1,3,4-Thiadiazole, 1,3,4-Thiadiazine, 1,3,6-Thiadiazepane and Quinoxaline Derivatives from Symmetrical Hydrazine-1,2-dicarbothioamide as well as N, N''-Ethane-1,2-diylbis(thiourea) Derivatives

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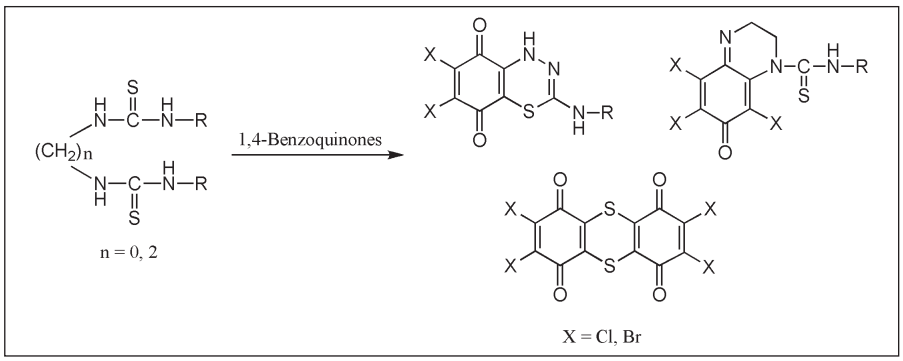
Dedicated to Professor Dietrich Döpp on the occasion of his 65th birthday



Reactions of N,N'-disubstituted hydrazine-1,2-carbothioamides **8a-c** and substituted N,N''-ethane-1,2-diylbis(thioureas) **9a-c** with 2,3,5,6-tetrachloro-1,4-benzoquinone (chloranil, **10a**) and 2,3,5,6-tetrabromo-1,4-benzoquinone (bromanil, **10b**) to form N,N'-disubstituted 1,3,4-thiadiazole-2,5-diamines **11a-c**, substituted 3-amino-6,7-dichloro-2,3-dihydro-1*H*-4,2,1-benzothiadiazine-5,8-diones **12a-c**, 2,3,7,8-tetrahalothianthrene-1,4,6,9-tetrones **13a,b**, substituted 5,6,8-trihalo-7-oxo-3,7-dihydroquinoxaline-2*H*-carbothioamides **14a-c**, **15a-c** and 7-substituted imino-1,3,6-thiadiazepane-2-thiones **16a-c** are reported.

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Introduction.

Addition of nitrogen nucleophiles to benzo-, and naphthoquinones represents a common synthetic route to many dyestuffs and medicinals [1-13]. The reactions of 2,3-dichloro-1,4-naphthoquinone (**1**) with thioacetamide or with thiourea to give 2-methyl- and 2-amino-2,3-dihydronaphtho[2,3-*d*]thiazole-4,9-diones **3** and **4**, as well as the synthesis of bisthiazole **7** from **1** and dithiooxamide were first reported by Hammam *et al.* [14]. They claimed that also the intermediate, 2-thioamido-3-chloro-1,4-naphthoquinones **5** and **6** were isolated from the reaction medium and could be separately transformed to thiazoles by boiling in aqueous ethanol containing sodium bicarbonate. Later, this work was repeated by Katritzky *et al.* [15,16] and, in agreement with the earlier work, they found that **1** reacted with a variety of thioamides in dimethylformamide or in dimethylsulfoxide in the presence of triethylamine yielding the corresponding thiazoles **3** and **4**, and with dithiooxamides to form the bisthiazole **7**.

Matsuoka and co-workers [17-19] subsequently claimed that the previous work was in error and the reactions of **1** with thioacetamide, thiourea and dithiooxamide all gave the same product, namely dibenzo[*b*,*i*]thianthrene-5,7,12,14-tetrone (**2**) but not the thiazoles **3**, **4** and **7**.

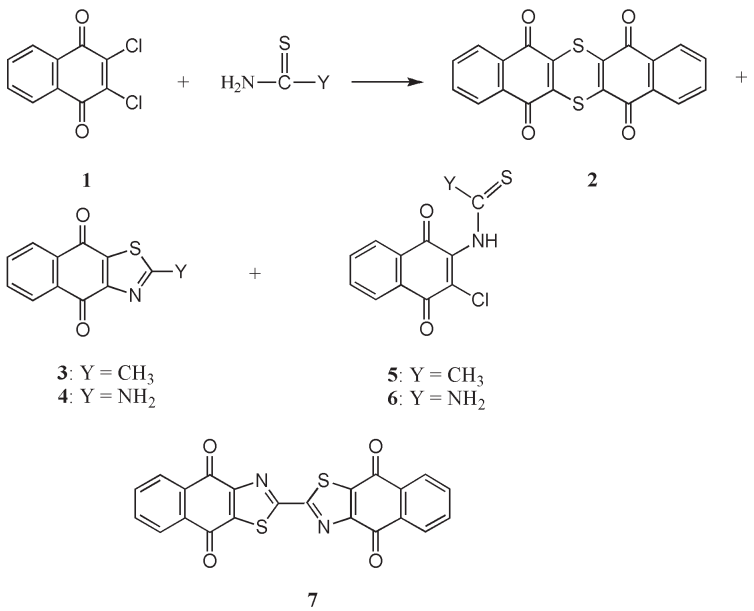
In view of these discrepancies, Katritzky and co-workers subsequently reexamined some of those reactions [20]. Although the product isolated by Matsuoka *et al.* was indeed formed, in all cases the 1,4-dithiine was accompanied by the corresponding 1,3-thiazole, although in some cases product separation was difficult.

Several authors have investigated under various conditions the heterocyclization of compounds having an extended urea-like chain such as 1,4- and 2,4-disubstituted thiosemicarbazides [21-23], 1-substituted-3-thiosemicarbazides [24], 1-acylbithiourea [25], 1,6-disubstituted-2,5-dithiobiureas [26], 1-aryl/alkyl-2-thiobiureas [27] and thiocarbohydrazides [28]. We report herein the results of our recent investigations on the reactions of symmetrical hydrazine-1,2-dicarbothioamide as well as *N,N''*-ethane-1,2-diylbis(thiourea) derivatives with both chloranil (**10a**) and bromanil (**10b**).

Results and Discussion.

On adding tetrahydrofuran (THF) solutions of **8a-c** (2 equivalents) to solutions of **10a,b** in the same solvent, the appearance of a green colour, which gradually changed to blue was observed. When the reaction was monitored spectrophotometrically (at 10 °C), an absorption maximum was observed in the visible region at 536-508 nm that was assigned to the formation of an unstable charge-trans-

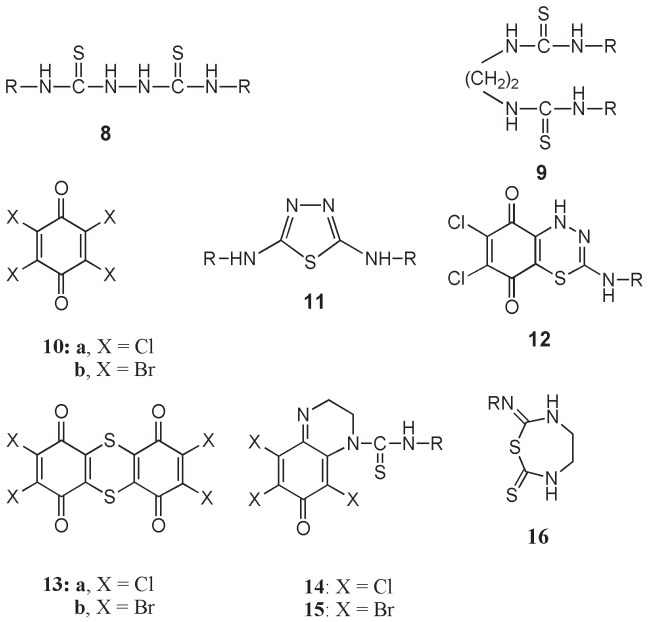
Scheme 1



fer complex (CTC), since neither the thiourea derivatives **8a-c** nor **10a,b** absorb alone in this region. After standing for 48 hours at room temperature, 2,3,7,8-tetrahalothianthrene-1,4,6,9-tetrones **13a,b** were precipitated as the major products (41-44 %). From the filtrate the substituted 3-amino-6,7-dichloro-2,3-dihydro-1*H*-4,1,2-benzothiadiazine-5,8-diones **12a-c** (22-28 %), together with 2,5-disubstituted 1,3,4-thiadiazoles-2,5-diamines **11a-c** (12-15 %) were isolated by preparative thin layer chromatography from the reaction of **8a-c** with **10a**. On the other hand, the filtrate from the reaction between **8a-c** and **10b** contains compound **11a-c** (21-26%).

As an example, the structural assignment of **12a** was supported by the following spectral data. In its ^{13}C-nmr spectrum, the characteristic resonance signal of the carbonyl carbon atoms of chloranil (**10a**) appeared at δ = 170.2, 171.4 ppm [29]. The ^{1}H-nmr spectrum of **12a** showed two broad signals at 8.68 and 7.80 ppm, due to the NH attached to the phenyl ring and the thiadiazine-NH, respectively, in addition to the phenyl protons. The ir spectrum of **12a** (KBr disk) showed sharp bands at 3330, 3270 and 1680 cm^{-1} for the secondary amino and carbonyl groups respectively. The thianthrenetetrones **13a,b** exhibited absorptions at 1700-1695 cm^{-1} for the quinone carbonyl groups. The ^{13}C-nmr spectra of **13a,b** showed absorption signals around 171.4 – 170.9 ppm for the chloranil or bromanil carbonyl carbon atoms. The formation of **13a,b** was further confirmed by mass spectrometry. Besides the molecular ions at 416/412 or 594/590, the characteristic fragment ion patterns of the substituted tetrahalo compounds were observed [30].

Chart 1



8, **9**, **11-12**, **14-16**: **a**, R = Ph; **b**, R = PhCH$_2$; **c**, R = allyl

It has been reported that ethylenediamine on reaction with allylisothiocyanate furnishes a linear thiourea, which in turn is cyclized to a bisthiazoline [31]. The present work was also undertaken to examine the reactions of **9a-c** with **10a,b**. Thus, two equivalents of substituted N,N''-ethane-1,2-diylbis(thioureas) **9a-c** reacted with **10a,b** in boiling tetrahydrofurane to afford substituted imino-1,3,6-thiadiazepane-2-thiones **16a-c** as minor (14-19 %) and N-substi-

tuted trihalo-7-oxo-3,7-dihydroquinoxaline-2*H*-carbothioamides **14a-c/15a-c** as major products (41-49 %), in addition to the corresponding dihydrobenzoquinone derivatives. The structures of **14a-c** and **15a-c** were confirmed on the basis of elemental analyses, mass spectra, ^{1}H- and ^{13}C-nmr data. The ir spectra of **14a-c/15a-c** showed characteristic absorption bands for the secondary-NH between 3330 and 3310 cm^{-1} and between 1690-1680 cm^{-1} for the C=O groups. The ^{1}H-nmr spectrum of **14a** shows the resonances of the methylene protons at C3 and C2 in the δ = 3.46 - 3.60 and 3.64 - 3.87 ppm range, respectively. The presence of methylene groups is also evident from the ^{13}C-DEPT-nmr spectrum, which exhibits negative signals at δ= 48.8 and 55.3 ppm. In addition, the ^{1}H-nmr spectrum exhibited a broad singlet centered at 9.69 ppm due to the NH-attached to phenyl and C=S groups. The decoupled carbon spectrum of **14a** showed signals at δ = 170.2 and 180.3 ppm, assigned to C=O and C=S, respectively [30,32].

EXPERIMENTAL

Equipment: all the melting points were determined in open glass capillaries on a Gallenkamp melting point apparatus and are uncorrected. The ir spectra were recorded with a Shimadzu 408 or Bruker Vector 22 FT-IR spectrophotometers using potassium bromide pellets. A Bruker WM 300 spectrometer was used to determine ^{1}H- (300.13 MHz) and ^{13}C- (75.47 MHz) nmr spectra. Assignment of carbon the resonances have been supported by DEPT experiments. Mass spectra were obtained with a Varian MAT 311 doubly focusing instrument using electron impact ionization (70 eV). Elemental analyses were determined at the Microanalytical Center, Cairo University, Egypt. uv/vis spectra were recorded on a Perkin-Elmer Lambda 2-spectrophotometer equipped with a thermostated cell. Preparative thin layer chromatography (plc) was carried out on 1 mm thick layers of silica gel slurry (Merck Pf_{254}) applied on 48 cm wide x 20 cm high glass plates using the solvents mentioned below. Zones were detected by quenching of fluorescence upon exposure to 254 nm light and the compounds were extracted from the plates with acetone.

Materials: Chloranil (2,3,5,6-Tetrachlorobenzo-1,4-quinone, **10a**) and bromanil (2,3,5,6-tetrabromobenzo-1,4-quinone, **10b**) were used as received from Aldrich. *N*,*N*'-disubstituted hydrazine-1,2-carbothioamides **8a-c** and substituted *N*',*N*'''-ethane-1,2-diylbis[*N*-substituted(thioureas)] **9a-c** were prepared according to the literature procedures [31,33-37].

Reactions of 8a-c with Chloranil (10a) and Bromanil (**10b**).

A solution of **8a-c** (2.0 mmol) in anhydrous THF (20 mL) was added dropwise with stirring to a solution of chloranil (**10a**) or bromanil (**10b)** (1.0 mmol) in the same solvent (20 mL). The colour of the reaction changed gradually from deep green to a blue colour. Stirring was continued for 48 hours with admission of air to complete the reaction. The reaction mixture was filtered and the blue precipitate was washed several times with cold THF and identified as the tetrahalothianthrenetetrones **13a,b**. The filtrate was concentrated *in vacuo* and the residue separated by plc using cyclohexane/ethyl acetate (2:1) mixture into three zones. The fastest moving zone contained the thiadiazoles **11a-c** (in case of reaction with **10a** and **10b),** the second zone, compounds **12a-c** (isolated from the reaction with **10a**) and the slowest migrating zone contained the dihydrobenzoquinones **10a**-H_2 or **10b**-H_2. The zones were extracted with acetone.

N,*N*'-Diphenyl-[1,3,4]thiadiazole-2,5-diamine (**11a**).

This compound had mp 239-241°, yield (80 mg, 15 % in case of **10a** and 139 mg, 26 % in case of **10b**), colourless crystals from DMF (lit. [38] 240-243 °C).

N,*N*'-Dibenzyl-[1,3,4]thiadiazole-2,5-diamine (**11b**).

This compound had mp 250-252°, yield (71 mg, 12 % in case of **10a** and 124 mg, 21 % in case of **10b**), colourless crystals from methanol (lit. [34] 251 °C).

N,*N*'-Diallyl-[1,3,4]thiadiazole-2,5-diamine (**11c**).

This compound had mp 133-135°, yield (55 mg, 14 % in case of **10a** and 90 mg, 23 % in case of **10b**), colourless crystals from ethanol (lit. [36,37] 135 °C).

6,7-Dichloro-3-(phenylamino)-1*H*-benzo[*e*][1,3,4]thiadiazine-5,8-dione (**12a**).

This compound had mp 277-279°, orange crystals from acetonitrile, yield 190 mg (28 %); ir: 3330, 3270 (NH), 1680 (C=O), 1620 (C=N), 1590 (Ar-C=C) cm^{-1}; ^{1}H nmr: δ 7.11-7.32 (m, 5H, Ph), 7.80 (br, s, 1H, thiadiazine-NH), 8.68 (br, s, 1H, NHPh); ^{13}C nmr: δ 125.1, 128.6, 129.3 (Ph-CH), 142.4 (q-C), 127.0 (C-4a), 139.2, 141.2 (C-6,7), 152.2 (C-3), 155.6 (C-8a), 170.2, 171.4 (C-5,8); EI-MS m/z: % 341/339 (M$^+$, 9), 303 (8), 267 (14), 132 (52), 104 (31), 91 (100), 77 (76), 65 (44).

Anal. Calcd. for $C_{13}H_7Cl_2N_3O_2S$: C, 45.90; H, 2.07; Cl, 20.84; N, 12.35; S, 9.43. Found: C, 46.06; H, 1.93; Cl, 20.69; N, 12.48; S, 9.56.

3-(Benzylamino)-6,7-dichloro-1*H*-benzo[*e*][1,3,4]thiadiazine-5,8-dione (**12b**).

This compound had mp 291-293°, orange crystals from methanol, yield 177 mg (25 %); ir: 3340, 3255 (NH), 1675 (C=O), 1630 (C=N), 1585 (Ar-C=C) cm^{-1}; ^{1}H nmr: δ 4.64 (br, s, 2H, CH_2Ph), 7.06-7.24 (m, 5H, Ph), 7.70 (br, s, 1H, thiadiazine-NH), 8.43 (br, s, 1H, NHCH$_2$Ph); ^{13}C nmr: δ 47.9 (CH_2Ph), 126.6, 127.2, 128.4(Ph-CH), 141.4 (q-C), 127.2 (C-4a), 139.4, 141.1 (C-6,7), 151.8 (C-3), 155.4 (C-8a), 170.0, 170.8 (C-5,8); EI-MS m/z: % 355/353 (M$^+$, 11), 317 (5), 281 (8), 104 (27), 91 (83), 71 (100).

Anal. Calcd. for $C_{14}H_9Cl_2N_3O_2S$: C, 47.47; H, 2.56; Cl, 20.02; N, 11.86; S, 9.05. Found C, 47.31; H, 2.73; Cl, 19.88; N, 11.98; S, 8.93.

3-(Allylamino)-6,7-dichloro-1*H*-benzo[*e*][1,3,4]thiadiazine-5,8-dione (**12c**).

This compound had mp 189-199°, pale orange crystals from methanol, yield 134 mg (22 %); ir: 3340, 3260 (NH), 2960, 2840 (Ali-CH), 1685 (C=O), 1610 (C=N) cm^{-1}; ^{1}H nmr: δ 4.22 (m, 2H, allyl-CH_2N), 5.14-5.17 (m, 2H, allyl-CH_2=), 5.92-6.04 (m, 1H, allyl-CH=), 7.54 (br, s, 1H, allyl-NH), 7.86 (br, s, 1H, thiadiazine-NH); ^{13}C nmr: δ 43.7 (allyl-CH_2N), 115.1 (allyl-CH_2=), 134.9 (allyl-CH=), 127.2 (C-4a), 139.2, 141.1 (C-6,7), 151.4 (C-3), 154.8 (C-8a), 170.8, 171.5 (C-5,8); EI-MS m/z: % 305/303 (M$^+$, 21), 267 (14), 231 (9), 203 (11), 99 (100), 41 (61).

Anal. Calcd. for $C_{10}H_7Cl_2N_3O_2S$: C, 39.49; H, 2.32; Cl, 23.31; N, 13.82; S, 10.54. Found C, 39.35; H, 2.24; Cl, 23.51; N, 14.01; S, 10.34.

2,3,7,8-Tetrachlorothianthrene-1,4,6,9-tetrone (**13a**).

This compound had mp 342-344°, blue crystals from DMF, yield 170 mg (41 %); ir: 1695 (C=O) cm^{-1}; ^{13}C nmr : δ 143.5 (C-2,3,7,8), 149.3 (C-4a,5a,9a,10a), 171.4 (C-1,4,6,9); EI-MS m/z: % 416/412 (M^+, 100), 398 (39), 379 (12), 349 (16), 321 (19), 115 (55), 87 (91), 64 (36), 36 (69).

Anal. Calcd. for $C_{12}Cl_4O_4S_2$: C, 34.81; Cl, 34.25; S, 15.49. Found C, 34.66; Cl, 34.41; S, 15.63.

2,3,7,8-Tetrabromothianthrene-1,4,6,9-tetrone (**13b**).

This compound had mp >360°**,** blue crystals from DMF, yield 260 mg (44 %); ir: 1700 (C=O) cm^{-1}. ^{13}C nmr: δ 138.2 (C-2,3,7,8), 149.1 (C-4a,5a,9a,10a), 170.9 (C-1,4,6,9); EI-MS m/z: % 594/590 (M^+, 100), 512 (20), 496 (26), 416 (18), 260 (66), 188 (56), 142 (33), 116 (83), 60 (54).

Anal. Calcd. for $C_{12}Br_4O_4S_2$: C, 24.35; Br, 54.00; S, 10.84; Found C, 24.51; Br, 53.86; S, 11.02.

Reactions of **9a-c** with Chloranil (**10a**) and Bromanil (**10b**).

A solution of **9a-c** (2.0 mmol) in anhydrous THF (15 mL) was added dropwise with stirring to a solution of **10a**,**b** (1.0 mmol) in anhydrous THF (20 mL). The mixture was heated under reflux for 5 hours, during which it turned from yellow into reddish orange. The mixture was concentrated under vacuum and the residue separated by plc using cyclohexane/ethyl acetate (3:1) as developing solvent to give numerous coloured zones, three of which (with the highest intensity) were extracted and removed. The fastest migrating one, which quenched all indicator fluorescence upon exposure to 254 nm UV-light, contained the thiadiazepanes **16a-c**, the second zone (which was always characterized by an orange colour) contained the quinoxalines **14a-c** and **15a-c**, while the third zone contained the dihydrobenzoquinones **10a**-H_2 and **10b**-H_2.

5,6,8-Trichloro-7-oxo-*N*-phenyl-2,3-dihydroquinoxaline-1(7*H*)-carbothioamide (**14a**).

This compound had mp 254-256°, brown crystals from ethanol, yield 189 mg (49 %); ir: 3325 (NH), 2965 (Ali-CH), 1685 (C=O), 1590 (Ar-C=C) cm^{-1}; ^1H nmr: δ 3.46-3.60 (m, 2H, quinoxaline-3-H_2), 3.64-3.87 (m, 2H, quinoxaline-2-H_2), 7.08-7.37 (m, 5H, Ph), 9.69 (br, s, 1H, NHPh); ^{13}C nmr: δ 48.8, 55.3 (quinoxaline-C-3,2), 120.1 (C-8), 124.8, 125.3, 128.9 (Ph-CH), 139.4 (q-C), 138.5, 141.3 (C-5,6), 151.1 (C-4b), 158.4 (C-4a), 170.2 (C-7), 180.3 (C=S); EI-MS m/z: % 387/383 (M^+, 36), 349 (11), 277 (8), 221 (21), 205 (9), 135 (57), 91 (100), 77 (81), 65 (64).

Anal. Calcd. for $C_{15}H_{10}Cl_3N_3OS$: C, 46.59; H, 2.61; Cl, 27.51; N, 10.87; S, 8.29. Found C, 46.68; H, 2.53; Cl, 27.38; N, 11.03; S, 8.44.

N-Benzyl-5,6,8-trichloro-7-oxo-2,3-dihydroquinoxaline-1(7*H*)-carbothioamide (**14b**).

This compound had mp 269-271°, brown crystals from acetonitrile, yield 188 mg (47 %); ir: 3320 (NH), 2960, 2870 (Ali-CH), 1690 (C=O), 1600 (Ar-C=C) cm^{-1}; ^1H-nmr: δ 3.50-3.61 (m, 2H, quinoxaline-3-H_2), 3.70-3.85 (m, 2H, quinoxaline-2-H_2), 4.60 (br, s, 2H, CH_2Ph) 7.0-7.29 (m, 5H, Ph), 9.42 (br, s, 1H, $NHCH_2Ph$); ^{13}C nmr: δ 48.7, 55.2 (quinoxaline-C-3,2), 50.2 (CH_2Ph), 119.8 (C-8), 126.5, 127.1, 129.0 (Ph-CH), 140.1 (q-C), 138.4, 141.2 (C-5,6), 150.8 (C-4b), 158.8 (C-4a), 170.0 (C-7), 181.1 (C=S); EI-MS m/z: % 400/397 (M^+, 22), 363 (17), 263 (27), 235 (11), 149 (42), 91 (62), 77 (100), 65 (83).

Anal. Calcd. for $C_{16}H_{12}Cl_3N_3OS$: C, 47.96; H, 3.02; Cl, 26.54; N, 10.49; S, 8.00. Found C, 48.12; H, 2.96; Cl, 26.39; N, 10.66; S, 7.86.

N-Allyl-5,6,8-trichloro-7-oxo-2,3-dihydroquinoxaline-1(7*H*)-carbothioamide (**14c**).

This compound had mp 167-169°, pale brown crystals from ethanol, yield 154 mg (44 %); ir: 3330 (NH), 2970, 2890 (Ali-CH), 1685 (C=O) cm^{-1}; ^1H nmr: δ 3.48-3.57 (m, 2H, quinoxaline-3-H_2), 3.68-3.86 (m, 2H, quinoxaline-2-H_2), 4.22 (m, 2H, allyl-CH_2N), 5.17-5.20 (m, 2H, allyl-CH_2=), 5.84-5.92 (m, 1H, allyl-CH=), 7.54 (br, s, 1H, allyl-NH); ^{13}C nmr: δ 43.6 (allyl-CH_2N), 48.6, 55.1 (quinoxaline-C-3,2), 115.0 (allyl-CH_2=), 119.9 (C-8), 134.8 (allyl-CH=), 138.6, 141.1 (C-5,6), 151.1 (C-4b), 158.6 (C-4a), 170.1 (C-7), 180.7 (C=S); EI-MS m/z: % 351/347 (M^+, 32), 313 (18), 277 (6), 241 (11), 185 (24), 99 (76), 41 (100), 36 (54).

Anal. Calcd. for $C_{12}H_{10}Cl_3N_3OS$: C, 41.10; H, 2.87; Cl, 30.33; N, 11.98; S, 9.14. Found C, 41.26; H, 2.69; Cl, 30.13; N, 12.11; S, 9.26.

5,6,8-Tribromo-7-oxo-*N*-phenyl-2,3-dihydroquinoxaline-1(7*H*)-carbothioamide (**15a**).

This compound had mp 273-275°, reddish-brown crystals from ethanol, yield 239 mg (46 %); ir: 3310 (NH), 2960 (Ali-CH), 1680 (C=O), 1600 (Ar-C=C) cm^{-1}; ^1H nmr: δ 3.44-3.61 (m, 2H, quinoxaline-3-H_2), 3.66-3.85 (m, 2H, quinoxaline-2-H_2), 7.10-7.35 (m, 5H, Ph), 9.65 (br, s, 1H, NHPh); ^{13}C nmr: δ 48.8, 55.1 (quinoxaline-C-3,2), 103.3 (C-8), 124.3, 125.2, 128.8 (Ph-CH), 139.4 (q-C), 127.7, 130.2 (C-5,6), 150.7 (C-4b), 158.4 (C-4a), 170.1 (C-7), 180.4 (C=S); EI-MS m/z: % 519/515 (M^+, 18), 489 (12), 461 (14), 437 (21), 357 (18), 277 (12), 142 (38), 91 (67), 77 (83), 65 (100).

Anal. Calcd. For $C_{15}H_{10}Br_3N_3OS$: C, 34.64; H, 1.94; Br, 46.10; N, 8.08; S, 6.17. Found C, 34.51; H, 2.12; Br, 45.93; N, 7.96; S, 6.29.

N-Benzyl-5,6,8-tribromo-7-oxo-2,3-dihydroquinoxaline-1(7*H*)-carbothioamide (**15b**).

This compound had mp 282-284°, reddish-brown crystals from acetonitrile, yield 219 mg (41 %); ir: 3330 (NH), 2965, 2840 (Ali-CH), 1690 (C=O), 1590 (Ar-C=C) cm^{-1}; ^1H nmr: δ 3.53-3.64 (m, 2H, quinoxaline-3-H_2), 3.68-3.83 (m, 2H, quinoxaline-2-H_2), 4.64 (br, s, 2H, CH_2Ph), 6.98-7.28 (m, 5H, Ph), 9.45 (br, s, 1H, $NHCH_2Ph$); EI-MS m/z: % 533/529 (M^+, 18), 503 (11), 474 (6), 451 (27), 371 (18), 291 (16), 142 (36), 91 (100), 77 (67), 65 (43).

Anal. Calcd. for $C_{16}H_{12}Br_3N_3OS$: C, 35.98; H, 2.26; Br, 44.88; N, 7.87; S, 6.00. Found C, 36.14; H, 2.18; Br, 45.08; N, 7.96; S, 5.87.

N-Allyl-5,6,8-tribromo-7-oxo-2,3-dihydroquinoxaline-1(7*H*)-carbothioamide (**15c**).

This compound had mp 185-187°, reddish brown crystals from ethanol, yield 208 mg (43 %); ir: 3310 (NH), 2970, 2890 (Ali-CH), 1685 (C=O) cm^{-1}; ^1H nmr: δ 3.46-3.58 (m, 2H, quinoxaline-3-H_2), 3.62-3.78 (m, 2H, quinoxaline-2-H_2), 4.18 (m, 2H, allyl-CH_2N), 5.18-5.22 (m, 2H, allyl-CH_2=), 5.92-6.03 (m, 1H, allyl-CH=), 7.58 (br, s, 1H, allyl-NH); EI-MS m/z: % 483/479 (M^+, 21), 401 (16), 321 (11), 241 (6), 213 (17), 185 (32), 86 (53), 41 (100).

Anal. Calcd. for $C_{12}H_{10}Br_3N_3OS$: C, 29.78; H, 2.08; Br, 49.53; N, 8.68; S, 6.63. Found C, 29.64; H, 1.96; Br, 49.68; N, 8.52; S, 6.47.

7-(Phenylimino)-1,3,6-thiadiazepane-2-thione (**16a**).

This compound had mp 233-237°, yield (45 mg, 19 %), colourless crystals from methanol (lit. [37] 235-237 °C).

7-(Benzylimino)-1,3,6-thiadiazepane-2-thione (**16b**).

This compound had mp 130-132°, yield (40 mg, 16 %), colourless crystals from ethanol (lit. [37] 128-130 °C).

7-(Allylimino)-1,3,6-thiadiazepane-2-thione (**16c**).

This compound had mp 100-101°, yield (28 mg, 14 %), colourless crystals from ethanol (lit. [37] 98-100 °C).

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REFERENCES AND NOTES

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[1] S. Patai and Z. Rappoport "The Chemistry of Quinonoid Compounds"; Wiley Interscience Publ.: New York, (1988), Vol. **2**, part 1, pp. 552- 570.

[2] J. H. Billman, D. G.Thomas and D. K. Barnes, *J. Am. Chem. Soc.,* **68**, 2103 (1946).

[3] K. Kouno, C. Ogawa, Y. Shimoura, H. Yano and Y. Veda, *Chem. Pharm. Bull.,* **29**, 301 (1981).

[4] P. Ballesteros, R. M. Claramunt, C. Escolastico and M. D. Santa Maria, *J. Org. Chem.*, **57**, 1873 (1993).

[5] R. Foster, N. Kulevsky and D. S. Wanigasekera, *J. Chem. Soc. Perkin Trans. 1*, 1318 (1974).

[6] A. H. Khan and J. S. Driscoll, *J. Med. Chem.*, **19**, 313 (1976).

[7] F. Chan, A. H. Khan and J. S. Driscoll, *J. Med. Chem.*, **19**, 1302 (1976).

[8] A. A. Hassan, N. K. Mohamed, A. A. Aly and A. E. Mourad, *Pharmazie,* **52**, 282 (1997).

[9] A. A. Hassan, N. K. Mohamed, Y. A.Ibrahim and A. E. Mourad, *Liebigs Ann. Chem*., 695 (1993).

[10] Y. A. Ibrahim, A. A. Hassan, N. K. Mohamed and A. E. Mourad, *Arch. Pharm. (Weinheim)*, **325**, 389 (1992).

[11] A. A. Hassan, N. K. Mohamed, A. A. Aly and A. E. Mourad, *Bull. Soc. Chim. Belg.*, **105**, 159 (1996).

[12] A. A. Hassan, N. K. Mohamed, A. A. Aly and A. E. Mourad, *Pharmazie,* **52**, 23 (1997).

[13] A. A. Hassan, N. K. Mohamed, Y. A. Ibrahim, K. U. Sadek and A. E. Mourad, *Bull. Chem. Soc. Jpn*., **66**, 2612 (1993).

[14] A. S. Hammam and B. E. Bayoumy, *Collect. Czech. Chem. Commun*., **50**, 71 (1985).

[15] A. R. Katritzky and W. Q. Fan, *J. Heterocyclic Chem*., **25**, 901 (1988).

[16] A. R. Katritzky, W. Q. Fan, Q. I. Linand and S. Bayyuk, *J. Heterocyclic Chem.*, **26**, 885 (1989).

[17] M. Matsuoka, A. Iwamoto, N. Furukawa and T. Kitao, *J. Heterocyclic Chem*., **28**, 1445 (1991).

[18] M. Matsuoka, A. Iwamoto, N. Furukawa and T. Kitao, *J. Heterocyclic Chem.*, **29**, 439 (1992).

[19] M. Matsuoka and A. Iwamoto, *J. Heterocyclic Chem*., **30**, 173 (1993).

[20] A. R. Katritzky and W. Q. Fan, *J. Heterocyclic Chem.*, **30**, 1679 (1993).

[21] M. Dobosz, and A. Pachuta-Stec, *Acta Pol. Pharm*., **53**, 123 (1996).

[22] M. Dobosz, and A. Pachuta-Stec, *Acta Pol. Pharm*., **51**, 457 (1994).

[23] L. Korzycka, M. Glowka and J. Janicka, *Pol. J. Chem.*, **72**, 73 (1998).

[24] H. W. Altland and P. A. Graham, *J. Heterocyclic Chem.,* **15**, 377 (1978).

[25] T. Okawara, Y. Tateyama, T. Yamasaki and M. Furukawa, *J. Heterocyclic Chem.,* **25**, 1071 (1988).

[26] E. V. P. Tao, S. Rolski, *Org. Prep. Proced Int.,* **18**, 272 (1986).

[27] M. M. Suni, V. A. Nair and C. P. Joshua, *Tetrahedron*, **57**, 2003 (2001).

[28] E. P. Invidiata, G. Furno, I. Lampronti and D. Simoni, *J. Heterocyclic Chem.*, **34**, 1255 (1997).

[29] H. O. Kalinowski, S. Berger, S. Braun, *^{13}C-NMR Spectroscopy*; Georg Thieme Verlag: Stuttgart, **1984**.

[30] R. M. Silverstein, Spectrometric Identification of Organic Compounds; John Wiley and Sons, Inc.; New York, **1974**.

[31] L. T. Mizrakh, L. Yu.Polanskaya, A. N. Gvozdetskii, A. M. Vosil'ev, T. M. Ivanova and N. I. Lisina, *Khim-Farm Zn*., **21**, 322 (1987).

[32] J. Reiter and J. Barkôczy, *J. Heterocyclic Chem.*, **30**, 333 (1993).

[33] V. Kepe, F. Pozvàn, A. Golobič, S. Polanc and M. Koéevar, *J. Chem. Soc. Perkin Trans. 1,* 2813 (1998).

[34] E. Heinz and R. Berscheid, *Sofw J.*, **120**, 286 (1994); *Chem. Abstr*., **124**, 55859w (1996).

[35] A. I. Simiti, N. Cosma and I. Proinov, *Acad. Rep. Pop. Rom., Filiala Cluj, studii cercetavdri Chim*., **8**, 315 (1957).

[36] P. C. Guha, *J. Am. Chem. Soc.*, **45**, 1036 (1923).

[37] A. A. Hassan, A. E. Mourad, K. M. El-Shaieb, A. H. Abou-Zied and D. Döpp, *J. Heteroatom Chem.*, **14**, 535 (2003).

[38] W. Ried and R. Oxenius, *Chem. Ber.*, **106**, 484 (1973).