . In the mass spectrum of compound **7a**, the base peak is observed at m/z 206 (M^+-32) corresponding to loss of hydrazine, which is additional evidence for the postulated structure. In the mass spectra of compounds **8a,b**, molecular ion peaks M^+ were observed at m/z 408 and 532, respectively.

The reaction of crude **3b**, contaminated with elemental sulfur, with phenyl hydrazine in refluxing 2-propanol furnished bis(3,7-dimethyl-4-oxo-4,6-dihydro-pyrazolo[5,1-*c*][1,2,4]- triazin-8-yl)-disulfide (**9**) which was also prepared by refluxing pure **3b** with elemental sulfur and phenyl hydrazine. While, the reaction of **3a,b** with methyl and/or phenyl hydrazine (**10a,b**) in the presence of a few drops of acetic acid in refluxing 2-propanol yielded the corresponding hydrazono derivatives (**11a-d**) (*cf.* Scheme 3). In the ^{1}H nmr and ^{13}C nmr spectra of compound **9**, aromatic protons or carbons were not observed, showing that the phenyl group is not present. The ^{1}H nmr spectrum of compound **11b** showed the presence of a singlet corresponding to the NH-hydrazono at 9.2 ppm and a singlet corresponding to the pyrazolo NH at 13.0 ppm. In addition, a signal corresponding to the 8-CO carbon was not observed in ^{13}C nmr spectrum of **11**. The mass spectrum of compound **9** showed a molecular ion peak M^+ at m/z 390 and the base peak ($^1/_2$ M^+) at m/z at 195, which is a strong evidence for the disulfide structure of **9**.

Condensation of **3a,b** with hydroxylamine hydrochloride in refluxing 2-propanol in the presence of triethylamine afforded the corresponding oxime derivatives (**12a,b**) which were reacted with benzoyl chloride in anhydrous pyridine at 0 ˚C to give the corresponding benzoyloxyimino derivatives (**13a,b**) through protection of the hydroxyl group (*cf.* Scheme 3). A singlet corresponding to the OH protons at 10.8 and 11.7 ppm, respectively, was observed in the ^{1}H nmr spectra of compounds **12a,b**. The ^{13}C nmr spectrum of compound **12b** showed that the 8-CO carbon is no longer present. The ^{1}H nmr spectra of compounds **13a,b** showes that the OH groups are no longer present, and the singlets at 13.0 and 13.6 ppm show that the NH groups are present, which confirmed that protection occurred on the OH groups not the NH groups.

EXPERIMENTAL

Melting points were measured in open capillary tubes and are uncorrected. The nmr spectra were recorded on a Bruker 250 FT nmr spectrometer, with tetramethylsilane as internal standard. Mass spectra were recorded using electron ionization (EI) on a varian Mat 311A spectrometer. The ir spectra were recorded on a Perkin-Elmer 1720 spectrometer. The microanalysis were measured at the microanalysis unit, Faculty of Science, Tanta University.

General Procedure for the Preparation of 3,7-Dimethyl-6H-pyrazolo[5,1-*c*][1,2,4]triazin-4-one (**3a-e**).

Method A

To a solution of active methylene diketones (2,4-pentandione, 1-phenylbutane-1,3-dione, 3-oxobutyramide, 3-oxo-*N*-phenylbutyramide and/or *N*-(4-chlorophenyl)-3-oxobut-yramide) (**2a-e**) (0.0064 mol) in ethanol (50 ml.), *N*-bromosuccinimide (1.36 g., 0.0076 mol) and benzoyl peroxide (0.05 g.) were added and the reaction mixture was stirred for 30 minutes at room temperature. Compound **1** (1 g., 0.0064 mol) was then added and the reaction mixture was refluxed for 2 hours until the starting material was consumed (tlc). On cooling, the solid that formed was ioslated by filtration, dried and recrystallized from methanol to give **3a-e**.

8-Acetyl-3,7-dimethyl-6*H*-pyrazolo[5,1-*c*][1,2,4]triazin-4-one (**3a**).

Compound 3a was obtained in 90% yield, mp 300-02 ˚C; ^{1}H nmr (DMSO-d_6): δ 2.3 (s, 3H, 7-CH_3), 2.4 (s, 3H, 3-CH_3), 2.6 (s, 3H, $COCH_3$), 13.2 (s, 1H, NH); ^{13}C nmr (DMSO-d_6): δ 15.2 (CH_3 of C-7), 16.3 (CH_3 of C-3), 29.5 (CH_3CO), 103.6 (C-8), 141.5 (C-7), 145.1 (C-3), 148.5 (C-4), 153.5 (C-9), 191.4 ($COCH_3$); ir (potassium bromide): 3412, 1713, 1644, 1594 cm^{-1}; hrms Calcd. for $C_9H_{10}N_4O_2$: 206.0800. Found: 206.0450.

8-Benzoyl-3,7-dimethyl-6*H*-pyrazolo[5,1-*c*][1,2,4]triazin-4-one (**3b**).

Compound **3b** was obtained in 56% yield, mp 240-42 °C; ^{1}H nmr (DMSO-d_6): δ 2.0 (s, 3H, 7-CH_3), 2.2 (s, 3H, 3-CH_3), 7.2-7.6 (m. 5H, Ar), 13.3 (s, 1H, NH); ^{13}C nmr (DMSO-d_6): δ 15.3 (CH_3 of C-7), 16.7 (CH_3 of C-3), 102.9 (C-8), 128.4, 128.9 132.3, 139.6 (C_{arom}), 141.7 (C-7), 145.9 (C-3), 148.9 (C-4), 153.8 (C-9), 189.5 (*C*OPh); ir (potassium bromide): 3439, 1712, 1619, 1551 cm^{-1}; hrms Calcd. for $C_{14}H_{12}N_4O_2$: 268.0960. Found: 268.0620.

3,7-Dimethyl-4-oxo-4,6-dihydropyrazolo[5,1-*c*][1,2,4]triazine-8-carboxamide (**3c**).

Compound **3c** was obtained in 46% yield, mp >350 °C; ^{1}H nmr (DMSO-d_6): δ 2.2 (s, 3H, 7-CH_3), 2.5 (s, 3H, 3-CH_3), 7.2 (s, 2H, NH_2), 13.3 (s, 1H, NH); ^{13}C nmr (DMSO-d_6): δ 14.3 (CH_3 of C-7), 16.1 (CH_3 of C-3), 97.9 (C-8), 139.8 (C-7), 145.6 (C-3), 149.7 (C-4), 153.0 (C-9), 164.7 (*C*O of C-8); ir (potassium bromide): 3443, 3340, 3246, 1701, 1654, 1599 cm^{-1}; hrms Calcd. for $C_8H_9N_5O_2$: 206.0756. Found: 206.0588.

N-Phenyl3,7-dimethyl-4-oxo-4,6-dihydropyrazolo[5,1-*c*]-[1,2,4]triazine-8-carboamide (**3d**).

Compound **3d** was obtained in 35% yield, mp 295-97 °C; ^{1}H nmr (DMSO-d_6): δ 2.3 (s, 3H, 7-CH_3), 2.6 (s, 3H, 3-CH_3), 7.1-7.7 (m, 5H, Ar), 9.56 (s, 1H, NHCO) 13.7 (s, NH); ^{13}C nmr (DMSO-d_6): δ 14.3 (CH_3 of C-7), 16.5 (CH_3 of C-3), 97.8 (C-8), 120.5, 123.8, 128.8, 139.1 (C_{arom}), 139.2 (C-7), 144.2 (C-3), 149.1 (C-4), 153.0 (C-9), 160.7 (CONH) ppm.; ir (potassium bromide): 3417, 3268, 1717, 1635, 1597 cm^{-1}.

Anal. Calcd. for $C_{14}H_{13}N_5O_2$: C, 59.36; H, 4.63; N, 24.72. Found: C, 59.13; H, 4.52; N, 24.34.

N-(4-chloro-phenyl)-3,7-dimethyl-4-oxo-4,6-dihydropyrazolo[5,1-*c*][1,2,4]triazine-8-carboxamide (**3e**).

Compound **3e** was obtained in 32% yield, mp >350 °C; ^{1}H nmr (DMSO-d_6): δ 2.4 (s, 3H, 7-CH_3), 2.6 (s, 3H, 3-CH_3), 7.4-7.7 (m, 5H, Ar), 9.7 (s, 1H, NHCO); ^{13}C nmr (DMSO-d_6): δ

14.8 (CH_3 of C-7), 17.10 (CH_3 of C-3), 98.4 (C-8), 122.6, 127.9, 129.3, 138.8 (C_{arom}), 139.8 (C-7), 144.9 (C-3), 149.7 (C-4), 153.8 (C-9), 161.4 (CONH); ir (potassium bromide): 3420, 3325, 1706, 1650, 1609 cm^{-1}.

Anal. Calcd. for $C_{14}H_{12}ClN_5O_2$: C, 52.92; H, 3.81; N, 22.04. Found: C, 52.51; H, 3.75; N, 21.95.

Method B.

To a solution of **1** (3.16 g., 0.02 mol) in ethanol (80 ml), 3-chloro-2,4-pentandione (2.4 ml, 0.02 mol) was added in one portion and refluxed for $1^1/_2$ hour at which time the starting material was consumed (tlc). On cooling, the solid that separated out was isolated by filtration, dried and recrystallized from methanol to give 8-acetyl-3,7-dimethyl-6*H*-pyrazolo[5,1-*c*]-[1,2,4]triazin-4-one (**3a**); yield 3.9 g. (95%); mp 300-02 °C. Melting point depression was not observed in a mixed melting point experiment with an authentic sample of **3a**.

Methyl and/or ethyl 3,7-dimethyl-4-oxo-4,6-dihydropyrazolo[5,1-I][1,2,4]triazine-8-carboxylate (**3f,g**).

To a solution of (**1a**) (3.16 g., 0.02 mol) in ethanol (70 ml), methyl and/or ethyl 2-chloroacetoacetate (**5f,g**) (0.02 mol) was added in one portion and refluxed for $11/_2$ hour at which time the starting material was consumed (tlc). On cooling, the solid that separated out was filtered off and recrystallized from methanol to give **3f,g**.

Methyl 3,7-Dimethyl-4-oxo-4,6-dihydro-pyrazolo[5,1-*c*]-[1,2,4]triazine-8-carboxylate (**3f**).

Compound **3f** was obtained in 76% yield, mp 250-52 °C; ^{1}H nmr (DMSO-d_6): δ 2.3 (s, 3H, 7-CH_3), 2.4 (s, 3H, 3-CH_3), 3.8 (s, 3H, OCH_3), 13.4 (s, 1H, NH); ^{13}C nmr (DMSO-d_6): δ 13.8 (CH_3 of C-7), 16.3 (CH_3 of C-3), 51.0 (OCH_3), 92.5 (C-8), 140.5 (C-7), 144.9 (C-3), 148.6 (C-4), 154.8 (C-9), 161.9 (*C*OO of C-8); ir (potassium bromide): 3288, 1719, 1681, 1621 cm^{-1}.

Anal. Calcd. for $C_9H_{10}N_4O_3$: C, 48.65; H, 4.54; N, 25.21. Found: C, 48.32; H, 4.47; N, 25.11.

Ethyl 3,7-Dimethyl-4-oxo-4,6-dihydro-pyrazolo[5,1-*c*][1,2,4]-triazine-8-carboxyate (**3g**).

Compound **3g** was obtained in 71% yield, mp 200-02 °C; ^{1}H nmr (DMSO-d_6): δ 1.3 (t, 3H, CH_3CH_2), 2.3 (s, 3H, CH_3), 2.4 (s, 3H, CH_3),4.3 (9, 2H, OCH_2CH_3),13.4 (s,1H, NH); ^{13}C nmr (DMSO-d_6): δ 14.0 (CH_3-CH_2), 14.4 (CH_3 of C-7), 16.3 (CH_3 of C-3), 60.6 (OCH_2), 93.6 (C-8), 141.4 (C-3), 145.9 (C-4), 155.6 (C-9), 162.5 (COO of C-8); ir (potassium bromide): 3252, 1712, 1673, 1624 cm^{-1}; hrms Calcd. for $C_{10}H_{12}N_4O_3$: 236.0909. Found: 236.0325.

Hydrazinium 8-Acyl-3,7-dimethyl-6*H*-pyrazolo[5,1-*c*][1,2,4]-triazin-on-6-ides (**7a,b**).

Compounds **3a,b** (0.01mol) and hydrazine hydrate 80% (0.45 ml., 0.015 mol) in 2-propanol (50 ml) were stirred at room temperature for 6 hours at which time the starting material has been consumed (tlc). The solid product that formed was separated out and recrystallized from ethanol to give **7a,b**.

Hydrazinium 8-Acetyl-3,7-dimethyl-6*H*-pyrazolo[5,1-*c*]-[1,2,4]triazin-4-on-6-ide (**7a**).

Comound **7a** was obtained in 85% yield, mp 150-152 °C, ^{1}H nmr (DMSO-d_6): δ 2.4 (s, 3H, 7-CH_3), 2.5 (s, 3H, 3-CH_3), 2.6 (s, 3H, $COCH_3$), 6.9 (br s, 5H, hydrazinum-H's); ^{13}C nmr (DMSO-d_6): δ 16.4 (CH_3 of C-7), 17.5 (CH_3 of C-3), 30.8 (CH_3CO), 104.6 (C-8), 139.5 (C-7), 149.8 (C-3), 153.1 (C-4), 155.7 (*C*-9), 191.6 (*C*O of C-8); ir (potassium bromide): 3332, 3247, 1711, 1631, 1541, 1461 cm^{-1}.

Anal. Calcd. for $C_9H_{14}N_6O_2$: C, 45.37; H,5.92; N, 35.27 . Found: C, 45.12; H, 5.83; N, 35.11.

Hydrazinium 8-Benzoyl-3,7-dimethyl-6*H*-pyrazolo[5,1-*c*]-[1,2,4]triazin-4-on-6-ide (**7b**).

Compound **7b** was obtained in 93% yield, mp 110-112°C, ir (potassium bromide): 3425, 3247, 1699, 1612, 1513, 1425 cm^{-1}.

Anal. Calcd. for $C_{14}H_{16}N_6O_2$: C, 55.99; H, 5.37; N, 27.98. Found: C, 55.38; H, 5.21; N, 27.71.

N,N'-Bis[(3,7-dimethyl-4-oxo-4,6-dihydropyrazolo[5,1-*c*]-[1,2,4]triazin-8-yl)-alkylidene]-hydrazine (**8a,b**).

Method A.

Compound **7a,b** (0.005 mol) and glacial acetic acid (0.5 ml) were refluxed in 2-propanol for 2 hours until the starting material was consumed (tlc). The solid product that formed was separated out and recrystallized from dimethylformamid/water (DMF/H_2O) to give (**8a,b**).

Method B.

Compound **3a,b** (0.01 mol), and hydrazine hydrate 80% (0.25 ml, 0.0052 mol) in 2-propanol (50 ml) in the presence of acetic acid (1 ml) were refluxed for $2^1/_2$ hours until the starting material was consumed (tlc). The solid product that formed was separated out and recrystallized from DMF/H_2O to give **8a,b**.

N,N'-Bis[(3,7-dimethyl-4-oxo-4,6-dihydropyrazolo[5,1-*c*]-[1,2,4]triazin-8-yl)-ethylidene]hydrazine (**8a**).

Compund **8a** was obtained in 38% yield (method A), 56% (method B), mp >300 °C, ^{1}H nmr (DMSO-d_6): δ 2.1 (s, 3H, 7-CH_3), 2.3 (s, 3H, 3-CH_3), 2.5 (s, 3H, hydrazono-CH_3) ppm; ir (potassium bromide): 3278, 1703, 1602, 1546 cm^{-1}.

Anal. Calcd. for $C_{18}H_{20}N_{10}O_2$: C, 52.93; H, 4.94; N, 34.29. Found: C, 52.73; H, 4.81; N, 34.13.

N,N'-Bis[(3,7-dimethyl-4-oxo-4,6-dihydropyrazolo[5,1-*c*]-[1,2,4]triazin-8-yl)-benzylidene]hydrazine (**8b**).

Compound **8b** was obtained in 36% yield (method A), 52% (method B); mp >300 °C, ^{1}H nmr (DMSO-d_6): δ 2.1 (s, 3H, 7-CH_3), 2.4 (s, 3H, 3-CH_3), 7.2-7.7 (m, 5H, Ar), 8.98 (br s, 1H, NH); ^{13}C nmr (DMSO-d_6): δ 14.1 (CH_3 of C-7), 17.0 (CH_3 of C-3), 92.2 (C-8), 125.8, 127.8, 129.1, 133.9 (Ar), 137.5 (C-7), 139.3 (C-3), 142.6 (C=N of C-8) 150.5 (C-4), 154.1 (C-9) ppm; ir (potassium bromide): 3426, 1694, 1624, 1546 cm^{-1}.

Anal. Calcd. for $C_{28}H_{24}N_{10}O_2$: C, 63.15; H, 4.54; N, 26.30. Found: C, 62.89; H, 4.38; N, 26.21.

Bis(3,7-dimethyl-4-oxo-4,6-dihydropyrazolo[5,1-*c*][1,2,4]-triazin-8-yl)-disulfide (**9**).

Compound **3b** (1.34 g., 0.005 mol) contaminated with elemental sulfur (as a crude material) and phenyl hydrazine (0.55 ml, 0.005 mol) in 2-propanol (25 ml) were refluxed for 2 hours until the starting material was consumed (tlc). The solid product that formed was filtered off and recrystallized from methanol to give 1.1 g of **9**. Yield 56%, mp >300 °C; ^{1}H nmr (DMSO-d_6): δ 2.1 (s, 3H, 7-CH_3), 2.3 (s, 3H, 3-CH_3), 13.8

(s, 1H, NH); ^{13}C nmr (DMSO-d_6): δ 11.5 (*C*H_3 of C-7), 16.1 (*C*H_3 of C-3), 90.3 (C-8), 138.9 (C-7), 145.6 (C-3), 148.8 (C-4), 156.9 (C-9); ir (potassium bromide): 3431, 1685, 1599 cm^{-1}.

Anal. Calcd. for $C_{14}H_{14}N_8O_2S_2$: C, 43.07; H, 3.61; N, 28.70. Found: C, 42.88; H, 3.51; N, 28.56.

For more confirmation of the above reaction, the pure compound **3b** (1.34 g, 0.005 mol), elemental sulfur (0.32 g, 0.01 mol), and phenylhydrazine (0.55 ml, 0.005 mol) in 2-propanol (25 ml) were refluxed for 2 hours until the starting material was consumed (tlc). The solid product that formed was filtered off and recrystallized from methanol to give 1.5 g of **9** (Yield 77%, mp >300 °C).

3,7-Dimethyl-8-[1-(methylhydrazono)-alkyl and/or aryl]-6*H*-pyrazolo[5,1-*c*] [1,2,4]triazin-4-ones (**11a-d**).

Compound **3a,b** (0.01mol) and methyl (and/or phenyl) hydrazine (**11a,b**) (0.01 mol) in 2-propanol (50 ml) in the presence of acetic acid (1 ml) were ref luxed for 1 hour until the starting material was consumed (tlc). The solid product that formed was separated out and recrystallized from DMF/H_2O to give **11a-d**.

3,7-Dimethyl-8-[1-(methylhydrazono)-ethyl]-6*H*-pyrazolo-[5,1-*c*][1,2,4]triazin-4-one (**11a**).

Compound **11a** was obtained in 65% yield, mp >300 °C; ir (potassium bromide): 3402, 3232, 1702, 1583, 1540 cm^{-1}; hrms Calcd. for $C_{10}H_{14}N_6O$: 234.1229. Found: 234.1955.

3,7-Dimethyl-8-[1-(phenylhydrazono)-ethyl]-6*H*-pyrazolo-[5,1-*c*][1,2,4]triazin-4-one (**11b**).

Compound **11b** was obtained in 72% yield, mp 280-282 °C, ^{1}H nmr (DMSO-d_6): δ 2.3 (s, 3H, 7-CH_3), 2.4 (s, 3H, 3-CH_3), 2.5 (s, 3H, CH_3), 6.7-7.3 (m. 5H, Ar), 9.17 (s, 1H, hydrazono-NH), 13.0 (s, 1H, pyrazolo-NH); ^{13}C nmr (DMSO-d_6): δ 14.7 (*C*H_3 of C-7), 16.0 (*C*H_3 of C-3), 16.1 (hydrazono-*C*H_3), 101.5 (C-8), 113.9, 119.9, 130.1, 137.4, (C_{arom}), 138.4 (C-7), 141.9 (C=N-NH), 147.9 (C-3), 150.4 (C-4), 153.4 (C-9); ir (potassium bromide): 3437, 3318, 1682, 1599, 1502 cm^{-1}; hrms Calcd. for $C_{15}H_{16}N_5O$: 296.1385. Found: 296.2814.

3,7-Dimethyl-8-[1-(methylhydrazono)-1-phenyl-methyl]-6*H*-pyrazolo[5,1-*c*][1,2,4]triazin-4-one (**11c**).

Compound **11c** was obtained in 74% yield, mp >300 °C, ^{1}H nmr (DMSO-d_6): δ 2.1 (s, 3H, 7-CH_3), 2.4 (s, 3H, 3-CH_3), 3.0 (s, 3H, hydrazono-CH_3) 7.3-7.5 (m. 5H, Ar), 10.0 (br s, 1H, NH); ^{13}C nmr (DMSO-d_6): δ 14.1 (*C*H_3 of C-7), 16.9 (*C*H_3 of C-3), 38.2 (s, 3H, CH_3-NH), 92.8 (C-8), 125.7, 127.7, 129.1,131.2 (C_{arom}), 137.5 (C-7), 139.0 (C=N-NH), 142.7 (C-3), 150.5 (C-4), 154.1 (*C*-9) ppm; ir (potassium bromide): 3431, 3244, 1694, 1620 cm^{-1}.

Anal. Calcd. for $C_{15}H_{16}N_6O$: C, 60.80; H, 5.44; N, 28.36. Found: C, 60.54; H, 5.31; N, 28.06.

3,7-Dimethyl-8-[1-phenyl-1-(phenylhydrazono)methyl]-6*H*-pyrazolo[5,1-*c*][1,2,4]triazin-4-one (**11d**).

Compound **11d** was obtained in 67% yield, mp 260-262°C, ^{1}H nmr (DMSO-d_6): δ 2.1 (s, 3H, 7-CH_3), 2.4 (s, 3H, 3-CH_3), 6.8-7.6 (m. 10 H, Ar), 9.4 (s, 1H, hydrazono-NH), 13.5 (br s, 1H, pyrazolo-NH); (DMSO-d_6): δ 11.6 (*C*H_3 of C-7), 16.2 (*C*H_3 of C-3), 90.3 (C-8), 138.9 (C-7), 145.6 (C-3), 148.8 (C-4), 156.9 (C-9); ir (potassium bromide): 3248, 3140, 1693, 1609, 1549 cm^{-1}.

Anal. Calcd. for $C_{20}H_{18}N_6O$: C, 67.03; H, 5.06; N, 23.45. Found: C, 66.96; H, 5.02; N, 23.23.

8-(1-Hydroxyiminoalkyl)-3,7-dimethyl-6*H*-pyrazolo[5,1-*c*]-[1,2,4]triazin-4-ones (**12a,b**).

Compound **3a,b** (0.01 mol) and hydroxylamine hydrochloride (0.94 g. 0015 mol) in 2-propanol (60 ml) in the presence of triethyl amine (0.2 ml) were heated gradually to 90 °C followed by refluxing for 3 hours until the starting material was consumed (tlc). The solid product that formed was separated out and recrystallized from methanol.

8-(1-Hydroxyiminoethyl)-3,7-dimethyl-6*H*-pyrazolo[5,1-*c*]-[1,2,4]triazin-4-one (**12a**).

Compound **12a** was obtained in 94% yield, mp 225-227 °C, ^{1}H nmr (DMSO-d_6): δ 2.0 (s, 3H, 7-CH_3), 2.2 (s, 3H, C*H*$_3$-C=NOH), 2.3 (s, 3H, 3-CH_3), 10.9 (s, 1H, OH) ppm; ir (potassium bromide): 3227, 3042, 1691, 1631, 1600 cm^{-1}.

Anal. Calcd. for $C_9H_{11}N_5O_2$: C, 48.87; H, 5.01; N, 31.66. Found: C, 48.76; H, 4.98; N, 31.25.

8-(1-Hydroxyimino-1-phenylmethyl)-3,7-dimethyl-6*H*-pyrazolo[5,1-*c*][1,2,4]triazin-4-one (**12b**).

Compound **12b** was obtained in 63% yield, mp 2258-260 °C, ^{1}H nmr (DMSO-d_6): δ 2.0 (s, 3H, CH_3), 2.3 (s, 3H, triazine-CH_3), 7.4-7.5 (m. 5H, Ar), 11.8 (s, 1H, OH); ^{13}C nmr (DMSO-d_6): δ 14.6 (*C*H_3 of C-7), 17.0 (*C*H_3 of C-3), 93.7 (C-8), 127.7, 129.4, 129.9, 136.5 (C_{arom}), 137.8 (C-7), 142.6 (Ph-C=NOH), 147.4 (C-3), 150.1 (C-4), 153.7 (C-9) ppm; ir (potassium romide): 3294, 3034, 1713, 1636, 1558 cm^{-1}.

Anal. Calcd. for $C_{14}H_{13}N_5O_2$: C, 59.36; H, 4.63; N, 24.72. Found: C, 59.11; H, 4.53; N, 24.33.

8-(1-Benzoyloxyiminoalkyl)-3,7-dimethyl-6*H*-pyrazolo[5,1-*c*]-[1,2,4]triazin-4-ones (**13a,b**).

A mixture of (**12a,b**) (0.005 mol) and benzoyl chloride (0.9 ml 0.0075 mol) was stirred in anhydrous pyridine (25 ml) at 0 °C for 6 hours until the starting material was consumed (tlc). The reaction mixture was poured on ice cold water. The solid product obtained was isolated by filtration, dried and stirred with carbon tetrachloride (20 ml) at 30 °C to remove the residual benzoic acid. The solid was again isolated by filtration and recrystallized from methanol to give **13a,b**.

8-(1-Benzoyloxyiminoethyl)-3,7-dimethyl-6*H*-pyrazolo[5,1-*c*]-[1,2,4]triazin-4-one (**13a**).

Compound **13a** was obtained in 72% yield, mp 176-178 °C, ^{1}H nmr (DMSO-d_6): δ 2.3 (s, 3H, 7-CH_3), 2.6 (s, 6H, 7-CH_3 and C*H*$_3$-C=N-OCOPh), 7.6-8.13 (m. 5H, Ar), 13.0 (s, 1H, NH); ir (potassium bromide): 3461, 1713, 1609, 1543, 1498 cm^{-1}.

Anal. Calcd. for $C_{16}H_{15}N_5O_3$: C, 59.07; H, 4.65; N, 21.53. Found: C, 59.01; H, 4.62; N, 21.45.

8-(1-Benzoyloxyimino-1-phenylmethyl)-3,7-dimethyl-6*H*-pyrazolo[5,1-*c*][1,2,4]triazin-4-one (**13b**).

Compound **13b** was obtained in 68% yield, mp 209-211°C, ^{1}H nmr (DMSO-d_6): δ 1.9 (s, 3H, 7-CH_3), 2.4 (s, 6H, 3-CH_3), 7.4-7.8 (m. 10H, Ar), 13.6 (s, 1H, NH); ir (potassium bromide): 3129, 1743, 1624, 1590, 1533 cm^{-1}. Ms, peak matching for $C_{10}H_{12}N_4O_3$: Calcd., 387.1331. Found, 387.2130.

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