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Synthesis of 1,3,4-Thiadiazole, 1,3,4-Thiadiazine, 1,3,6-Thiadiazepane and Quinoxaline Derivatives from Symmetrical Dithiobiureas and Thioureidoethylthiourea Derivatives

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

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Abstract: Reactions of *N,N`*-disubstituted hydrazinecarbothioamides **8a-c** and substituted thioureidoethylthioureas **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**, 6,7-dichloro-3-substituted amino-1*H*-benzo[1,3,4]-thiadiazine-5,8-diones **12a-c**, 2,3,7,8-tetrahalothianthrene-1,4,6,9-tetraones **13a,b**, 5,6,8-trihalo-7-oxo-3,7-dihydro-2*H*-quinoxaline-1-carbothioic acid substituted amides **14a-c**, **15a-c** and 7-substituted imino-[1,3,6]thiadiazepane-3-thiones **16a-c** are reported. Rationales for the observed conversions are presented.

Keywords: Tetrahalo-1,4-benzoquinones; Cyclocondensation; Heterocyclic compounds.

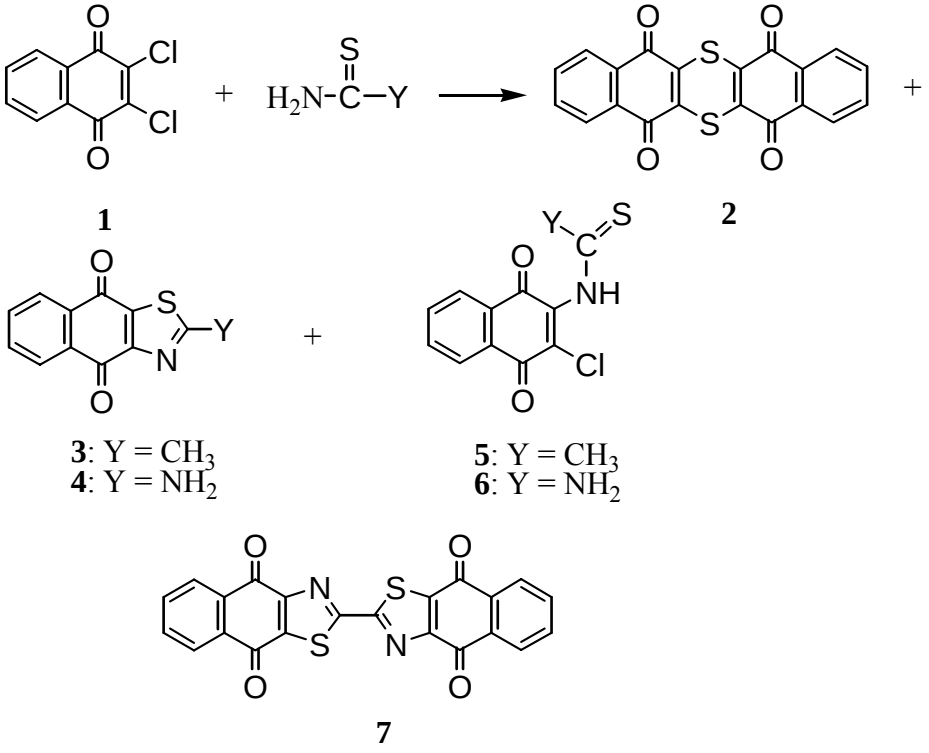
Introduction

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-aminonaphtho[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 also claimed that the intermediates, 2-thioamido-3-chloro-1,4-naphthoquinones **5** and **6** could be isolated from the reaction medium and separately transformed into 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 results, 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-tetraone (**2**) but not the thiazoles **3**, **4** and **7**.

Scheme 1



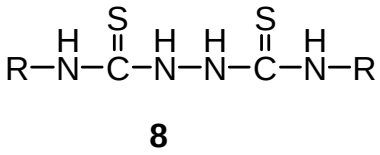
In view of these discrepancies, Katritzky and co-workers subsequently reexamined some of those reactions [20]. Although the product reported to have been isolated by Matsuoka *et al.* was indeed formed, in all cases the 1,4-dithiine was accompanied by the corresponding 1,3-thiazole, although in some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

Several authors have investigated the heterocyclization of 1,6-disubstituted dithiobiureas in basic or acidic media [21-28]. We report herein the results of our recent investigations on the reactions of symmetrical dithiobiureas as well as thioureidoethylthiourea derivatives with both chloranil (**10a**) and bromanil (**10b**).

Results and Discussion

On adding tetrahydrofuran (THF) solutions of **8a-c** to 2:1 solutions of **10a,b** in the same solvent, 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-transfer 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-tetraones **13a,b** were precipitated as the major products (41-44%). From the filtrate the substituted amino-6,7-dichloro-benzo[1,3,4]-thiadiazine-5,8-diones **12a-c** (22-28%), together with 2,5-disubstituted amino-1,3,4-thiadiazoles **11a-c** (12-15 % in case of **10a**, 21-26%) in case of **10b**), were isolated as minor products by preparative thin layer chromatography.



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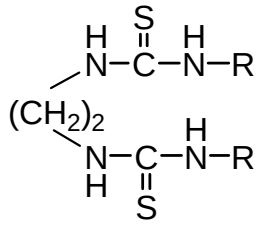

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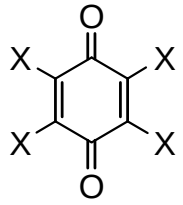
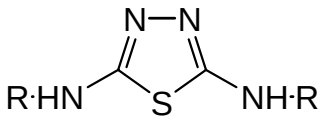


10: a, X = Cl
b, X = Br



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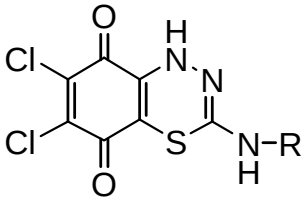

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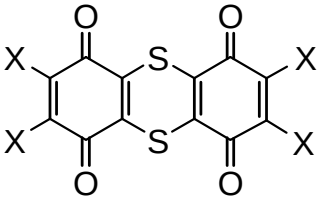
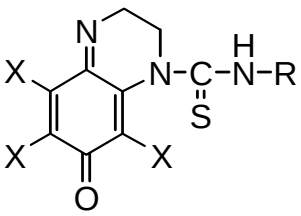
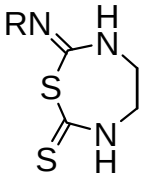


13: a, X = Cl
b, X = Br



14: X = Cl
15: X = Br



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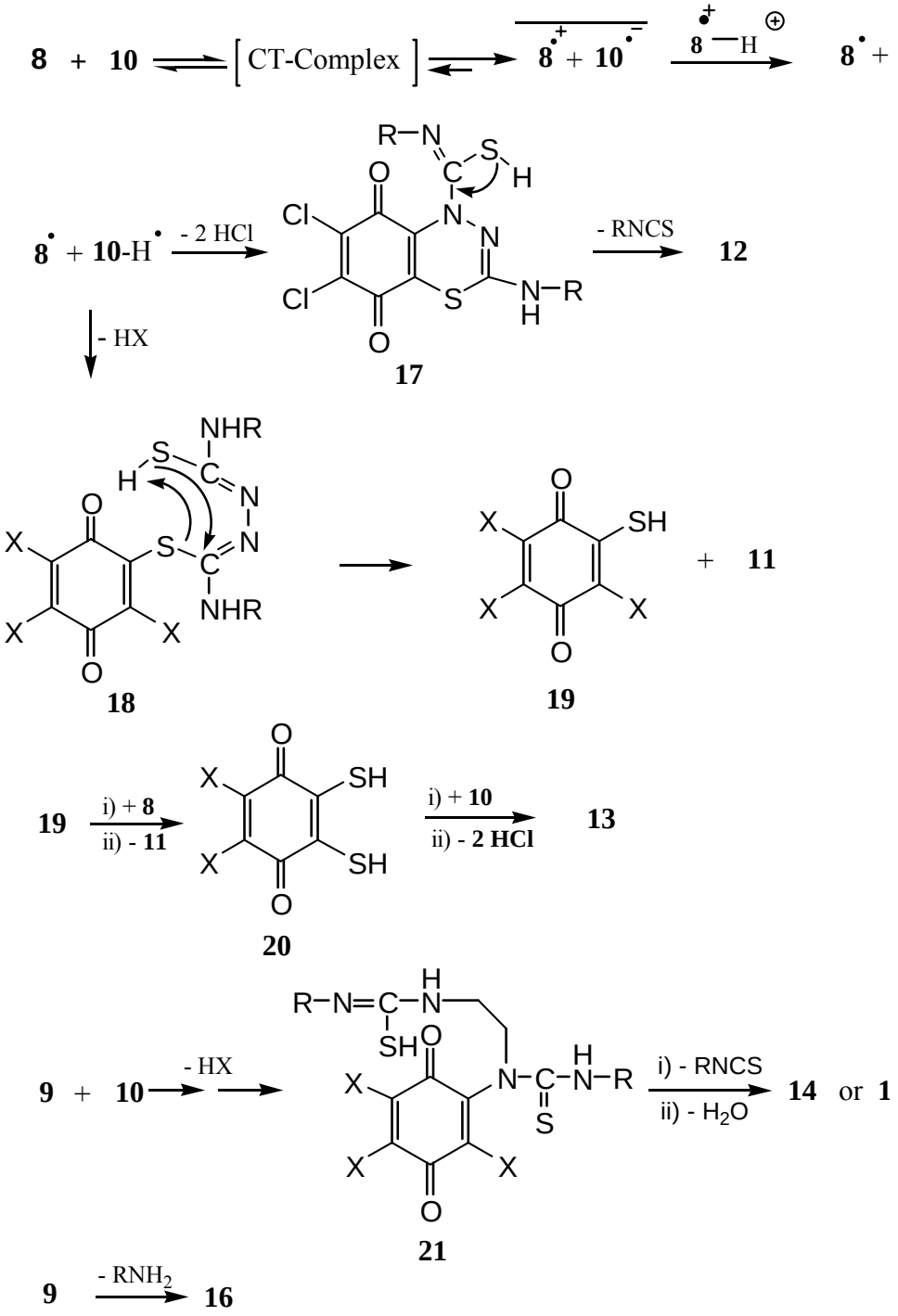
8, **9**, **11-12**, **14-16**: **a**, R = Ph; **b**, R = $PhCH_2$; **c**, R = allyl

As an example, the structural assignment of **12a** was supported by the following spectral data: in its ^{13}C-NMR spectrum, the characteristic absorption signal of the carbonyl carbon atoms of chloranil (**10a**) appeared at δ = 170.20, 171.36 ppm [29]. The ^{1}H-NMR spectrum of **12a** showed two broad signals at 7.68 and 8.80 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 thianthrenetetraones **13a,b** exhibited absorptions at 1700-1695 cm^{-1} for the quinine carbonyl groups. The ^{13}C-NMR spectra of **13a,b** showed absorption signals around 171.36 – 170.86 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].

Formation of these products may be rationalized by the mechanism shown in Scheme 2: an unstable CTC is formed followed by the formation of radicals **8**$^{\bullet}$ and **10-H**$^{\bullet}$. Two routes could be suggested for the formation of compounds **11-13** after the recombination of the two radicals **8**$^{\bullet}$ and **10-H**$^{\bullet}$. The first one is the elimination of two molecules of HCl to form the intermediate **17**, which splits off a molecule of substituted isothiocyanate to give the benzothiadiazine derivatives **12a-c**. The second route is the elimination of one molecule of HX to give the intermediate **18**. Nucleophilic attack by the 2-thiol group on the C=N and detachment of the HS-moiety affords the intermediate **19** along with thiadiazoles **11a-c**. The tetrahalothianthrenetetraones **13a,b** could be formed *via* the intermediates **19** and **20** (Scheme 2).

Scheme 2



It has been reported that ethylenediamine upon 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 thioureidoethylthiourea derivatives **9a-c** reacted with **10a,b** in THF at room temperature to afford substituted imino-[1,3,6]-thiadiazepane-2-thiones **16a-c** as minor (14-19%) and trihalo-7-oxo-quinoxaline-1-carbothioic acid substituted amides **14a-c**/**15a-c** as major products (41-49%), in addition to the corresponding dihydro-benzoquinone 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 = 48.77 and 55.33 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 = 170.17 and 180.34 ppm, assigned to C=O and C=S, respectively [30,32].

The formation of quinoxaline products **14** and **15** may be rationalized through the successive substitution of one chlorine atom and elimination of a molecule of substituted isothiocyanate followed by cyclization *via* a condensation reaction (Scheme 2).

Acknowledgements

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Experimental

General

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 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.

Starting materials

Chloranil (*2,3,5,6-Tetrachloro-1,4-benzoquinone*, **10a**) and bromanil (*2,3,5,6-tetrabromo-1,4-benzoquinone*, **10b**) were used as received from Aldrich. *N,N`*-disubstituted hydrazinecarbothioamides **8a-c** and substituted thioureidoethylthioureas **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 tetrahalothianthrenetetraones **13a,b**. The filtrate was concentrated in vacuum 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**, the second zone, compounds **12a-c** and the slowest migrating zone contained the dihdrobenzoquinones **14**-H_2 or **15**-H_2. The zones were extracted with acetone.

N,N`-Diphenyl-[1,3,4]thiadiazole-2,5-diamine (**11a**). Yield (80 mg, 15 % in case of **10a** and 139 mg, 26 % in case of **10b**), colourless crystals from DMF, m.p. 239-241 °C (lit. [38] 240-243 °C).

N,N`-Dibenzyl-[1,3,4]thiadiazole-2,5-diamine (**11b**). Yield (71 mg, 12 % in case of **10a** and 124 mg, 21 % in case of **10b**), colourless crystals from methanol, m. p. 250-252 °C (lit. [34] 251 °C).

N,N`-Diallyl-[1,3,4]thiadiazole-2,5-diamine (**11c**). Yield (55 mg, 14 % in case of **10a** and 90 mg, 23 % in case of **10b**), colourless crystals from ethanol, m.p. 133-135 °C (lit. [36,37] 135 °C).

3-Phenylamino-6,7-dichloro-1H-benzo[1,3,4]thiadiazine-5,8-dione (**12a**). Orange crystals from acetonitrile, m.p. 277-179 °C, Yield 190 mg (28 %); IR cm^{-1}: 3330, 3270 (NH), 1680 (C=O), 1620 (C=N), 1590 (Ar-C=C); ^{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): 125.11, 128.56, 129.32 (Ph-CH), 142.43 (q-C), 127.00 (C-4a), 139.16, 141.22 (C-6,7), 152.16 (C-3), 155.63 (C-8a), 170.20, 171.36 (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 $C_{13}H_7Cl_2N_3O_2S$ (340.19): 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-1H-benzo[1,3,4]thiadiazine-5,8-dione (**12b**). Orange crystals from methanol, m.p. 291-293 °C, Yield 177 mg (25 %); IR cm^{-1}: 3340, 3255 (NH), 1675 (C=O), 1630 (C=N), 1585 (Ar-C=C); ^{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_2Ph); ^{13}C-NMR (δ): 47.94 (CH_2Ph), 126.56, 127.18, 128.41(Ph-CH), 141.42 (q-C), 127.24 (C-4a), 139.36, 141.11 (C-6,7), 151.83 (C-3), 155.42 (C-8a), 169.96, 170.83 (C-5,8); EI-MS m/z (%): 355/353 (M^+, 11), 317 (5), 281 (8), 104 (27), 91 (83), 71

(100); Anal. Calcd. for $C_{14}H_9Cl_2N_3O_2S$ (354.22): 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-1H-benzo[1,3,4]thiadiazine-5,8-dione (**12c**). Pale orange crystals from methanol, m.p. 189-199 °C, Yield 134 mg (22 %); IR cm^{-1}: 3340, 3260 (NH), 2960, 2840 (Ali-CH), 1685 (C=O), 1610 (C=N); ^{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): 43.66 (allyl-CH_2N), 115.12 (allyl-CH_2=), 134.86 (allyl-CH=), 127.18 (C-4a), 139.22, 141.10 (C-6,7), 151.36 (C-3), 154.76 (C-8a), 170.76, 171.48 (C-5,8); EI-MS m/z (%): 305/303 (M^+, 21), 267 (14), 231 (9), 203 (11), 99 (100), 41 (61); Anal. Calcd. for $C_{10}H_7Cl_2N_3O_2S$ (304.16): 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-tetraone (**13a**). Blue crystals from DMF, m.p. 342-344 °C, Yield 170 mg (41 %); IR cm^{-1}: 1695 (C=O); ^{13}C-NMR (δ): 143.47 (C-2,3,7,8), 149.32 (C-4a,5a,9a,10a), 171.36 (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 $C_{12}Cl_4O_4S_2$ (414.07): 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-tetraone (**13b**). Blue crystals from DMF, m.p. >360 °C, Yield 260 mg (44 %); IR cm^{-1}: 1700 (C=O). ^{13}C-NMR (δ): 138.16 (C-2,3,7,8), 149.11 (C-4a,5a,9a,10a), 170.86 (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 $C_{12}Br_4O_4S_2$ (591.87): 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** (1.0 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 **14**-H_2 and **15**-H_2.

5,6,8-Trichloro-7-oxo-3,7-dihydro-2H-quinoxaline-1-carbothioic acid phenyl amide (**14a**). Brown crystals from ethanol, m.p. 254-256 °C, Yield 189 mg (49 %); IR cm^{-1}: 3325 (NH), 2965 (Ali-CH), 1685 (C=O), 1590 (Ar-C=C); ^{1}H-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): 48.77, 55.33 (quinoxaline-C-3,2), 120.11 (C-8), 124.83, 125.31, 128.86 (Ph-CH), 139.41 (q-C), 138.46, 141.33 (C-5,6), 151.12 (C-4b), 158.36 (C-4a), 170.17 (C-7), 180.34 (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

$C_{15}H_{10}Cl_3N_3OS$ (386.68): 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.

5,6,8-Trichloro-7-oxo-3,7-dihydro-2H-quinoxaline-1-carbothioic acid benzyl amide (**14b**). Brown crystals from acetonitrile, m.p. 269-271 °C, Yield 188 mg (47 %); IR cm^{-1}: 3320 (NH), 2960, 2870 (Ali-CH), 1690 (C=O), 1600 (Ar-C=C); ^{1}H-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): 48.68, 55.19 (quinoxaline-C-3,2), 50.24 (CH_2Ph), 119.82 (C-8), 126.52, 127.14, 128.95 (Ph-CH), 140.13 (q-C), 138.37, 141.20 (C-5,6), 150.76 (C-4b), 158.82 (C-4a), 169.93 (C-7), 181.12 (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 $C_{16}H_{12}Cl_3N_3OS$ (400.71): 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.

5,6,8-Trichloro-7-oxo-3,7-dihydro-2H-quinoxaline-1-carbothioic acid allyl amide (**14c**). Pale brown crystals from ethanol, m.p. 167-169 °C, Yield 154 mg (44 %); IR cm^{-1}: 3330 (NH), 2970, 2890 (Ali-CH), 1685 (C=O); ^{1}H-NMR ((δ): 3.48-3.57 (m, 2H, quinoxaline-3-H_2), 3.86-3.86 (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): 43.62 (allyl-CH_2N), 48.61, 55.12 (quinoxaline-C-3,2), 114.96 (allyl-CH_2=), 119.86 (C-8), 134.76 (allyl-CH=), 138.56 141.13 (C-5,6), 151.10 (C-4b), 158.63 (C-4a), 170.12 (C-7), 180.66 (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 $C_{12}H_{10}Cl_3N_3OS$ (350.65): 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-3,7-dihydro-2H-quinoxaline-1-carbothioic acid phenyl amide (**15a**). Reddish-brown crystals from ethanol, m.p. 273-275 °C, Yield 239 mg (46 %); IR cm^{-1}: 3310 (NH), 2960 (Ali-CH), 1680 (C=O), 1600 (Ar-C=C); ^{1}H-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): 48.76, 55.12 (quinoxaline-C-3,2), 103.34 (C-8), 124.34, 125.16, 128.83 (Ph-CH), 139.42 (q-C), 127.66, 130.18 (C-5,6), 150.66 (C-4b), 158.36 (C-4a), 170.10 (C-7), 180.36 (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 $C_{15}H_{10}Br_3N_3OS$ (520.04): 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.

5,6,8-Tribromo-7-oxo-3,7-dihydro-2H-quinoxaline-1-carbothioic acid benzyl amide (**15b**). Reddish-brown crystals from acetonitrile, m.p. 282-284 °C, Yield 219 mg (41 %); IR cm^{-1}: 3330 (NH), 2965, 2840 (Ali-CH), 1690 (C=O), 1590 (Ar-C=C); ^{1}H-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 $C_{16}H_{12}Br_3N_3OS$ (534.06): 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.

5,6,8-Tribromo-7-oxo-3,7-dihydro-2H-quinoxaline-1-carbothioic acid allyl amide (**15c**). Reddish brown crystals from ethanol, m.p. 185-187 °C, Yield 208 mg (43 %); IR cm^{-1}: 3310 (NH), 2970, 2890

(Ali-CH), 1685 (C=O); ^{1}H-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 $C_{12}H_{10}Br_3N_3OS$ (484.01); 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-3-thione (**16a**). Yield (45 mg, 19 %), colourless crystals from methanol, m.p. 233-235 °C (lit. [37] 235-237 °C).

7-Benzylimino-[1,3,6]thiadiazepane-3-thione (**16b**). Yield (40 mg, 16 %), colourless crystals from ethanol, m.p. 130-132 °C (lit. [37] 128-130 °C).

7-Allylimino-[1,3,6]thiadiazepane-3-thione (**16c**). Yield (28 mg, 14 %), colourless crystals from ethanol, m.p. 100-101 °C (lit. [37] 98-100 °C).

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Sample availability: Samples of compounds **2, 11, 13a** and **16** are available from MDPI.