Thermolysis of *N*,*N*''-1,ω-Alkanediyl-bis[N'-organylthiourea] Derivatives

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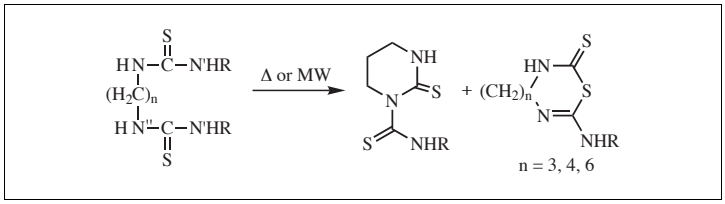

The course of microwave assisted or conventional thermal intramolecular heterocyclization of the title compounds has been found to be dependent on the length of the alkanediyl chain. While 1,3-propanediyl-bisthioureas **5a**-**c** gave both 2-thioxoperhydropyrimidine-1-carbothioamides **8a**-**c** and 8-amino-3,4,5,6-tetrahydro-1,3,7-thiadiazocine-2-thiones **10a**-**c**, thermolysis of 1,4-butanediyl-bisthioureas **6a**-**c** and 1,6-hexanediyl-bisthioureas **7a**-**c** under the same conditions gave solely 9-amino-4,5,6,7-tetrahydro-1,3,8-thiadiazonine-2-thiones **11a-c** and 11-amino-1-thia-3,10-diazacycloundec-10-ene-2-thiones **12a-c**, respectively. Symmetric *N*,*N*'-diorganylthioureas **4a**-**c** were formed in all cases as minor byproducts.

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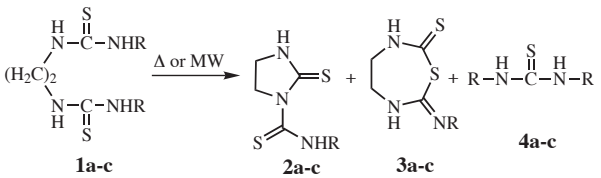
Introduction.

When either conventionally heated or activated in a microwave oven in absence of any solvents, the thioureidoethylthioureas **1a**-**c** underwent a cyclocondensation with loss of one molecule of amine yielding the 2-thioxoimidazoline-1-carbothioic amides **2a**-**c**, the 7-organylimino-1,3,7-thiadiazepane-2-thiones **3a**-**c** and the symmetric thioureas **4a**-**c** [1] (Scheme 1). This unique reactivity warrants a more detailed investigation. Therefore we undertook to prepare a series of three higher homologues of **1**, namely the substituted thioureidopropyl-, butyl- and hexylthioureas **5a**-**c**, **6a**-**c** and **7a**-**c**, respectively, and to investigate their thermolysis reactions under the abovementioned conditions.

Results and Discussion.

Compounds **5a** [2], **5b** [3], **6a** [4], **7a** [5] and **7c** [6] were known from the literature and were prepared according to published procedures, and samples **5c**, **6b,c** and **7b** were prepared analogously. When samples of neat powdered compounds **5**, **6**, and **7** were either heated to melt in an oil bath (method A) or subjected to irradiation in a microwave (MW) oven (method B, see Table 1 for details) a sticky residue was always obtained. Chromatographic separation gave numerous zones, and from the most intense of which the symmetric thioureas **4a**-**c** and the cyclisation products **8a**-**c** and **10a-c** (from **5a**-**c**) or **11a**-**c** (from **6a**-**c**) and **12a**-**c** (from **7a**-**c**) could be isolated (see Table 1 and Scheme 2).

Scheme 1

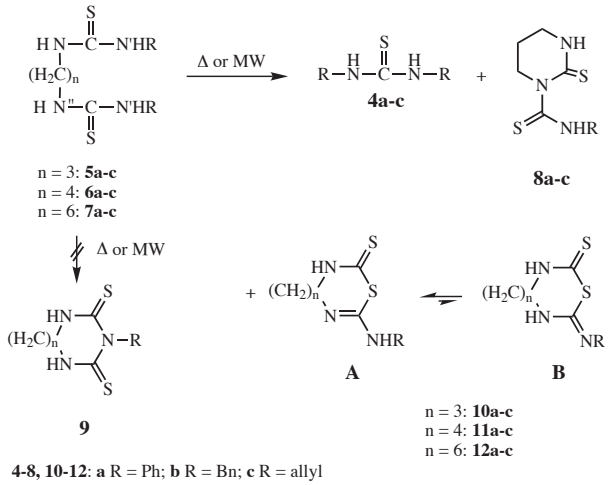


1-4	R
a	Ph
b	Bn
c	Allyl

While **4a**-**c** are known compounds, the structures of all new cyclic products were assigned on the basis of their ir- and nmr-spectral data. For all new compounds the gross compositions were derived from satisfactory elemental analyses, and the molecular masses were extracted in all cases from the EI-mass spectra, the common features of which will also be briefly discussed further below.

The salient features of the nmr-spectra (including ^{13}C DEPT 135/90 spectra) of products **8** and **10**-**12** are the following: Unlike in the published [4] ^{1}H and ^{13}C spectra of the starting materials **5a** and **6a** as well as of the newly prepared compounds **5c**, **6b**,**c** and **7b** there are no pairs of truly isochronous CH_2-groups, thus symmetric structures of type **9** are ruled out. Whereas compounds **8a**,**b** show two different thioxo carbon signals around 175.6 for the carbothioamide function and around 180.2 for the ring thione function, compounds **10a,b**, **11a**-**c** and **12a**-**c** show only one thioxocarbon signal between 182.1 and 184.6 ppm, but in addition a signal each from 151.2 to 151.9 ppm, a range close to the chemical shift (157.15) of the functional C atom of *N*-phenylisothiourea [7]. These

Scheme 2



signals are therefore assigned to carbon atoms 8 (in **10a-c**), 9 (in **11a-c**) and 11 (in **12a-c**), respectively. These data would also fit the tautomeric structures **B**, but structures **A** of **10**, **11**, and **12** are preferred, since endocyclic double bonds lead to relief of eclipsing strain in medium sized rings [8]. All cyclic products show two NH proton signals each. Whereas the range of chemical shifts for the ring N*H* is relatively narrow (7.46 to 7.54 for **8a-c**, 7.31 – 7.80 for **10-12**), the δ-values for the carbothioamide (in **8a-c**) or exocyclic N*H*R groups (in **10-12**) are dependent on the nature of R (around 9.5 for R = Ph, 7.8 for R = Bn and 7.4 – 7.5 for R = allyl).

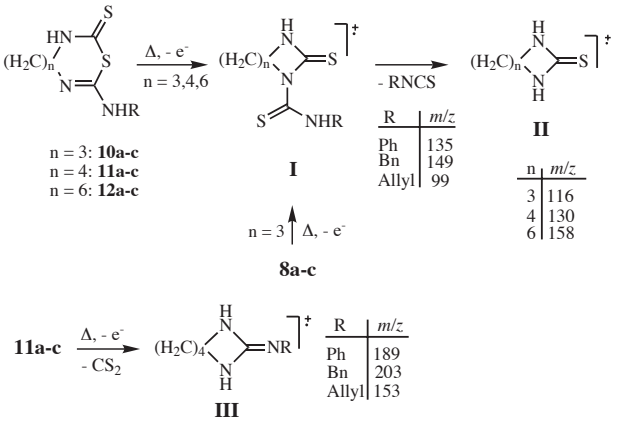
Table 1

Thermolysis of 1.5 g each of pulverized neat starting materials by conventional heating (A) and MW irradiation (B).

Starting materials (mmol)	Reaction conditions	Yields of products in mg (%)	Method **A**	Method **B**
5a	**A**: 145-147 °C.	**4a**	63 (7)	87 (9)
(4.36)	**B**: Full power, 6 min.	**8a**	103 (9)	154 (14)
		10a	620 (57)	685 (63)
5b	**A**: 123-124 °C.	**4b**	60 (6)	111 (11)
(4.03)	**B**: Full power, 6 min.	**8b**	122 (12)	184 (17)
		10b	560 (52)	602 (56)
5c	**A**: 146-148 °C.	**4c**	44 (5)	61 (7)
(5.51)	**B**: Full power, 6 min.	**8c**	140 (12)	196 (17)
		10c	540 (46)	604 (51)
6a	**A**: 184-186 °C.	**4a**	124 (13)	162 (17)
(4.19)	**B**: Full power, 8 min.	**11a**	618 (56)	754 (68)
6b	**A**: 184-186 °C.	**4b**	132 (13)	178 (18)
(3.88)	**B**: Full power, 8 min.	**11b**	548 (51)	652 (60)
6c	**A**: 80-82 °C.	**4c**	112 (14)	144 (18)
(5.24)	**B**: Power 70%, 4 min.	**11c**	618 (51)	732 (61)
7a	**A**: 158-159 °C.	**4a**	93 (11)	128 (14)
(3.88)	**B**: Full power, 7 min	**12a**	685 (60)	796 (70)
7b	**A**: 164-166 °C.	**4b**	78 (8)	111 (12)
(3.62)	**B**: Full power, 7 min.	**12b**	528 (47)	661 (59)
7c	**A**: 113-115 °C.	**4c**	92 (12)	126 (17)
(4.78)	**B**: Power 70%, 6 min.	**12c**	611 (41)	770 (52)

All products **8** and **10-12** are also characterized in their ir-spectra by sharp bands at 1541-1574 due to (NH-deformation and C-N stretching) and intense band in the range of 1348 – 1373 and 972-1030 cm^{-1} assigned to strongly coupled between C=S and C-N vibrations [9-11]. The EI-mass spectra need a brief comment (see Scheme 3). For **8a-c** m/z = 116 represents the 2-thioxoperhydropyrimidinyl fragment (**II**, n = 3) formed by release of the corresponding isothiocyanate from the molecular ion. Since fragment ions with the masses of these isothiocyanates are also found it is concluded that the positive charge may remain alternatively either with the ring or the isothiocyanate fragment. For **10**, **11** and **12** the same fragmentation process is observed, although a *N*-carbamoyl function as in **8** is definitely absent in products **10-12**. Since it has been demonstrated that compounds **3** could thermally be converted into the more stable isomers **2** [1] it seems most logical to assume that in the mass spectrometer compounds **10-12** are also transformed into their isomeric radical cations **I** prior to fragmentation yielding ions **II**. Since the nine-membered ring compounds **11a-c** are fragmented alternatively also by loss of mass 76 (which is assigned to represent carbon disulfide), another mode of ring contraction seems to be significant for these three products, namely loss of CS_2 to generate ions **III** (Scheme 3).

Scheme 3

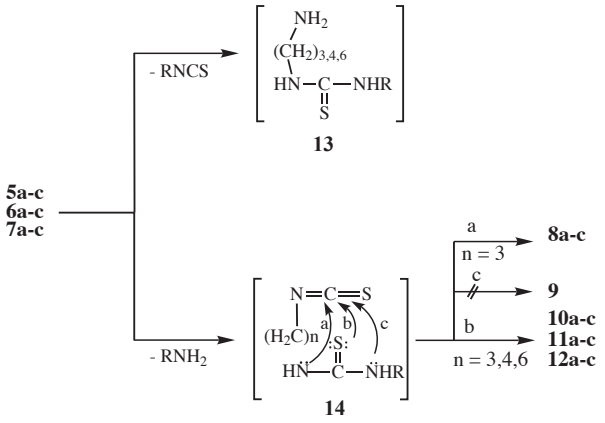


The formation of products **4**, **8** and **10-12**, respectively, from **5**, **6** and **7**, respectively, may be rationalized as follows (Schemes 4 and 5): Thioureas may thermally be fragmented to isothiocyanates and amines [12-14], and in some cases a plethora of additional fragmentation products has been reported [15,16]. Thus under both conditions employed in this study (A and B, see Table 1) bisthioureas **5-7** may release either the isothiocyanates

R-NCS to generate fragments **13** or one molecule of amine R-NH_2 to generate the thioureidoisothiocyanates **14**. Fragments **14** being more reactive than their precursors **5**-**7**, have three options for further reaction by intramolecular attack of nucleophilic centers on the isothiocyanate carbon atom: (i) attack of the thioureido N generating **8a**-**c** (path a, valid for n = 3), (ii) attack by the thione sulfur atom with formation of the medium ring compounds **10**-**12** (path b, valid for n = 3, 4, 6), and finally (iii) attack of the thioureido N' (path c). The latter option is not used since products **9** have not been found. Path a is also tantamount to direct displacement of N' of one thioureido group in **5**-**7** by the central N of the other, but the process involving intermediate **14** is preferred here due to the tendency of thioureas to form guanidines when reacted with amines [17-19]. It is not clear at present whether this type of reaction, here with **5**-**7** and the amine R-NH_2 liberated, may affect the yields of **8** and **10-12** by partially consuming the available starting material **5**, **6** or **7**.

Last, the symmetric thioureas **4a**-**c** may be formed from the isocyanates R-NCS liberated by either addition of R-NH_2 or by absorbing moisture to generate the thiocarbamic acid, which may react with a second molecule of isothiocyanate to a thiocarbamic anhydride which in turn

Scheme 4

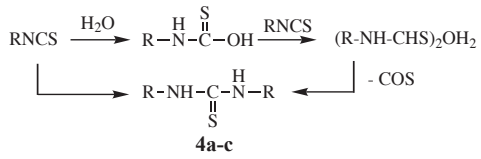


is degraded to COS and **4** analogous to the so-called "self-condensation" of isothiocyanates described earlier [20]. Amino group exchange reactions between thioureas and isothiocyanates [21] and between thioureas and primary amines [22], probably involving an isothiocyanate intermediate, have been reported in the early literature and in our previous paper [1].

Conclusion.

Thermolysis of the easily accessible neat title compounds allows the solvent-free preparation of fully or

Scheme 5



4a: R = Ph; **4b**: R = Bn; **4c**: R = Allyl

partly saturated normal or medium sized diaza- or diazathia-heterocycles owing to the typical and versatile reactivity of the isothiocyanato and thioureido groups. Yields may be moderately enhanced by microwave application instead of conventional thermal activation.

EXPERIMENTAL

The uncorrected melting points were determined with a Reichart thermover hot stage microscope. The ir spectra were recorded from KBr disks on Shimadzu 408 or Bruker Vector 22 FT-IR instruments. ^{1}H (300.13 MHz) and ^{13}C (75.47 MHz) nmr spectra (DMSO-d_6 as solvent, TMS as internal standard) were recorded on a Bruker WM300 instrument. Assignment of carbon resonances has been supported by DEPT experiments. The mass spectra were recorded on a double focusing AMD 604 spectrometer in the EI Mode at 70 eV ionization energy. Elemental analyses were determined at the Microanalytical Centre, Cairo University, Egypt and Carlo Erba Model 1106 Elemental Analyzer (Universität Duisburg- Essen). A Samsung MX 45 microwave oven was used at its full power 1400 W, 100 % and 70 % power level for the experiments recorded for this study. Preparative layer chromatography (PLC): Glass plates (48 cm x 20 cm) were coated with silica gel Merck PF_{254} (applied as an aqueous slurry and air-dried affording a 1mm layer). Zones were detected by indicator fluorescence quenching upon 254 nm illumination, removed from the plates and extracted with acetone or tetrahydrofuran.

General Procedure for Preparation of Starting Materials.

To a stirred solution of the diamine (1,3-diaminopropane, 1,4-diaminobutane or 1,6-diaminohexane) (10 mmol) in 30 ml of dimethylformamide, phenyl-, benzyl-, or allyl isothiocyanate (20 mmol) was added dropwise at room temperature. Stirring at room temperature was continued for 3 h, the mixture was set aside overnight and then added to ice/water. A colourless precipitate was formed which was recrystallized from a suitable solvent.

N,*N*''-1,3-Propanediylbis[*N*'-phenylthiourea] (**5a**).

This compound was obtained as colourless crystals (ethanol), mp 133-135° (Lit. [2] 135-137°), yield (92%); ir: NH 3310, 3195, (NH def. and C-N str.) 1555, (C=S, C-N) 1354, 955 cm^{-1}; ^{1}H nmr δ = 1.78 (m, 2H, CH_2), 3.12 (m, 4H, CH_2), 7.11-7.41 (m, 10H, phenyl H), 7.62 (br, 2H, NH), 9.42 ppm (br, 2H, N*H*Ph).

N,*N*''-1,3-Propanediylbis[*N*'-(phenylmethyl)thiourea] (**5b**).

This compound was obtained as colourless crystals (ethanol), mp 113-115° (Lit. [3] 113-114°), yield (84%); ir: NH 3324,

3216, (NH def. and C-N str.) 1563, (C=S, C-N) 1360, 972 cm^{-1}; ^1H nmr: δ = 1.75 (m, 2H, CH_2), 3.26 (m, 4H, CH_2), 4.65 (br, 2H, CH_2Ph), 7.20-7.46 (m, 10H, phenyl H), 7.55 (br, 2H, NH), 7.90 ppm (br, 2H, N*H*CH_2Ph).

N,*N*''-1,3-Propanediylbis[*N*'-(2-propenyl)thiourea] (**5c**).

This compound was obtained as colourless crystals (ethanol), mp 136-138°, yield (76%); ir: NH 3240, 3170, (NH def. and C-N str.) 1558, (C=S, C-N) 1361, 966 cm^{-1}; ^1H nmr: δ = 1.70 (m, 2H, CH_2), 3.08 (m, 4H, CH_2), 4.05 (br, 4H, allyl 1-H_2), 5.08-5.12 (m, 4H, allyl 3-H_2), 5.71-5.89 (m, 2H, allyl 2-H), 7.42 (br, 4H, NH) ppm; ms: m/z 272 (M^+, 18), 215 (21), 173 (11), 99 (91), 56 (100), 41 (53).

Anal. Calcd. for $C_{11}H_{20}N_4S_2$ (272.44): C, 48.50; H, 7.40; N, 20.57; S, 23.54. Found C, 48.34; H, 7.52; N, 20.66; S, 23.41 %.

N,*N*''-1,4-Butanediylbis[*N*'-phenylthiourea] (**6a**).

This compound was obtained as colourless crystals (ethanol), mp 173-175° (Lit. [4] 174-176°), yield (89%); ir: NH 3288, (NH def. and C-N str.) 3176, 1560, (C=S, C-N) 1358, 978 cm^{-1}; ^1H nmr: 1.52 (m, 4H, CH_2), 3.32-3.44 (m, 4H, CH_2), 7.24-7.47 (m, 10H, phenyl H), 7.60 (br, 2H, NH), 9.40 ppm (br, 2H, N*H*Ph).

N,*N*''-1,4-Butanediylbis[*N*'-(phenylmethyl)thiourea] (**6b**).

This compound was obtained as colourless crystals (dioxane), yield (81%), mp 174-176°, ir: NH 3358, 3212, (NH def. and C-N str.) 1558, (C=S, C-N) 1373, 963 cm^{-1}; ^1H nmr: 1.48 (m, 4H, CH_2), 3.36 -3.43 (m, 4H, CH_2), 4.64 (br, 4H, *C*H_2Ph), 7.23-7.35 (m, 10H, phenyl H), 7.49 (br, s, 2H, NH), 7.82 ppm (br, s, 2H, NH); ms: m/z 386 (M^+, 10), 279 (18), 237 (8), 149 (88), 106 (63), 91 (100), 65 (33), 41 (48).

Anal. Calcd. for $C_{20}H_{26}N_4S_2$ (386.58): C, 62.14; H, 6.78; N, 14.49; S, 16.59. Found C, 62.28; H, 6.62; N, 14.57; S, 16.44 %.

N,*N*''-1,4-Butanediylbis[*N*'-(2-propenyl)thiourea] (**6c**).

This compound was obtained as colourless crystals (ethanol), yield (77%), mp 70-72°; ir: NH 3237, (NH def. and C-N str.) 1567, 1361, (C=S, C-N) 993 cm^{-1}; ^1H nmr: 1.47 (m, 4H, CH_2), 3.39-3.46 (m, 4H, CH_2), 4.02 (br, 4H, allyl 1-H_2), 5.05-5.16 (m, 4H, allyl 3-H_2), 5.77-5.90 (m, 2H, allyl 2-H), 7.45 ppm (br, 4H, NH); ms: m/z: 286 (M^+, 12), 229 (9), 187 (13), 174 (11), 99 (79), 56 (90), 41 (100).

Anal. Calcd. for $C_{12}H_{22}N_4S_2$ (286.46): C, 50.31; H, 7.74; N, 19.56; S, 22.39. Found C, 50.48; H, 7.85; N, 19.39; S, 22.53 %.

N,*N*''-1,6-Hexanediylbis[*N*'-phenylthiourea] (**7a**).

This compound was obtained as colourless crystals (ethanol), mp 148-150° (Lit. [5] 148-149°), yield (94%); ir: NH 3344, 3222, NH def. and C-N str.) 1560, (C=S, C-N) 1366, 976cm^{-1}; ^1H nmr: 1.24 (m, 4H, CH_2), 1.46 (m, 4H, CH_2), 3.38-3.41 (m, 4H, CH_2), 7.16-7.42 (m, 10H, phenyl H), 7.62 (br, 2H, NH), 9.44 ppm (br, 2H, N*H*Ph).

N,*N*''-1,4-Hexanediylbis[*N*'-(phenylmethyl)thiourea] (**7b**).

This compound was obtained as colourless crystals (ethanol), yield (76%), mp 154-156°. Ir: NH 3328, 3221, (NH def. and C-N str.) 1568, (C=S, C-N) 1368, 996 cm^{-1}; ^1H nmr: 1.26 (m, 4H, CH_2), 1.47 (m, 4H, CH_2), 3.36-3.44 (m, 4H, CH_2), 4.65 (br, 4H, *C*H_2Ph), 7.21-7.41 (m, 10H, phenyl H), 7.49 (br, s, 2H, NH), 7.80 ppm (br, s, 2H, NH). ms: m/z 414 (M^+, 11), 307 (8), 265 (12), 200 (18), 149 (77), 91 (100), 77 (46).

Anal. Calcd. for $C_{22}H_{30}N_4S_2$ (414.63): C, 63.73; H, 7.29; N, 13.51; S, 15.47. Found C, 63.61; H, 7.42; N, 13.67; S, 15.31 %.

N,*N*''-1,4-Hexanediylbis[*N*'-(2-propenyl)thiourea] (**7c**).

This compound was obtained as colourless crystals (ethanol), mp 103-105° (Lit. [6] 100-102°), yield (78%); ir: NH 3288, (NH def. and C-N str.) 3194, 1567, (C=S, C-N) 1361,990 cm^{-1}; ^1H nmr: 1.32 (m, 4H, CH_2), 1.53 (m, 4H, CH_2), 3.32-3.40 (m, 4H, CH_2), 4.10 (br, 4H, allyl 1-H_2), 5.05-5.20 (m, 4H, allyl 3-H_2), 5.82-6.00 (m, 2H, allyl 2-H), 7.50 ppm (br, 4H, NH).

Heterocyclization of Neat **5a-c**, **6a-c** and **7a-c**.

Method A: By Conventional Heating.

Samples of (1.5 g) were heated in an oil bath to 10 °C above their melting point. After cooling, tetrahydrofuran (30 ml) was added and the mixture was subjected to PLC using cyclohexane/ethyl acetate (1:1) as developing solvent to give numerous zones. From the thermolyses of **5a-c** three intense zones were extracted with acetone. The fastest migrating zone contained the disubstituted thiourea **4a-c**, the second zone contained the 2-thioxotetrahydropyrimidine-1-carbothioic acid amide **8a-c** and the slowest zone contained the amino-3,4,5,6-tetrahydro-[1,3,7]thiadiazocine-2-thiones **10a-c**. On the other hand, chromatographic separation of the residue from the thermolysis of **10a-c**, **11a-c** or **12a-c** using $CHCl_3$/MeOH (20:1) as eluent afforded two main zones (extracted with THF). The faster migrating one contained the disubstituted thiourea **4a-c** and the second zone the amino-4,5,6,7-tetrahydro-3*H*-[1,3,8]thiadiazonine-2-thiones **11a-c** or the amino-1-thia-3,10-diazacycloundec-10-ene-2-thiones **12a-c**.

Method B: By Microwave Irradiation.

Samples of 1.5 g of powdered starting materials were MW-irradiated to melting in an open glass tube (for the time listed in Table 1). After completion of the reaction as monitored by TLC, the residue was separated as reported above. Comparison of the yields from both methods is given in Table 1.

1,3-Diphenylthi ourea (**4a**).

This compound had mp: 151-153° (Lit. [23] 152-153° [24], 151-152 °).

1,3-Dibenzylthiourea (**4b**).

This compound had mp: 146-148° (Lit. [23] 145-147° [24], 146-147°).

1,3-Diallylthiourea (**4c**).

This compound had mp: 48-50° (Lit. [24], 48-49°).

N-Phenyl-2-thioxotetrahydropyrimidine-1(2*H*)-carbothioamide (**8a**).

This compound was obtained as colourless crystals (acetonitrile), mp: 150-152°; ir: broad NH 3171, (NH def. and C-N str.) 1556, (C=S, C-N) 1360, 992 cm^{-1}, (CCl_4, 10^{-3} M, d = 3 cm) (broad NH assoc.) 3188 and (C=S, C-N) 1336, 972 cm^{-1}; ^1H nmr: 1.68-1.76 (m, 2H, 5-H_2), 3.08 (m, 2H, 6-H_2), 3.48 (m, 2H, 4-H_2) 7.08-7.11, 7.29-7.32 and 7.36-7.38 (m, 5H, phenyl H), 7.48 (br, s, 1H, 3-NH), 9.54 ppm (br, s, 1H, N*H*Ph), the latter two signals fade upon treatment of the DMSO-d_6 solution with D_2O; ^{13}C nmr: 31.20 (C-5), 50.40 (C-6), 55.80 (C-4), 123.22,

124.25, 128.70 (phenyl CH), 139.10 (phenyl C-1), 175.60 (acyclic C=S), 180.27 ppm (cyclic C=S); ms: m/z 251 (M^+, 4), 135 (21), 116 (100), 93 (20), 77 (17), 59 (23).

Anal. Calcd. for $C_{11}H_{13}N_3S_2$ (251.37): C, 52.56; H, 5.21; N, 16.72; S, 25.51. Found C, 52.69; H, 5.32; N, 16.58; S, 25.64 %.

N-Benzyl-2-thioxotetrahydropyrimidine-1(2*H*)-carbothioamide (**8b**).

This compound was obtained as colourless crystals (ethanol), mp 54-56°; ir: NH 3220, (NH def. and C-N str.) 1568, (C=S, C-N) 1358, 986 cm^{-1}; ^1H nmr: 1.64-1.76 (m, 2H, 5-H_2), 3.09 (m, 2H, 6-H_2), 3.36 (m, 2H, 4-H_2), 4.61 (m, 2H, C*H*$_2$Ph), 7.12-7.36 (m, 5H, phenyl H), 7.46 (br, 1H, 3-NH), 7.83 ppm (br, s, 1H, N*H*CH$_2$Ph); ^{13}C nmr: 30.80 (C-5), 46.80 (*C*H$_2$Ph), 50.20 (C-6), 55.70 (C-4), 126.52, 127.40, 128.10 (phenyl CH), 141.63 (phenyl C-1), 175.58 (acyclic C=S), 180.12 (2-C=S); ms: m/z 265 (M^+, 7), 178 (12), 149 (51), 116 (62), 91 (100).

Anal. Calcd. for $C_{12}H_{15}N_3S_2$ (265.07): C, 54.31; H, 5.70; N, 15.83; S, 24.16. Found C, 54.19; H, 5.83; N, 15.91; S, 24.04 %.

N-Allyl-2-thioxotetrahydropyrimidine-1(2*H*)-carbothioamide (**8c**).

This compound was obtained as colourless crystals (ethanol), mp 124-126°; ir: NH 3210, (NH def. and C-N str.) 1570, (C=S, C-N) 1362, 976 cm^{-1}; ^1H nmr: 1.68-1.70 (m, 2H, 5-H_2), 3.02 (m, 2H, 6-H_2), 3.34 (m, 2H, 4-H_2), 4.10 (br, 2H, allyl 1–H_2), 5.06-5.18 (m, 2H, allyl 3-H_2), 5.77-5.90 (m, 1H, allyl 2-H), 7.46 (br, 1H, allyl-NH), 7.54 ppm (br, 1H, 3-NH); ms: m/z 215 (M^+, 4), 200 (51), 158 (32), 116 (32), 99 (84), 56 (96), 41 (100).

Anal. Calcd. for $C_8H_{13}N_3S_2$ (215.34): C, 44.62; H, 6.08; N, 19.51; S, 29.78. Found C, 44.79; H, 6.16; N, 19.38; S, 29.61 %.

8-Phenylamino-3,4,5,6-tetrahydro-1,3,7-thiadiazocine-2-thione (**10a**).

This compound was obtained as colourless crystals (ethanol), mp 112-114°; ir: NH 3210, 3190, (NH def. and C-N str.) 1560, (C=S, C-N) 1366, 992 cm^{-1}; ^1H nmr: 1.78-1.82 (m, 2H, 5-H_2), 3.05 (m, 2H, 4-H_2), 3.37 (m, 2H, 6-H_2) 7.10-7.39 (m, 5H, phenyl H), 7.80 (br, 1H, 3-NH), 9.54 ppm (br, 1H, N*H*Ph); ^{13}C nmr: 30.22 (C-5), 39.90 (C-4), 42.70 (C-6), 112.66, 126.40, 128.90 (phenyl CH), 139.60 (phenyl C-1), 151.20 (C-8), 184.60 ppm (C=S); ms: m/z 251 (M^+, 7), 135 (88), 116 (41), 93 (100), 77 (71), 51 (42).

Anal. Calcd. for $C_{11}H_{13}N_3S_2$ (251.37): C, 52.56; H, 5.21; N, 16.72; S, 25.51. Found C, 52.41; H, 5.32; N, 16.54; S, 25.67 %.

8-Benzylamino-3,4,5,6-tetrahydro-2*H*-1,3,7-thiadiazocine-2-thione (**10b**).

This compound was obtained as colourless crystals (methanol), mp 138-140°; ir: NH 3230, 3190, (NH def. and C-N str.) 1568, (C=S, C-N) 1356, 996 cm^{-1}; ^1H nmr: 1.72-1.77 (m, 2H, 5-H_2), 3.10 (m, 2H, 4-H_2), 3.39 (m, 2H, 6-H_2), 4.63 (br, 2H, C*H*$_2$Ph), 7.22-7.34 (m, 5H, phenyl H), 7.50 (br, 1H, 3-NH), 7.85 ppm (br, 1H, N*H*CH$_2$Ph); ^{13}C nmr: 30.26 (C-5), 38.40 (C-4), 43.10 (C-6), 46.66 (*C*H$_2$Ph), 122.00, 127.36, 128.60 (phenyl CH), 139.24 (phenyl C-1), 151.90 (C=N), 184.44 ppm (C=S); ms: m/z 265 (M^+, 8), 149 (100), 130 (36), 107 (74), 77 (66), 51 (44).

Anal. Calcd. for $C_{12}H_{15}N_3S_2$ (265.07): C, 54.31; H, 5.70; N, 15.83; S, 24.16. Found C, 54.47; H, 5.57; N, 15.69; S, 24.31 %.

Allylamino-3,4,5,6-tetrahydro-2*H*-1,3,7-thiadiazocine-2-thione (**10c**).

This compound was obtained as colourless crystals (acetonitrile), mp 138-140°, ir: NH 3260, 3170, (NH def. and C-N str.) 1562, (C=S, C-N) 1350, 975 cm^{-1}; ^1H nmr: 1.66-1.70 (m, 2H, 5-H_2), 3.20 (m, 2H, 4-H_2), 3.34 (m, 2H, 6-H_2), 4.00 (br, 2H, allyl 1-H_2), 5.03-5.15 (m, 2H, allyl 3-H_2), 5.76-5.88 (m, 1H, allyl 2-H), 7.46 (br, 1H, allyl-NH), 7.54 ppm (br, 1H, 3-NH); ms: m/z 215 (M^+, 7), 116 (41), 99 (90), 56 (96), 41 (100).

Anal. Calcd. for $C_8H_{13}N_3S_2$ (215.34): C, 44.62; H, 6.08; N, 19.51; S, 29.78. Found C, 44.46; H, 6.19; N, 19.44; S, 29.91 %.

9-Phenylamino-2,3,4,5,6,7-hexahydro-1,3,8-thiadiazonine-2-thione (**11a**).

This compound was obtained as colourless crystals (acetonitrile), mp 162-164°; ir NH 3260, 3164, week; C=N 1620, (NH def. and C-N str.) 1541, (C=S, C-N) 1308, 1256 cm^{-1}; ^1H nmr: 1.57 (m, 4H, 5-H_2 and 6-H_2), 3.32 (m, 2H, 4-H_2), 3.49 (m, 2H, 7-H_2) 7.12-7.41 (m, 5H, phenyl H), 7.78 (br, 1H, 3-NH), 9.48 ppm (br, 1H, N*H*Ph); ^{13}C nmr: 30.59 (C-5,6), 43.79 (C-4), 44.97 (C-7), 124.25, 125.09, 128.81 (phenyl CH), 139.42 (phenyl C-1), 151.64 (C-9), 183.46 ppm (C=S); ms: m/z 265 (M^+, 6), 189 (4), 135 (62), 130 (8), 91 (100), 77 (42), 65 (44).

Anal. Calcd. for $C_{12}H_{15}N_3S_2$ (265.40): C, 54.31; H, 5.70; N, 15.83; S, 24.16. Found C, 54.46; H, 5.52; N, 15.71; S, 24.33 %.

9-Phenylmethylamino-2,3,4,5,6,7-hexahydro-1,3,8-thiadiazonine-2-thione (**11b**).

This compound was obtained as colourless crystals (ethanol), mp 168-170°; ir: NH 3225, (NH def. and C-N str.) 1558, (C=S, C-N) 1351, 964 cm^{-1}; ^1H nmr: 1.46 (m, 4H, 5-H_2 and 6-H_2), 3.34 (m, 2H, 4-H_2), 3.41 (m, 2H, 7-H_2), 4.64 (br, 2H, C*H*$_2$Ph) 7.19-7.34 (m, 5H, phenyl H), 7.51 (br, 1H, 3-NH), 7.79 ppm (br, 1H, N*H*CH$_2$Ph); ^{13}C nmr: 30.60 (C-5,6), 40.52 (C-4), 43.36 (C-7), 126.94, 127.41, 128.40 (phenyl CH), 139.33 (phenyl C-1), 151.63 (C-9), 182.68 ppm (C=S); MS: m/z 279 (M^+, 4), 203 (3), 149 (48), 130 (12), 106 (66), 91 (100), 77 (36), 65 (38).

Anal. Calcd. for $C_{13}H_{17}N_3S_2$ (279.43): C, 55.88; H, 6.13; N, 15.04; S, 22.95. Found C, 55.71; H, 5.98; N, 14.91; S, 23.12 %.

9-(2-Propenyl)amino-2,3,4,5,6,7-hexahydro-1,3,8-thiadiazonine-2-thione (**11c**).

This compound was obtained as colourless crystals (ethanol), mp 144-146°; ir: NH 3266, 3164, (NH def. and C-N str.) 1541, (C=S, C-N) 1356, 1016 cm^{-1}; ^1H nmr: 1.46 (m, 4H, 5-H_2 and 6-H_2), 3.36 (m, 2H, 4-H_2), 3.46 (m, 2H, 7-H_2) 4.03 (br, 2H, allyl 1-H_2), 5.05-5.16 (m, 2H, allyl 3-H_2), 5.77-5.90 (m, 1H, allyl 2-H), 7.36 (br, 1H, 3-NH), 7.47 ppm (br, 1H, allyl-NH); ^{13}C nmr : 29.51 (C-5,6), 40.50 (C-4), 45.50 (C-7), 43.48 (allyl C-1), 115.46 (allyl C-3), 135.39 (allyl C-2), 151.80 (C-9), 182.10 ppm (C=S); ms: m/z 229 (M^+, 3), 172 (6), 153 (32), 130 (12), 99 (73), 56 (98), 41 (100).

Anal. Calcd. for $C_9H_{15}N_3S_2$ (299.37): C, 47.13; H, 6.59; N, 18.32; S, 27.96. Found C, 46.96; H, 6.71; N, 18.46; S, 28.12 %.

11-Phenylamino-1-thia-3,10-diazacycloundec-10-ene-2-thione (**12a**).

This compound was obtained as colourless crystals (methanol), mp 98-100°; ir: NH 3235, 3160, (NH def. and C-N str.) 1566, (C=S, C-N) 1348, 1030 cm^{-1}; ^1H nmr: 1.30 (m, 4H, 6-H_2 and 7-H_2), 1.54 (m, 4H, 5-H_2 and 8-H_2), 3.33 (m, 2H, 4-H_2), 3.46 (m, 2H, 9-H_2), 7.07-7.41 (m, 5H, phenyl H), 7.73 (br, 1H, 3-NH), 9.45 ppm (br, 1H, N*H*Ph); ^{13}C nmr: 26.40 (C-6,7), 28.63,

28.94 (C-5,8), 43.98, 44.30 (C-4,9), 124.16, 125.09, 128.75 (phenyl CH), 139.51 (phenyl C-1), 151.64 (C-11), 180.44 ppm (C=S); ms: m/z 293 (M^+, 6), 177 (28), 135 (100), 93 (96), 77 (94), 57 (61).

Anal. Calcd. for $C_{14}H_{19}N_3S_2$ (293.45): C, 57.30; H, 6.53; N, 14.32; S, 21.85. Found C, 57.44; H, 6.66; N, 14.19; S, 22.02 %.

11-Phenylmethylamino-1-thia-3,10-diazacycloundec-10-ene-2-thione (**12b**).

This compound was obtained as colourless crystals (acetonitrile), mp 128-130°, ir: NH 3261, 3212, (NH def. and C-N str.) 1574, (C=S, C-N) 1360, 1014 cm^{-1}; ^1H nmr: 1.26 (m, 4H, 6-H_2 and 7-H_2), 1.47 (m, 4H, 5-H_2 and 8-H_2), 3.33 (m, 2H, 4-H_2), 3.41 (m, 2H, 9-H_2), 4.65 (br, 2H, CH_2Ph), 7.21-7.34 (m, 5H, phenyl-H), 7.48 (br, 1H, 3-NH), 7.78 ppm (br, 1H, N*H*CH_2Ph); ^{13}C nmr: 26.94 (C-6,7), 28.90, 28.94 (C-5,8), 40.26 (C-4), 43.58 (C-9), 47.02 (*C*H_2Ph), 126.92, 127.40, 128.38 (phenyl CH), 139.60 (phenyl C-1), 151.62 (C-11), 182.62 ppm (C=S); ms: m/z 307 (M^+, 6), 149 (41), 106 (63), 91 (100), 77 (31), 65 (42).

Anal. Calcd. for $C_{15}H_{21}N_3S_2$ (307.48): C, 58.59; H, 6.88; N, 13.67; S, 20.86. Found C, 58.72; H, 7.04; N, 13.53; S, 20.93 %.

11-(2-Propenyl)amino-1-thia-3,10-diazacycloundec-10-ene-2-thione (**12c**).

This compound was obtained as colourless crystals (ethanol), mp 80-88°; ir: NH 3244, C=N 1610, (NH def. and C-N str.) 1567, (C=S, C-N) 1362, 1024 cm^{-1}; ^1H nmr: 1.27 (m, 4H, 6-H_2 and 7-H_2), 1.46 (m, 4H, 5-H_2 and 8-H_2), 3.33 (m, 2H, 4-H_2), 3.36 (m, 2H, 9-H_2), 4.03 (br, 2H, allyl 1-H_2), 5.05-5.16 (m, 2H, 3-H_2), 5.77-5.90 (m, 1H, allyl 2-H), 7.31 (br, 1H, 3-NH), 7.44 ppm (br, 1H, allyl-NH); ^{13}C nmr: 26.33 (C-6,7), 28.89, 28.93 (C-5,8), 43.98, 40.25 (C-4), 43.56 (C-9), 45.91 (allyl C-1), 115.06 (allyl C-3), 135.41 (allyl C-2), 151.61 (C-11), 182.36 ppm (C=S); ms: m/z 257 (M^+, 3), 158 (28), 99 (36), 57 (100), 41 (68).

Anal. Calcd. for $C_{11}H_{19}N_3S_2$ (257.42): C, 51.32; H, 7.44; N, 16.32; S, 24.91. Found C, 51.46; H, 7.53; N, 16.21; S, 25.08 %.

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