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Thermolysis of Symmetrical Dithiobiurea and Thioureidoethylthiourea Derivatives

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ABSTRACT: *Microwave and thermal heterocyclization of N,N′-disubstituted hydrazinecarbothioamide* **1a,b** *and substituted thioureidoethylthioureas* **2a–c** *as well as 1-phenyl-3[2-(3-phenylthio-ureido)phenyl]-thiourea* **6** *are reported.* © 2003 Wiley Periodicals, Inc. Heteroatom Chem 14:535–541, 2003; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10188

INTRODUCTION

Several authors have investigated the heterocyclization of 1,6-disubstituted dithiobiureas in basic or acidic media and under various reaction conditions [1–14]. *N*,*N*′-Diphenylhydrazine-1,2-dicarbothioamide(1,6-diphenyl-2,5-dithiobiurea) (**1a**) and substituted thioureidoethylthioureas **2b,d** reacted with mercury bis(phenylacetylide) under thermal decomposition affording heterocyclic systems **3, 4**, and **8** (Schemes 1 and 2) [1]. Alkali catalyzed thermal cyclization of 1-alkyl- and 1,6-dialkyl-2,5-dithiobiureas results in the formation of compounds **5** and **9** (R = Me, Et, and *n*-Pr) [6]. Under same conditions, 1-alkyl-6-aryl-2,5-dithiobiureas give thiadiazolethiones **9** and triazolidine-3,5-dithiones **5**, when the alkyl groups are methyl or ethyl [4,6]. The ring-closure of 1-ethoxycarbonyl- and 1,6-bis(ethoxycarbonyl)bithiourea proceed under the influence of acids giving 5-amino (or mercapto)-2-ethoxycarbonamide-1,3,4-thiadiazoles as well as 2,5-bis(ethoxycarbonamido)-1,3,4-thiadiazole [7]. The action of alkali or hydrazine on the same ethoxycarbonylbithiourea produces 1,2,4-triazole derivatives [7]. 3-Mercapto-4-phenyl-5-anilino-1,2,4-triazole is formed during the reaction of *p*-bromophenyl-6-phenyl-2,5-bithiourea with alkali and alkali/CH_3I [9]. Also, phase transfer catalyzed cyclization of dithiobiureas and reaction with α-bromoacetophenone affordes 1,3,4-thiadiazole [5,8], 1,2,4-triazole [8], and 1,2,4-triazoline-2-thione derivatives [13,14].

Recently it has been reported that the cyclization of compounds having an extended urea-like chain of more than five atoms is an excellent method for the synthesis of heterocycles such as 1,3,4-thiadiazoles, 1,2,4-triazoles, and 1,3,5-triazines [11]. Furthermore there is currently much interest in performing chemical reactions under solvent-free conditions since there are both financial and environmental benefits [15,16].

In addition microwave (MW) heating has been employed for the rapid synthesis of a wide variety of organic molecules [17–22], wherein chemical reactions are accelerated because of selective absorption of MW energy by polar molecules. The application of MW irradiation provides enhanced reaction rates, higher yields, greater selectivity, and the ease of manipulation.

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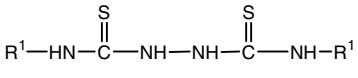
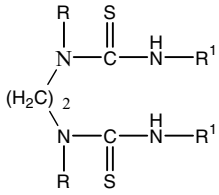


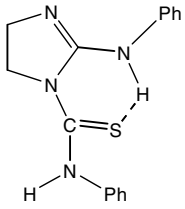
1

a, R^1 = Ph
b, R^1 = allyl



2

a, R = H, R^1 = Ph
b, R = H, R^1 = allyl
c, R = H, R^1 = $PhCH_2$
d, R = CH_3, R^1 = Ph



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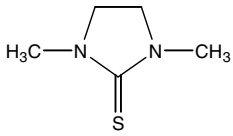

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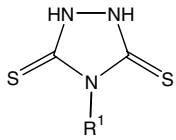
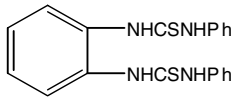


5, R^1 = Me, Et



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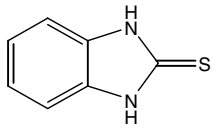

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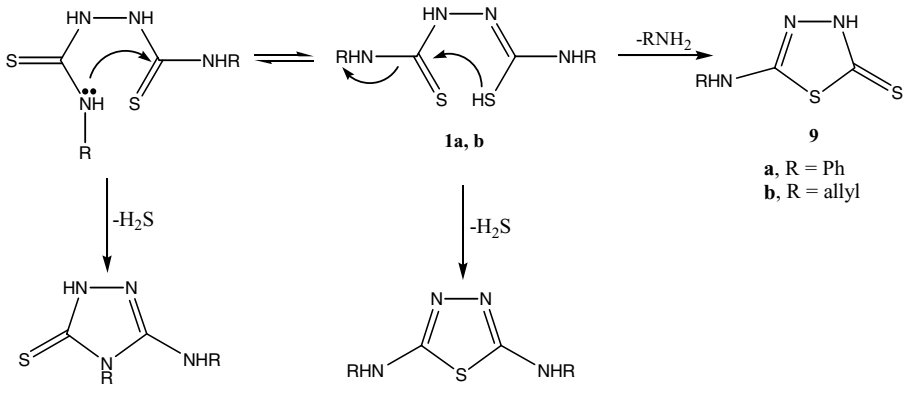
SCHEME 1

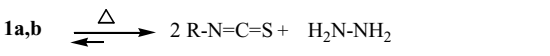


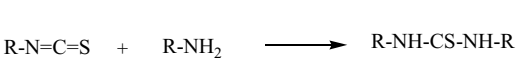
1a, b

9
a, R = Ph
b, R = allyl

10, R = Ph

8
a, R = Ph
b, R = allyl





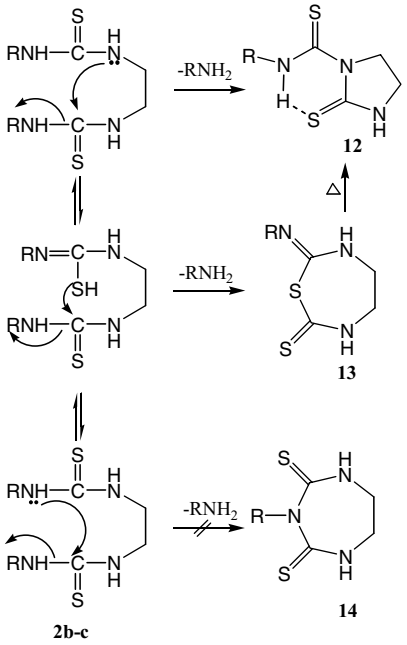
11
a, R = Ph
b, R = allyl
c, R = $PhCH_2$

SCHEME 2

As a part of our program directed for the development of new, simple and efficient, procedures for the synthesis of heterocyclic systems from thiosemicarbazide derivatives, we recently reported different successful approaches for the synthesis of thiazole, thiazine, thiadiazole, thiadiazine, thiadiazepine, oxathiadiazole, and indazole as well as pyridazine derivatives [23–27; A. A. Hassan, N. K. Mohamed, A. M. Shawky, and D. Döpp, manuscript in preparation]. The purpose of this work was to investigate an alternative, convenient and versatile, method for intramolecular heterocyclization of compounds **1** in the absence of alkaline or acidic catalyst.

RESULTS AND DISCUSSION

When compounds **1a,b**, **2a–c**, and **6** were heated or irradiated in a MW reactor, a sticky residue was obtained. Chromatographic separation of the residue gave numerous zones, from which products **7–13** could be isolated (Schemes 1–3). Their structures were assigned on the basis of elemental analyses and spectral data for unknown compounds and known compounds were identified by ^{1}H and ^{13}C NMR spectra. Their formation may be explained in terms of intramolecular nucleophilic attack by either the 2-thiol or the NH group and detachment of the RNH- or HS-moiety as depicted in Schemes 2 and 3. When aniline or allylamine is eliminated, the product would be a 5-substituted amino-3*H*-[1,3,4]thiadiazole-2-thione **9a,b**, whereas



SCHEME 3

when H_2S is displaced the product formed would be an *N*,*N*′-disubstituted[1,3,4]thiadiazole-2,5-diamine **8a,b**. On the other hand, if the lone pair of electrons on N-6 attacks the thiocarbonyl group at position 2 in **1a**, followed by displacing H_2S, the product formed would be 4-phenyl-5-phenylamino-4*H*[1,2,4]triazole-3-thiol (**10**).

Refluxing **1a** with acetic acid afforded acetanilide (0.041 g, 6%) in addition to compounds **8a**, **9a, 10**, and **11a**. The formation of 1,3-disubstituted thioureas **11a,b** and acetanilide confirmed the elimination of substituted amine during the heterocyclization of **1a,b**.

It has been reported that ethylenediamine when reacting with allylisothiocyanate furnishes a linear thiourea, which in turn is cyclized to a bis-thiazoline [10]. The present work was also undertaken to discuss the intramolecular heterocyclization of **2a–c**. Upon heating or MW irradiation of **2a–c** followed by chromatographic separation, **11–13** were isolated as products.

The structures of **12** and **13** were confirmed on the basis of elemental analysis, mass spectra, ^{1}H, and ^{13}C NMR data. The ^{1}H NMR spectrum of **12b** showed for the methylene groups at positions 5 and 4 resonances in the range $\delta = 3.54$–3.87 and 4.62–4.68 ppm respectively. The presence of methylene groups is also evident from the ^{13}C-DEPT-NMR spectrum exhibiting negative signals at $\delta = 40.28$ and 52.31. In addition, for imidazolidine-NH, the ^{1}H NMR spectrum exhibited a broad singlet centered at $\delta = 13.06$ ppm, as well as another broad singlet resonated at 6.83 ppm due to NH attached to allyl and C=S groups. The decoupled carbon spectra of **12b** showed signals at $\delta = 178.97$ and 179.76 assigned to acyclic and cyclic C=S, respectively [28], pointing out that the addition did not occur at the sulphur atom. Compound **12** was also assigned on the basis of intramolecular H bridge detected by IR (in dilute CCl_4) and ^{1}H NMR (see the Experimental section).

The presence of two multiplets in the ranges $\delta = 3.64$–3.77 and 4.38–4.52 ppm in the ^{1}H NMR of **13a** again are assigned to the C-4 and C-5 methylene groups. The ^{13}C-DEPT-NMR spectrum showed negative signals at $\delta = 41.64$ and 49.94 ppm, confirming the presence of two methylene groups, whereas the proton-decoupled ^{13}C-NMR spectrum showed two signals at $\delta = 158.70$ and 178.12 [28] for C=N and C=S groups, respectively.

The alternative structure **14** could be ruled out according to ^{1}H NMR spectra, as it would have shown different resonances for the methylene groups at positions 4 and 5 and the thiadiazepine-NHs. Also, compounds **12** and **13** are alternatives of each other; heating compound **13** afforded compound **12**.

Earlier it has been reported that when 1-phenyl-3-[2-(3-phenylthioureido)phenyl]thiourea **6** is heated with HCl or KOH at reflux temperature, 2-phenylamino-4,5-phenylene-7-thioxo-1,3,6-thiaheptadiazine is formed [29]. Recently, Sondhi et al. [30] reported that condensation of 4-isothiocyanatobutane-2-one with *o*-phenylenediamine in methanol gives a pyrimidobenzimidazole derivative [30]. Moreover, 2,3-diaminopyridine on condensation with 4-isothiocyanatobutan-2-one in refluxing acetic acid gives pyrido[2,3-d]imidazo-2 (1*H*)thione [30].

In the present investigation, 2-mercaptobenzimidazole (**7**) and diphenylthiourea **11a** were the only products found to be originating from intramolecular thermal cyclization of 1-phenyl-3-[2-(3-phenylthioureido)phenyl]thiourea **6**. Product **7** may also be obtained from the reaction of 5-phenyl-3*H*-1,3,4-oxadiazole-2-thione with *o*-phenylenediamine [31].

As shown in Table 1 the application of MW irradiation provided higher yields in comparison with yields obtained by application of thermal process.

EXPERIMENTAL

All the melting points were determined in open glass capillaries on Gallenkamp melting point apparatus and are uncorrected. The IR spectra were recorded with a Shimadzu 408 or a Bruker Vector 22 FT-IR instrument, using potassium bromide pellets. A Bruker WM 300 instrument was used to determine ^{1}H (300.13 MHz) and ^{13}C (75.47 MHz) NMR spectra. Assignment of carbon resonances has been supported by DEPT experiments. Mass spectra were obtained with a Varian MAT 311 doubly focussing instrument, using electron impact ionization (70 eV). Elemental analyses were determined at the Microanalytical Center, Cairo University, Egypt. A Samsung MX 145 MW oven was used at its full power 1400 W, 70% and 50% power level for the experiments recorded for this study. Preparative layer chromatography (PLC): Glass plates 48 × 20 cm covered with slurry applied and air dried layers of Merck silica gel PF_{254}. Detection of zones was carried out by fluorescence quenching after 254 nm excitation; zones were removed from the plates and extracted with cold acetone.

TABLE 1 Thermolysis of 1.5 g Each of Starting Materials **1a,b**, **2a–c**, and **6** by Conventional Heating (A) and MW Irradiation (B)

Starting Materials (Conditions)	*Products*	*Yield in g (%)* A	*Yield in g (%)* B
1a	**8a**	(22) 0.295	(26) 0.340
A: 188–190°C.	**9a**	(18) 0.217	(21) 0.217
B: 7 min, power 100%	**10**	(12) 0.157	(16) 0.213
	11a	(5) 0.055	(9) 0.097
1b	**8b**	(33) 0.422	(38) 0.492
A: 188–190°C.	**9b**	(24) 0.275	(30) 0.338
B: 6 min, power 100%	**11b**	(4) 0.044	(7) 0.073
2a	**11a**	(7) 0.069	(11) 0.111
A: 203–205°C.	**12a**	(11) 0.116	(15) 0.161
B: 6 min, power 100%	**13a**	(47) 0.505	(55) 0.596
2b	**11b**	(7) 0.059	(9) 0.078
A: 103–105°C.	**12b**	(5) 0.060	(8) 0.098
B: 4 min, power 50%	**13b**	(58) 0.680	(63) 0.739
2c	**11c**	(7) 0.073	(10) 0.108
A: 143–145°C.	**12c**	(10) 0.107	(14) 0.146
B: 6 min, power 70%	**13c**	(41) 0.427	(52) 0.544
6	**11a**	(6) 0.052	(10) 0.094
A: 153–155°C.	**7**	(46) 0.272	(60) 0.335
B: 7 min, power 100%			

General Procedure for Starting Materials

To a stirred solution of hydrazine hydrate or the respective diamine (10 mmol) in 20 ml dimethylformamide, phenyl-, allyl-, or benzylisothiocyanate (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 white precipitate was formed which was recrystallized from a suitable solvent: *N*,*N*′-Diphenylhydrazinecarbothioamide (**1a**) [32,33], *N*,*N*′-diallylhydrazinecarbothioamide (**1b**) [34], 1-phenyl-3-[2-(3-phenylthioureido)ethyl]thiourea (**2a**) [35], 1-allyl-3-[2(3-allylthioureido)ethyl]thiourea (**2b**) [10], and 1-phenyl-3-[2-(3-phenylthioureido)-phenyl]thiourea (**6**) [29].

*1-Benzyl-3-[2-(3-benzylthioureido)ethyl]thiourea (***2c***).* Colorless crystals from ethanol. Yield 71%, m.p. 143–145°C. IR: ν (KBr) cm^{-1} 3270, 3110 (NH), 2940 (Ali-CH), 1640, 1590 (C=N, C=C) and 1360 cm^{-1} (C=S). ^{1}H NMR (300 MHz, DMSO-d_6) δ 3.69 (s, 4H, 2CH_2), 4.66 (s, 4H, 2 benzyl-CH_2), 7.11–7.39 (m, 10H, Ar-H), 7.85 (s, br, 2H, 2 NH), 9.61 (s, br, 2H, 2NH). MS (70 eV) *m/z* (%) 358 (M^+, 19), 296 (53), 265 (43), 223 (8), 206 (13), 181 (39), 149 (87), 91 (100); $C_{18}H_{22}N_4S_2$ (358.53); calcd C, 60.30; H, 6.19; N, 15.63; S, 17.89; found C, 60.46; H, 6.03; N, 15.49; S, 18.06%.

Heterocyclization by Conventional Heating of Neat **1a,b, 2a–c***, and* **6**

1a,b, 2a–c or **6** (1.5 g) was heated in an oil bath to its melting point. After cooling, a 30 ml of ethanol were added, any insoluble material was filtered off and washed with ethanol to give compounds **8a,b**. The filtrate was concentrated and the residue was subjected

to PLC using cyclohexane/ethyl acetate (2:1) as developing solvent to give three zones from heating of **1a,b**. The fastest migrating zone contained **11a,b**, the second zone contained **9a,b** and the slowest zone contained **10**.

On the other hand, chromatographic separation of the residue from heating **2a–c** using cyclohexane/ethyl acetate (3:1) as eluent afforded three zones. The fastest moving one contained **11a–c**. The second zone contained **12a–c** while the last zone contained **13a–c**. Chromatographic separation of the residue from heating compound **6** using cyclohexane/ethyl acetate (2:1) as eluent afforded two zones, the fastest migrating one contained **11a**, and the second zone contained **7**. The zones were extracted with acetone, crystallized and identified.

Heterocyclization by Microwave Irradiation of **1a,b**, **2a–c**, *and* **6**

1.5 g of **1a,b**, **2a–c**, or **6** was irradiated in an open glass tube (the time of irradiation is 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 compounds **1, 2**, and **6** is given in Table 1.

*N,N-Diphenyl-[1,3,4]thiadiazole-2,5-diamine (***8a***).* Colorless crystals from DMF, m.p. 239–241°C (lit. [1,5] 240–243°C).

*N,N-Diallyl-[1,3,4]thiadiazole-2,5-diamine (***8b***).* Colorless crystals from ethanol. m.p. 133–135°C (lit. [36] 135°C). ^{1}H NMR (DMSO-d_6) $\delta = 3.75$ (br, s, 4H, 2CH_2N), 5.05–5.09 (m, 4H, 2CH_2=), 5.82–5.88 (m, 2H, 2CH=), 6.94 (br, s, 2H, 2NH). ^{13}C NMR (DMSO-d_6) 46.56 (CH_2—N), 115.82 (CH_2=), 135 (CH=), 159.81 (thiadiazole-C-2). MS (70 eV) *m/z* (%) 196 (M^+, 46), 181 (10), 155 (13), 114 (42), 100 (11), 81 (17), 56 (23), 41 (100). $C_8H_{12}N_4S$ (196.28); calcd C, 48.96; H, 6.16; N, 28.54; S, 16.34; found C, 48.81; H, 6.04; N, 28.66; S, 16.23%.

*5-Phenylamino-3H-[1,3,4]thiadiazole-2-thione (***9a***).* Pale yellow crystals from ethanol. m.p. 226–228°C (lit. [6] 228°C). ^{1}H NMR (DMSO-d_6) $\delta = 6.96$–6.99 (m, 1H, Ar-H), 7.28–7.41 (m, 4H, Ar-H), 10.14 (s, br, 1H, NH), 13.50 (s, br, 1H, thiadiazole-NH). ^{13}C NMR (DMSO-d_6) 117.6, 121.39, 129.14, 129.32, 129.59, 139.98 (Ar-CH), 157.08 (thiadiazole-C-5), 180.55 (C=S). MS (70 eV) *m/z* (%) 209 (M^+, 100), 135 (11), 93 (6), 77 (39). $C_8H_7N_3S_2$ (209.29); calcd C, 45.91; H, 3.32; N, 20.08; S, 30.64; found C, 46.11; H, 3.14; N, 19.96; S, 30.53%.

*5-Allylamino-3H-[1,3,4]thiadiazole-2-thione (***9b***).* Colorless crystals from cyclohexane. m.p. 56–58°C (lit. [25] 58°C). ^{1}H NMR ($CDCl_3$) $\delta = 4.31$–4.35 (m, 2H, allyl-CH_2N—), 5.16–5.28 (m, 2H, CH_2=), 5.90–5.99 (m, 1H, CH=), 7.53 (br, s, 1H, allyl-NH), 12.35 (s, br, 1H-thiadiazole-NH). ^{13}C NMR ($CDCl_3$) 45.93 (allyl-CH_2N), 116.89 (CH_2=), 133.71 (CH=), 149.14 (thiadiazole-C-5), 178.46 (C=S). MS (70 eV) *m/z* (%) 173 (M^+, 51), 115 (100), 100 (12), 56 (58), 41 (40). $C_5H_7N_3S_2$ (173.26); calcd C, 34.66; H, 4.07; N, 24.25; S, 37.01; found C, 34.81; H, 4.24; N, 24.36; S, 36.83%.

*4-Phenyl-5-phenylamino-4H-[1,2,4]triazole-3-thiol (***10***).* Colorless crystals from ethanol. m.p. 206–208°C (lit. [37,38] 206–209°C).

*1,3-Diphenylthiourea (***11a***).* Colorless powder from ethanol. m.p. 151–153°C (lit. [39,40] 153–154°C).

*1,3-Diallylthiourea (***11b***).* Colorless crystals from ether/hexane. m.p. 48–50°C (lit. [40] 47–49°C).

*1,3-Dibenzylthiourea (***11c***).* White crystals from ethanol. m.p. 146–148°C (lit. [40] 146–147°C).

*2-Thioxoimidazolidine-1-carbothioic Phenylamide (***12a***).* Colorless crystals. m.p. 174–176°C (lit. [41] 176–177°C).

*2-Thioxoimidazolidine-1-carbothioic Allylamide (***12b***).* Colorless crystals from acetonitrile. m.p. 126–128°C. IR: ν (KBr) 3191 (NH), 2928 (Ali-CH), 1531 (C=C) and 1354 cm^{-1} (C=S), ν (CCl_4, 10^{-3} M, $d = 3$ cm): 3170 (broad NH assoc.) and 1331 cm^{-1} (C=S, intramolecular H-bridge). ^{1}H NMR ($CDCl_3$) $\delta = 3.54$–3.78 (t, 2H, imidazolidine-5-CH_2, $J = 9.04$ Hz), 4.28–4.32 (br, s, 2H, allyl-CH_2N), 4.62–4.68 (t, 2H, imidazolidine-4-CH_2, $J = 9.02$ Hz), 5.21–5.38 (m, 2H, allyl CH_2=), 5.89–6.02 (m, 1H, allyl-CH=), 6.83 (s, br, 1H, allyl-NH), 13.06 (s, br, 1H, imidazolidine-NH) the latter two signals fade upon treatment of the $CDCl_3$-solution with D_2O. ^{13}C NMR ($CDCl_3$) $\delta = 40.28$ (imidazolidine-CH_2-5), 48.64 (allyl-CH_2N), 52.31 (imidazolidine-4-CH_2), 117.37 (allyl-CH_2=), 132.14 (allyl-CH=), 178.97 (acyclic-C=S), 179.76 (cyclic C=S). MS (70 eV) *m/z* (%) 201 (M^+, 100), 186 (96), 168 (8), 102 (55), 99 (12), 44 (99), 41 (42). $C_7H_{11}N_3S_2$ (201.31); calcd C, 41.76; H, 5.51; N, 20.87; S, 31.81; found C, 41.61; H, 5.64; N, 20.76; S, 31.90%.

*2-Thioxoimidazolidine-1-carbothioic Benzylylamide (***12c***).* Colorless crystals. m.p. 135–137°C (lit [42]. 135–136°C).

*7-Phenylimino-[1,3,6]thiadiazepane-2-thione (**13a**).* Colorless crystals from methanol. m.p. 235–237°C. IR: ν (KBr) 3410 (NH), 3020 (Ar-CH), 2920 (Ali-CH_2) and 1625, 1585 cm^{-1} (C=N, C=C). ^1H NMR (DMSO-d_6) $\delta = 3.67$–3.77 (t, 2H, thiadiazepane-5-CH_2, $J = 8.99$ Hz), 4.42–4.48 (t, 2H, thidiazepane-4-CH_2, $J = 9.01$ Hz), 7.23–7.29, 7.36–7.41, 7.71–7.97 (m, 5H, Ar-H), 9.67 (s, br, 1H, thiadiazepane-NH), 9.81 (s, br, 1H, thiadiazepane-NH). ^{13}C NMR (DMSO-d_6) 41.64 (C-5), 49.95 (C-4), 120.44, 121.52, 123.58, 126.05, 132.31, 148.26 (Ar-C), 158.72 (C-7), 178.12 (C=S). MS (70 eV) *m/z* (%) 237 (M^+,10), 235 (100), 163 (98), 150 (56), 136 (28), 135 (6), 43 (4). $C_{10}H_{11}N_3S_2$ (237.35); calcd C, 50.61; H, 4.68; N, 17.70; S, 27.02; found C, 50.49; H, 4.55; N, 17.61; S, 27.19%.

*7-Allylimino-[1,3,6]thiadiazepane-2-thione(**13b**).* Colorless crystals from ethanol. m.p. 98–100°C. IR: ν (KBr) 3219 (NH), 2921 (Ali-CH) and 1620, 1571 cm^{-1} (C=N, C=C). ^1H NMR (DMSO-d_6) $\delta = 3.39$ (br, t, 2H, thiadiazepane-5-CH_2), 3.49 (br, t, 2H, thiadiazepane-4-CH_2), 4.01 (br, s, 2H, allyl-CH_2N), 5.04–5.16 (m, 2H, allyl-CH_2=), 5.76–5.88 (m, 1H, allyl-CH=), 7.52 (br, s, 1H, thiadiazepane-NH), 7.63 (br, s, 1H, thiadiazepane-NH). ^{13}C NMR (DMSO-d_6) 36.81 (C-5), 43.01 (allyl-CH_2N), 46.09 (C-4), 115.66 (allyl-CH_2=), 135.13 (allyl-CH=), 158.12 (C-7), 182.38 (C=S). MS (70 eV) *m/z* (%) 201 (M^+, 78), 186 (82), 168 (7), 102 (64), 56 (100), 41 (76). $C_7H_{11}N_3S_2$ (201.31), calcd C, 41.76; H, 5.51; N, 20.87; S, 31.85; found C, 41.87; H, 5.44; N, 21.04; S, 31.97%.

*7-Benzylimino-[1,3,6]thiadiazepane-2-thione (**13c**).* Colorless crystals, m.p. 128–130°C (ethanol). IR: ν (KBr) 3310 (NH), 3025 (Ar-CH) 2945 (Ali-CH) and 1628, 1568 cm^{-1} (C=N, C=C). ^1H NMR (DMSO-d_6) $\delta = 3.61$–3.74 (t, 2H, thiadiazepane-5-CH_2, $J = 8.86$ Hz), 4.39–4.44 (t, 2H, thiadiazepane-4-CH_2, $J = 8.87$ Hz), 4.76 (s, 2H, CH_2), 7.21–7.28, 7.33–7.39, 7.68–7.94 (m, 5H, Ar-H), 9.65 (br, s, 1H, thiadiazepane-NH), 9.77 (br, s, 1H, thidiazepane-NH). ^{13}C NMR (DMSO-d_6) 40.14 (C-5), 48.53 (C-4), 49,22 (CH_2-Ph), 120.11, 120.86, 122.44, 125.31, 130.12, 140.41 (Ar-C), 158.62 (C-7), 181.16 (C=S). MS (70 eV) *m/z* (%) 251 (M^+, 16), 249 (100), 177 (84), 164 (49), 149 (11), 43 (6). $C_{11}H_{13}N_3S_2$ (251.37), calcd C, 52.56; H, 5.21; N, 16.72; S, 25.51; found C, 52.39; H, 5.34; N, 16.61; S, 25.68%.

*1,3-Dihydrobenzimidazole-2-thione (**7**).* White powder from acetonitrile. m.p. 301–303°C (lit. [31,43] 303–307°C).

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