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Reaction of *N*,*N* ’-disubstituted hydrazinecarbothioamides with 2-bromo-2-substituted acetophenones

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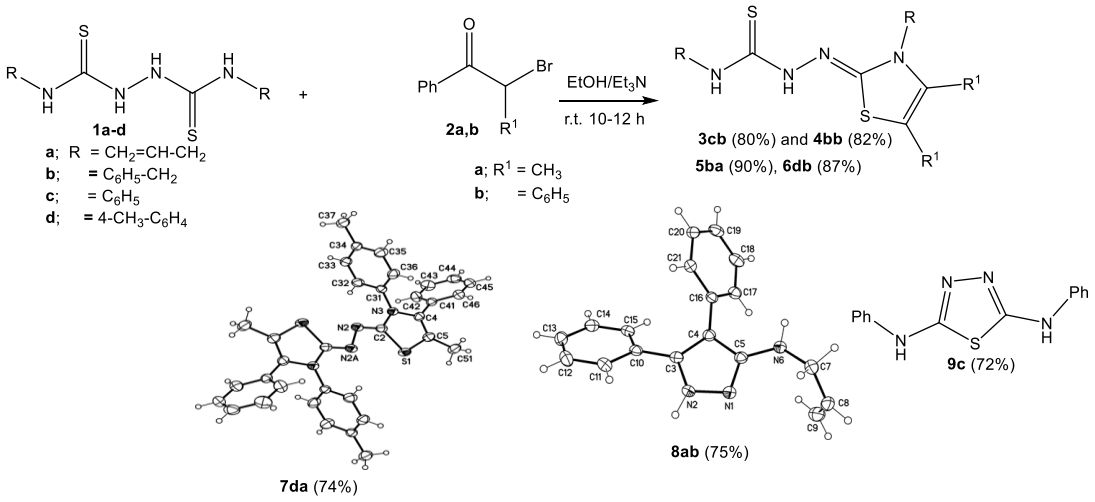
Abstract

Reaction of hydrazinecarbothioamides with 2-bromoacetophenones furnished the formation of thiazole-, bis-thiazole-, pyrazole- and 1,3,4-thiadiazole- derivatives in good yields. The mechanism was discussed. The structures of products were proved by MS, IR, NMR, elemental analyses and X-ray structure analyses.



Keywords: Hydrazinecarbothioamides, 2-bromoacetophenones, thiazoles, bis-thiazole, pyrazole

Introduction

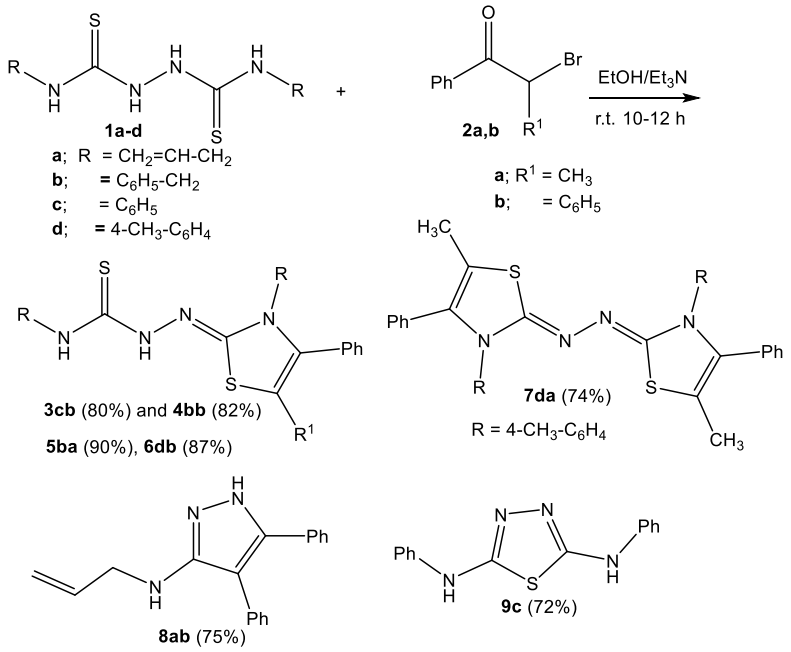
Substituted hydrazinecarbothioamides were found to exhibit antifungal,[1-3] antiviral[4] and antioxidant activities[5]. Free radicals and reactive sulfur species such as thiol radicals are frequently synthesized through many biological processes and may be considered as indicators of biological inadequacy. In recent times, the applications of thiazoles have found in drug development for the treatment of allergies[6], hypertension,[7] inflammation,[8] schizophrenia,[9] bacterial,[10] HIV infections,[11] and hypnotics[12]. Moreover, thiazoles have been used for the treatment of pain,[13] as fibrinogen receptor antagonists with antithrombotic activity[14] and as new inhibitors of bacterial DNA gyrase B.[15] Mukhija it was reported that thiourea reacted quantitatively with various 2-halocarbonyl compounds to form 2-amino salts of thiazoles.[16] Many classes of thiadiazole have been known to possess interesting widespread biological properties such as antimicrobial,[17] and anticancer.[18,19] Previously, we utilized by *N*,*N*'-disubstituted-hydrazinecarbothioamides in heterocyclic synthesis, such as 1,3-thiazin-2-ylidene-substituted hydrazides and 1,2,4-triazolo[3,4-*b*]-1,3-thiazine-5-carboxylates[20]. Continuation of our research program included the synthesis of various thiazoles,[21-26] we herein report the results of our investigation on the reactions of symmetrical hydrazinecarbothioamides **1a-d** with 2-bromoacetophenones **2a,b**.

Results and Discussion

Pleasingly, treatment of *N*,*N*'-disubstituted-hydrazinecarbothioamides **1a-d** with 2-bromoacetophenones **2a,b** at room temperature afforded the corresponding thiazoles **3cb** (80%), **4bb** (82%), **5ba** (90%), and **6db** (87%) (Scheme 1). (1*E*,2*E*)-1,2-Bis(5-methyl-4-phenyl-3-(*p*-tolyl)thiazol-2(3*H*)-ylidene)-hydrazine (**7da**) was also obtained in 74% yield (Scheme 1), during the reaction of **1d** with **2a**. Reaction of allyl hydrazinecarbothioamide derivative **1a** with **2b**, gave pyrazole **8ab** in 75% yield (Scheme 1). Finally, and on reacting **1c** with **2a**, the known 1,3,4-thiadiazole **9c** was obtained in 72% yield (Scheme 1).

The structures of thiazoles **3cb**, **4bb**, **5ba**, and **6db** were elucidated by IR, NMR, mass spectra and elemental analyses. For **3cb**, its molecular formula was proved from elemental analysis and mass spectrometry as $C_{28}H_{22}N_4S_2$ (Experimental section). The IR spectrum of **3cb** showed absorption band at ν = 3330-3320 cm^{-1} for the NH group. No absorption was noted for carbonyl or hydroxyl groups in the IR spectrum. The ^{1}H NMR spectrum of **3cb** showed two broad singlets; each for one proton at δ_H = 11.45 and 11.30 assigned to the two protons of thiourea. In ^{13}C NMR spectrum of **3cb**, it was observed carbon signals at δ_C = 181.0 for C=S, 154.0 (thiazole-C-2), and 118.4 ppm for C-5 of thiazole moiety (Experimental Section).

For compound **4bb**, its molecular formula was proved by mass spectrometry and elemental analysis as $C_{30}H_{26}N_4S_2$ (Experimental Section). Mass spectrum showed also the molecular ion peak at *m/z* = 506 (55%), whereas the basic ion peak at *m/z* = 91, which related to the prescence of benzylic fragment pattern. The IR spectra of **4bb** showed the NH groups at ν = 3220-3215 cm^{-1}. In the ^{1}H NMR spectral data of **4bb** (Experimental Section), it can be seen two broad singlets appeared at δ_H = 10.25 and 10.08 ppm, which assigned to the two NH thiourea protons. Moreover, the two-dissimilar benzylic-CH_2 protons resonated at δ_H = 4.86 and 5.02 ppm, respectively. The ^{13}C NMR spectra was also in accordance to the proposed structure and showed the functional groups of carbon signals δ_C = 181.0 for the thioamide carbon and the two benzylic carbons at δ_C = 48.9 and 46.9 (Experimental section). The thiazole carbon signals were also resonated at δ_C = 156.8 (C-2), 145.0 (C-4) and 118.3 (thiazole-C-5).



Scheme 1. Reactions of hydrazinecarbothioamides **1a-d** with 2-bromoacetophenones **2a,b**.

When, the derivative **1b** reacted with 2-bromo-1-phenylpropan-1-one (**2a**), the reaction gave thiazole **5ba** (Scheme 1). Mass spectrum of **5ba** showed the molecular peak at *m/z* = 444. The ^{1}H NMR spectrum of compound **5ba** gave two broad singlets at δ_H = 10.20 and 8.20 for the two NH thiourea protons (Experimental Section). Moreover, the asymmetrical structure was corroborated *via* appearance of three singlets at δ_H = 4.8, 5.0, 2.3 and 2.1 of the two benzylic-CH_2 protons, CH_3 and thiol-H, respectively. The ^{13}C NMR spectrum supported the ^{1}H NMR spectroscopic data due to the prescence of the thione-C, thiazole-C-2 and the two benzylic carbons at δ_C =179.7, 156.6, 48.9, and 46.4, respectively. (Experimental Section). Again, and in case of **6db**, the two NH protons absorbed as two broad singlets at δ_H =11.00 and 10.20. Most indicative that ^{13}C NMR spectrum of **6db** elucidated the asymmetric structure of **6db** *via* the appearance the two carbon signals of the *p*-toyl-methyl groups at δ_C = 21.2 and 21.4 (see Experimental Section).

Under the condition mentioned above, **1d** reacted with **2a** to give the bis-thiazole **7da** in 74% yield (Scheme 1). The IR spectrum of **7da** didn't reveal any absorption corresponding to NH, OH and C=S groups (Experimental Section). Mass and elemental analysis revealed that the molecular weight of **7da** equals to the sum of **1d** with two moles of **2a** accompanied with elimination of two molecules of hydrogen bromide. In the meanwhile, ^{13}C NMR spectrum reveal carbon signals of an asymmetric molecule. Disappearance of the thione carbon in ^{13}C NMR spectrum, indicated that it was involved in cyclization process. The structure of *E*-configuration in **7da** was ultimately proved by X-ray structural analysis (Figure 1).

The suggested mechanism described the formation of thiazoles **3cb**, **4bb**, **5ba** and **6db** was based upon attacking of thione-lone pair to the α-bromo-C in **2a,b** (Scheme 2). That was followed by salt formation as in intermediate **10**. Subsequently, salt **10** would be neutralized and nitrogen lone-pair would attack to the carbonyl-C to form intermediate **11**. Elimination of water and HBr from **11** would give the thiazoles **3cb**, **4bb**, **5ba** and **6db** (Scheme 2). Ultimately, addition of a second molecule of **2a** to **11** along with extrusion of two molecules of water and HBr, would produce **7da** (Scheme 2).

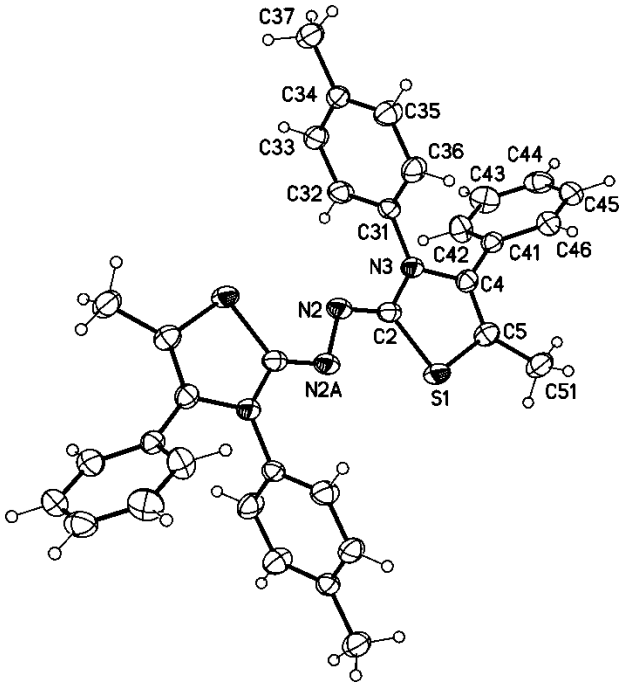
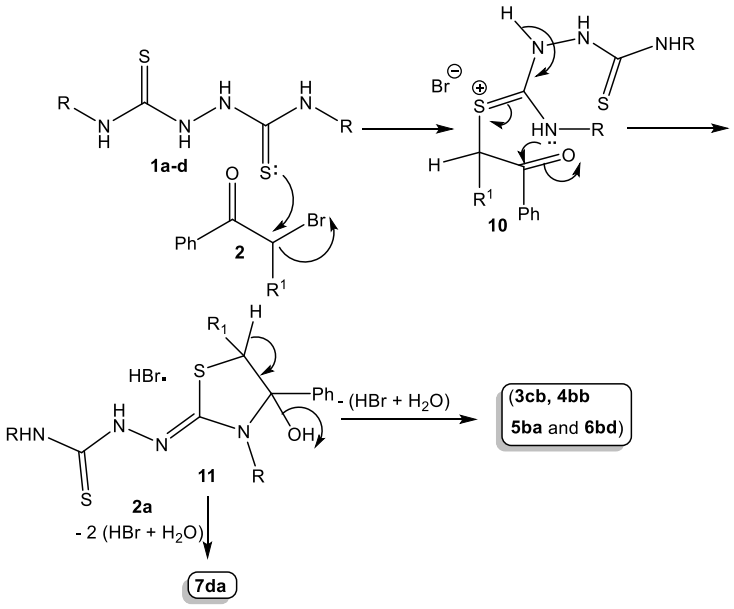


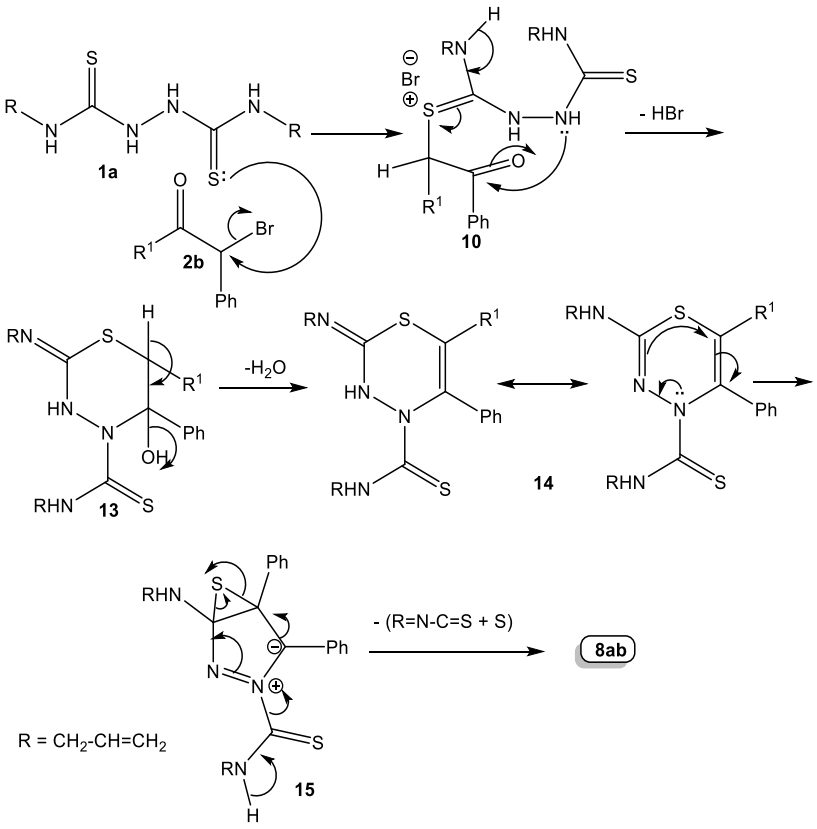
Figure 1. Molecular structure of **7da** (displacement parameters are drawn at 50% probability level).



Scheme 2. Suggested mechanism describing the formation of thiazoles **3cb**, **4bb**, **5ba**, **6bb** and free bis-thiazole **7da**.

In different manner, reaction of equal equivalents of both **1a** with 2-bromo-1,2-diphenylethan-1-one (**2b**) gave pyrazole **8ab** (Scheme 1). The IR spectrum of **8ab** showed the NH and aliphatic groups at ν = 3425-3400 and 2933-2974 cm^{-1}, respectively. The mass and elemental analysis elucidated the gross molecular formula of **8ab** as $C_{18}H_{17}N_3$. Mass spectrum showed the molecular ion peak at *m/z* = 275 (51%), whereas the base peak at *m/z* = 102. The ^{1}H NMR spectrum proved the prescence of allyl group and its protons. The NH-pyrazole was absorbed in ^{1}H NMR at δ_H =12.00 (Experimental Section). The ^{13}C NMR spectrum supported the ^{1}H NMR

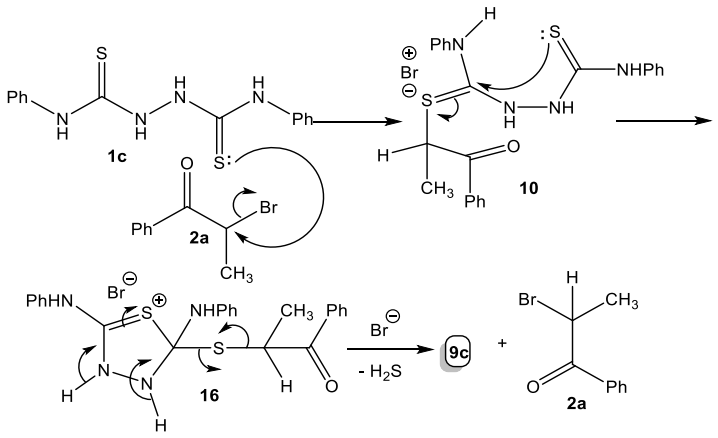
spectroscopic data *via* the appearance of the allylic-carbons at δ_C = 45.7, 114.8 and 133.3. The structure of **8ab** was corroborated by X-ray structure analysis (Figure 2).



Scheme 3. Suggested mechanism describing the formation of compound **8ab**.

The suggested mechanism for the formation of **8ab** starts also from the salt **10** (Scheme 3). Neutralization accompanied by elimination of HBr molecule, then addition of nitrogen-lone pair of the *N*-2 of the hydrazine group to the carbonyl-C would give intermediate **13** (Scheme 3). Elimination of water molecule from **13** would, thus, give **14**. Rearrangement was then occurred *via* amidine-like reaction to C-6 of the formed thiadiazine would led to salt **15**. Elimination of allyl isothiocyanate and extrusion of sulfur from **15** would, finally give **8ab** (Scheme 3).

Finally, on reacting hydrazinecarbothioamide derivative **1c** with **2a**, the reaction yielded the known product **9c**[27], Scheme 1). Heating the compound **1c** alone under the same condition didn't proceed to give **9c**, therefore we concluded that the presence of **2a** would enhance the formation of thiadiazole **9c**. Starting from the previous formed intermediate **10**, the other thione-lone pair would attack to the positively charged thiamido-C to form salt **16** (Scheme 4). Rearrangement and neutralization process in **16** and recombination of the eliminated Br anion would form **10** and recycled compound **2a** together with extrusion of H_2S (Scheme 4). Based upon TLC analysis with authentic sample of known *N*,*N'*-diphenyl-1,3,4-thiadiazole-2,5-diamine[27] and its IR and ^{1}H NMR, the structure compound **9c** was proved.



Scheme 4. Suggested mechanism describing formation of compound **9c** during reaction of **1c** with **2a**.

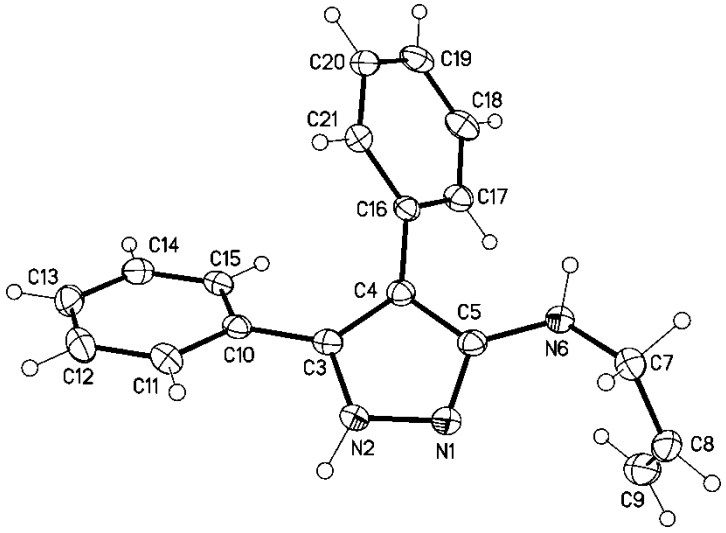


Figure 2. Molecular of **8ab** (displacement parameters are drawn at 50% probability level).

Conclusions

Our paper describes the synthesis of different types of heterocycles during the reactions of hydrazinecarbothioamides with electrophilic reagents. Therefore, much work will be done in our lab to investigate further reactions of hydrazinecarbothioamides.

Experimental Section

General. Melting points were determined on Stuart electrothermal melting point apparatus and were uncorrected. TLC analysis was performed on analytical Merck 9385 silica aluminum sheets (Kiselgel 60) with PF_{254} indicator. The IR spectra were recorded as KBr disks on Shimadzu-408 infrared spectrophotometer, Faculty of Science, Minia University. The NMR spectra were measured using a Bruker AV-400 spectrometer at the Karlsruhe Institut für Technologie (KIT), Institute of Organic Chemistry, Karlsruhe, Germany. Chemical

shifts were expressed as δ (ppm) with tetramethylsilane as internal reference. The samples were dissolved in DMSO-d_6, s = singlet, d = doublet, dd = doublet of doublet and t = triplet. Mass spectrometry were recorded on a Varian MAT 312 instrument in EI mode (70 eV), at the Karlsruhe Institut für Technologie (KIT), Institute of Organic Chemistry, Karlsruhe, Germany. Elemental analyses were carried out using Varian Elementary device in National Research Center, Giza, Egypt.

Starting materials. *N*,*N*'-Disubstituted-hydrazinecarbothioamides were prepared according to published procedures as were *N*,*N*'-diallylhydrazine-1,2-dicarbothioamide (**1a**)[27], *N*,*N*'-bis(benzyl)hydrazine-1,2-dicarbothioamide (**1b**), *N*,*N*'-diphenylhydrazine-1,2-dicarbothioamide (**1c**)[27], *N*,*N*'-bis(4'-methylphenyl)-hydrazine-1,2-dicarbothioamide (**1d**).[28] 2-Bromoacetophenones **2a,b** were bought from Aldrich.

General Procedure: reaction of hydrazinecarbothioamides 1a-d with 2-bromoacetophenones 1a,b. A mixture of hydrazinecarbothioamides (**1a-d**, 1 mmol) and 2-bromoacetophenones (**2a,b**, 1 mmol) in 30 mL dry EtOH together 0.5 mL of triethyl amine were stirred at room temperature for 10-12 h (the reaction was followed up by TLC analysis). In case of reaction between **1a** and **2b**, the reaction was completed after refluxing the reaction mixture for 3h. The formed precipitates were allowed to stand overnight and they were collected by suction filtration. The precipitates were then washed with cyclohexane, and dried at room temperature. Compounds **3cb**, **4bb**, **5ba**, **6db**, free bis-thiazole **7da**, pyrazole **8ab** and thiadiazole **9c** were obtained and were recrystallized from the stated solvents.

***N*-Phenyl-2-(3,4,5-triphenylthiazol-2(3*H*)-ylidene)hydrazine-1-carbothioamide (3cb)**. Yellow crystals (EtOH), yield: 0.38 g (80%), M.p.: 235 -7 °C (decomp.). IR (KBr): ν = 3330-3320 (NH), 3030 (Ar-CH), 1620 (C=N), 1590 (C=C), 1366 (C=S) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ_H = 11.45 (bs, 1H, NH), 11.30 (bs, 1H, NH), 7.80-7.75 (m, 2H, Ph-H), 7.70-7.65 (m, 2H, Ph-H), 7.56-7.46 (m, 5H, Ph-H), 7.30-7.15 (m, 5H, Ph-H), 7.00-6.85 (m, 4H, Ph-H), 6.80-6.75 (m, 2H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 181.0 (C=S), 154.0 (thiazole-C-2), 144.4 (thiazole-C-4), 138.3, 136.4 (Ar-*N*-C), 130.2, 130.0 (Ph-C), 128.4, 128.2, 127.8, 127.6, 127.4, 127.2, 127.0 (Ar-2CH), 126.8, 126.6, 126.4, 126.0 (Ar-CH), 125.8 (Ar-2CH), 118.4 (thiazole-C-5) ppm. MS (70 eV, Fab mass, %): *m/z* = 478 (92%), 385 (17), 328 (32), 268 (38), 152 (100). $C_{28}H_{22}N_4S_2$ (478.18): Calcd. C, 70.26; H, 4.63; N, 11.71. Found: C, 70.16; H, 4.60; N, 11.60.

***N*-Benzyl-2-(3-benzyl-4,5-diphenylthiazol-2(3*H*)-ylidene)hydrazine-1-carbothioamide (4bb).** Orange crystals (DMF/EtOH), yield: 0.41 g (82%), M.p.: 200-2 °C (decomp.).IR (KBr): ν = 3220-3215 (NH), 3030 (Ar-CH), 2777 (Aliph.-CH), 1581 (C=N), 1560 (C=C), 1370 (C=S) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ_H =10.25 (bs, 1H, NH), 10.08 (bs, 1H, NH), 7.80-7.76 (m, 2H, Ar-H), 7.70-7.50 (m, 5H, Ar-H), 7.30-7.15 (m, 4H, Ar-H), 7.00-6.86 (m, 2H, Ar-H), 6.80-6.50 (m, 7H, Ar-H), 5.02 (bs, 2H, CH_2-benzyl), 4.86 (bs, 2H, CH_2-benzyl) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 181.0 (C=S), 156.8 (thiazole-C-2), 145.0 (thiazole-C-4), 138.3, 136.4 (Ar-*N*-C), 131.6, 131.0 (Ph-C), 128.5, 128.3, 128.0, 127.9, 127.8, 127.6, 127.5, 127.2 (Ar-2CH), 126.4, 126.0, 125.8, 125.4 (Ar-CH), 118.3 (thiazole-C-5), 48.90, 46.9 (benzylic-CH_2) ppm. MS (70 eV, Fab mass, %): *m/z* = 506 (55%), 91 (100). $C_{30}H_{26}N_4S_2$ (506.16): Calcd. C, 71.12; H, 5.17; N, 11.06. Found: C, 71.00; H, 5.08; N, 11.10.

***N*-Benzyl-2-(3-benzyl-5-methyl-4-phenylthiazol-2(3*H*)-ylidene)hydrazine-1-carbothioamide (5ba).** Brown crystals (DMF/EtOH), 0.40 g (90%), M.p.: 260-2 °C (decomp.). IR (KBr): ν = 3330-3260 (NH), 3060-3030 (Ar-CH), 2900-2820 (Aliph.-CH), 1630, 1610 (C=N), 1560 (C=C) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ_H =10.20 (s, 1H, NH-thiourea), 8.20 (bs, 1H, NH-thiourea), 7.60-7.50 (m, 5H, Ar-H), 7.35-7.10 (m, 5H, Ar-H), 6.94-6.86 (m, 5H, Ar-H), 5.00 (bs, 2H, CH_2-benzyl), 4.80 (bs, 2H, CH_2-benzyl), 2.30 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 179.7 (C=S), 169.7 (C-2), 144.7 (C-5), 139.1 (C-4), 133.2, 132.1, 131.3 (Ar-C), 129.2, 128.8, 128.6, 127.8 (Ar-2CH), 126.8, 126.6, 126.2 (Ar-CH-*p*), 124.8, 124.4 (Ar-2CH), 48.9, 46.4 (benzyl-CH_2), 22.0 (CH_3) ppm. MS (70 eV,

Fab mass, %): *m/z* = 444 ([M^+, 100). $C_{25}H_{24}N_4S_2$ (444.62): Calcd. C, 67.54; H, 5.44; N, 12.60. Found: C, 67.40; H, 5.58; N, 12.70.

2-(4,5-Diphenyl-3-(*p*-tolyl)thiazol-2(3*H*)-ylidene-N-(*p*-tolyl)hydrazine-1-carbothioamide (6db). Brown crystals (DMF/EtOH), 0.45 g (87%), M.p. 282-4 °C (decomp.). IR (KBr): ν = 3340-3210 (NH), 3090 (Ar-CH), 2900-2820 (Aliph.-CH), 1630, 1620 (C=N), 1570 (C=C) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ_H =11.00 (s, 1H, NH-thiourea), 10.20 (bs, 1H, NH-thiourea), 7.60-7.57 (dd, 2H, *J* = 7.8, 0.7 Hz, Ar-H), 7.40-7.15 (m, 5H, Ar-H), 7.20-7.00 (m, 5H, Ar-H), 6.80-6.65 (m, 4H, Ar-H), 6.56-6.52 (dd, 2H, *J* = 7.8, 1.0 Hz, Ar-H), 2.40 (s, 3H, CH_3-Ar-C), 2.20 (s, 3H, CH_3-Ar-C) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 180.0 (C=S), 168.0 (C=N), 144.5 (C-5), 139.2 (C-4), 138.2, 138.0 (Ar-*N*-C), 136.2, 135.4 (Ar-C-CH_3), 132.3, 130.1 (Ar-C), 128.8, 128.7, 128.6, 128.0, 127.8, 127.6, 127.2 (Ar-2CH), 126.6, 126.4 (Ar-CH-*p*), 124.8 (Ar-2CH), 22.3, 22.1 (CH_3-Ar) ppm. MS (70 eV, Fab mass, %): *m/z* = 506 ([M^+], 100). $C_{30}H_{26}N_4S_2$ (506.68): Calcd. C, 71.11; H, 5.17; N, 11.06. Found: C, 71.20; H, 5.10; N, 11.28.

(1*E*,2*E*)-1,2-Bis(5-methyl-4-phenyl-3-(*p*-tolyl)thiazol-2(3*H*)-ylidene)hydrazine (7da). Yellow crystals (DMF/EtOH), yield: 0.41 g (74%), M.p. = 230-232 °C. IR (KBr): ν = 3030-3009 (Ar-CH), 2960, 2940 (Aliph-CH), 1630-1610 (C=N), 1560 (C=C) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ_H = 7.75-7.70 (dd, 4H, *J* = 8.0, 0.9 Hz, Ar-H), 7.40-7.20 (m, 6H, Ar-H), 7.10-6.80 (m, 8H, Ar-H), 2.26 (s, 6H, CH_3), 2.20 (s, 6H, Ar-CH_3) ppm.^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 163.2 (2C-2, thiazole), 147.8 (2C-4, thiazole), 139.8 (Ar-2C-N), 136.8, 131.0 (Ph-2C), 128.6, 128.5, 127.8 (Ar-4CH), 126.5 (Ph-2CH-*p*), 120.4 (Ar-4CH), 90.6 (2C-5, thiazole), 22.0, 18.9 ($2CH_3$) ppm. MS (70 eV, Fab mass, %): *m/z* = 559 (M + 1, 22), 558 (M^+, 34), 250 (100), 101 (30). $C_{34}H_{30}N_4S_2$ (558.76): Calcd. C, 73.09; H, 5.41; N, 10.03. Found: C, 73.30; H, 5.30; N, 10.0.

***N*-Allyl-4,5-diphenyl-1*H*-pyrazole-3-amine (8ab).** Buff crystals (EtOH), yield: 0.20 g (75%), M.p.: 140-142 °C. IR (KBr): ν = 3425-3400 (NH), 2933, 2974 (Aliph-CH), 1641-1601 (C=N), 1533 (C=C) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ_H = 12.00 (bs, 1H, Pyrazole- NH pyrazole), 7.80-7.60 (m, 6H, Ph-H), 7.45-7.30 (m, 5H, Ph-H, allyl-NH), 5.80 (m, 1H, allyl-CH=), 5.30-5.40 (m, 2H, allyl-CH_2), 3.90 (m, 2H, CH_2-allyl) ppm.^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 143.0 (pyrazole-C-3), 139.8 (pyrazole-C-5), 136.0, 133.4 (Ph-C), 133.3 (allyl-CH=), 129.0, 128.6, (Ar-2CH), 127.8, 127.8 (Ar-CH-*p*), 127.8, 127.4 (Ar-2CH), 114.8 (allyl-CH=0), 112.0 (pyrazole-C4), 45.7 (allyl-CH_2) ppm. MS (70 eV, Fab mass, %): *m/z* = 275 (51), 102 (100). $C_{18}H_{17}N_3$ (275.36): Calcd. C, 78.52; H, 6.22; N, 15.26. Found: C, 78.40; H, 6.10; N, 15.12.

N,N'*-Diphenyl-1,3,4-thiadiazole-2,5-diamine (9c*). Colorless crystals (MeOH), yield: 0.19 g (72%), M.p.: 240 °C (lit.[27] 239–240°C).

Crystal Structure Determinations. The single-crystal X-ray diffraction study were carried out on a Bruker D8 Venture diffractometer with Photon100 detector at 123(2) K using Cu-Kα radiation (λ= 1.54178 Å. Direct Methods (SHELXS-97)[29] were used for structure solution and refinement was carried out using SHELXL-2014 (full-matrix least-squares on F2)[30]. Hydrogen atoms were localized by difference electron density determination and refined using a riding model (H(N) free). Semi-empirical absorption corrections were applied. For **8ab** an extinction correction was applied.

7da: orange crystals, $C_{34}H_{30}N_4S_2$, Mr = 558.74, crystal size 0.12 × 0.08 × 0.06 mm, monoclinic, space group $P2_1/c$ (No. 14), a = 9.7213(3) Å, b = 13.9974(4) Å, c = 10.8289(3) Å, β = 103.137(2)°, V = 1434.96(7) $Å^3$, Z = 2, ρ = 1.293 Mg/m^{-3}, μ(Cu-Kα) = 1.911 mm^{-1}, F(000) = 588, $2\theta_{max}$ = 144.4°, 21286 reflections, of which 2822 were independent (Rint = 0.054), 183 parameters, R1 = 0.040 (for 2354 I > 2σ(I)), wR2 = 0.102 (all data), S = 1.05, largest diff. peak / hole = 0.322 / -0.211 e Å-3.

8ab: yellow crystals, $C_{18}H_{17}N_3$, Mr = 275.34, crystal size 0.36 × 0.30 × 0.06 mm, monoclinic, space group C2/c (No. 15), a = 29.1406(8) Å, b = 11.0744(3) Å, c = 9.2494(2) Å, β = 104.998(1)°, V = 2883.23(13) $Å^3$, Z = 8, ρ = 1.269 Mg/m^{-3}, μ(Cu-Kα) = 0.596 mm^{-1}, F(000) = 1168, $2\theta_{max}$ = 144.4°, 18490 reflections, of which 2847 were

independent (Rint = 0.031), 197 parameters, 2 restraints, R1 = 0.034 (for 2572 I > 2σ(I)), wR2 = 0.084 (all data), S = 1.04, largest diff. peak / hole = 0.217 / -0.201 e Å-3.
The CCDC 1553071 (**7da**), and CCDC 1553072 (**8ab**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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