

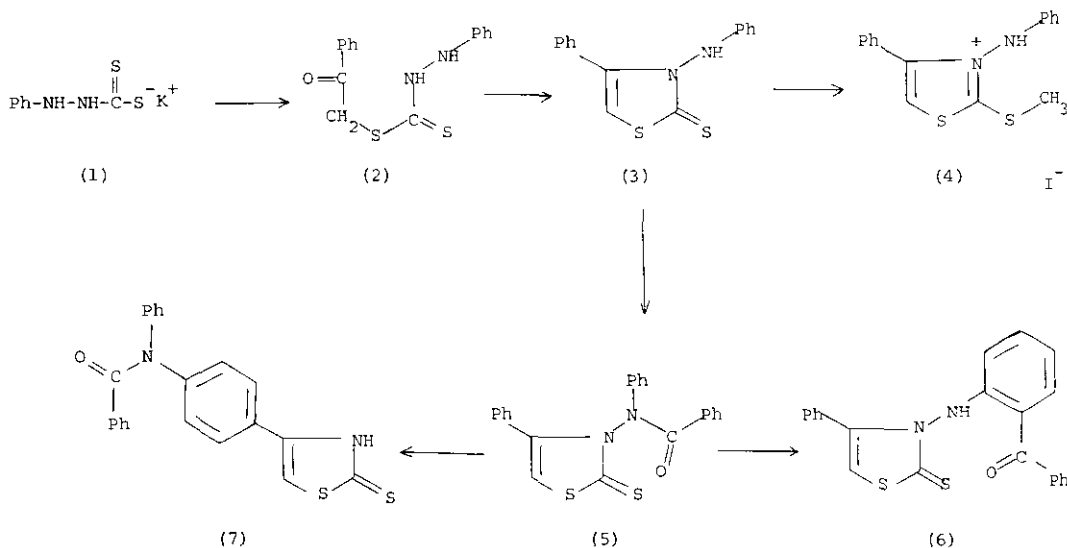
NOVEL REARRANGEMENT OF A 3-AMINO-1,3-THIAZOLE-2-THIONE

Alan R. Katritzky* and Shibli Bayyuk#

Department of Chemistry, University of Florida, Gainesville, FL 32611
U.S.A.

Abstract - Some new derivatives of 3-amino- and 3-phenylamino-4-phenyl-1,3-thiazole-2-thione have been prepared and characterized. When 3-(N-phenylbenzamido)-4-phenyl-1,3-thiazole-2-thione is rearranged thermally it gives 3-(2-benzoylphenylamino)-4-phenyl-1,3-thiazole-2-thione and 4-[4-(N-phenylbenzamido)phenyl]-1,3-thiazole-2-thione.

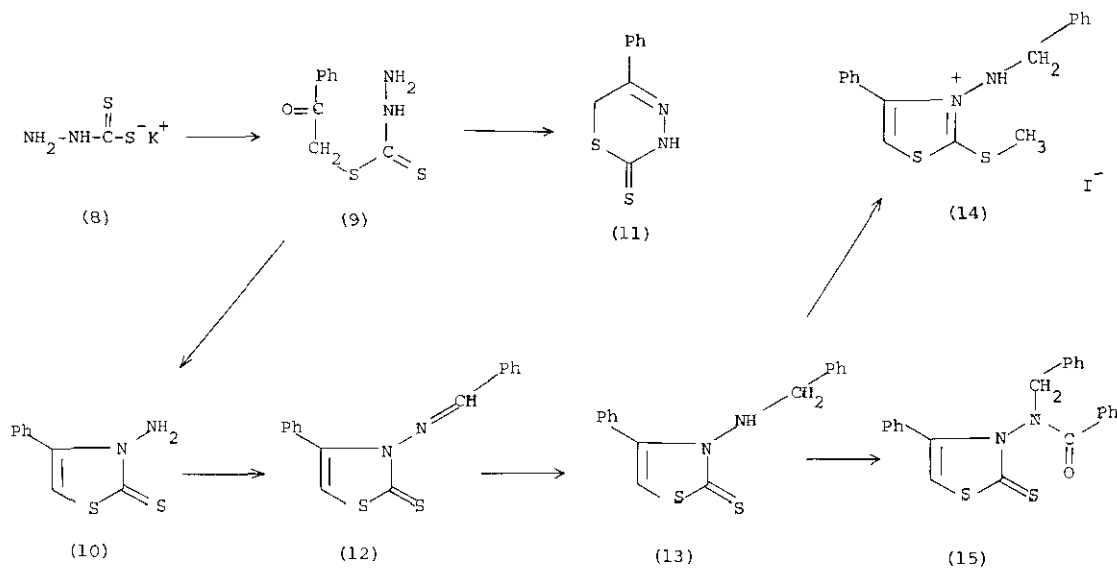
Considerable work has appeared on the chemistry of N-amino derivatives of heterocycles, and the subject has been well reviewed.^{1,2} Among this work, 3-amino-1,3-thiazol-2-ones and their 2-thione analogues have been prepared and some of their reactions explored.^{3,4,5} We now report an unusual thermally induced rearrangement of 3-(N-phenylbenzamido)-4-phenyl-1,3-thiazole-2-thione and some other reactions of 3-amino-4-phenyl-1,3-thiazole-2-thiones.



FORMULA FLOW CHART I

Permanent Address: Chemistry Department, University of Jordan, Amman, Jordan.

Following the work of Ege and his co-workers³, we have prepared 3-phenylamino-4-phenyl-1,3-thiazole-2-thione (3). Our melting point (69-70°C) was considerably different from that given in the literature (116-117°C), probably as a result of a different polymorphous form. Intermediate (2) had melting point in agreement with that given in the literature. The thione (3) formed a methiodide by alkylation of the sulfur atom as expected⁶ to give (4). The thiazole ring 5-CH signal shifted from delta 6.69 to 8.27 ppm upon methylation and the NH signal appeared at delta 9.80 ppm. Benzoylation of (3) in the presence of p-dimethylaminopyridine (DMAP) gave again as expected the benzoyl derivative (5).



FORMULA FLOW CHART II

We also prepared the corresponding 3-amino-4-phenyl-1,3-thiazole-2-thione (10) according to the method of Sandstrom⁴, and characterized for the first time the potassium salt (8). As previously reported, ring-closure of intermediate (9) gave varying amounts of the desired (10) together with a byproduct, to which we now assign the structure of 5-phenyl-3,6-dihydro-1,3,4-thiadiazine-2-thione (11). However, by prolonging the time of reaction, (9) was converted entirely into the desired (10) without formation of (11). Thus, the production of (11) from (9) is reversible and formation of (11) can be completely suppressed. The detailed structure of (11) is supported spectrally: ¹H nmr showed a CH₂ 2H-singlet at delta 4.10 ppm. ¹³C nmr (aided by INEPT) showed the CH₂ signal at delta 24.76 ppm; a signal at delta 187.69 ppm indicated the presence of C=S group, while that at delta 147.85 ppm corresponded to C₅ of the

thiadiazine-2-thione ring, the remaining 4 signals were characteristic of a C_6H_5 - group. The thione structure for (11) is in agreement with those assigned to similar compounds by Ege and coworkers^{3,7} on the basis of uv spectroscopy, but not with the alternative 2-mercaptothiadiazine tautomeric structure previously assigned by Mathes⁸ and Sandstrom.⁴

N-Amino compound (10) was converted into the benzylidene derivative (12) as previously reported⁴ but under similar conditions it failed to react with ketones probably due to steric factors. Imine (12) was reduced with sodium borohydride, and the resulting benzylamino compound (13) converted into a benzoyl derivative (15) and a methiodide (14). The structures of compounds (3), (5)-(7), (10) and (12)-(15) were also confirmed by their 1H , ^{13}C and mass spectra, and by elemental analysis.

On heating the benzoyl derivative (5), it underwent rearrangement. Out of the complex mixture, two major products (6) and (7) were isolated. The formation of (6) from (5) corresponds to a rearrangement of the Fries type, but the formation of (7) involves a deep seated rearrangement of the molecule that is reminiscent of the semidine rearrangement.^{9,10}

Attempts to grow large enough crystals from (6) and (7) for X-ray diffractometry failed and structural assignments were based on spectral and chemical evidence. The ir spectrum of compound (6) showed a strong N-H stretching at $3290-3280\text{ cm}^{-1}$ characteristic of acyclic amines and strong Nu C=O stretching at $1650-1635\text{ cm}^{-1}$. The absence of an amide functional group is supported by the inability of (6) to liberate benzoic acid upon protracted refluxing with 70% H_2SO_4 . In comparison, the parent compound (5) displayed no absorption attributable to Nu N-H but exhibited strong Nu C=O (amide) at $1690-1675\text{ cm}^{-1}$. That (6) is an isomer of (5) is evidenced by their mass spectra which both showed molecular ion base peaks at m/e 388, and by elemental analysis. The 1H nmr of (6) showed a broad multiplet at δ 7.38-8.03 and its ^{13}C spectrum showed characteristic signals for the C=S (δ 185.72 ppm) and C=O (δ 166.16 ppm) groups. In (5) these signals appeared at δ 185.64 and 165.92 ppm, respectively. ^{13}C nmr aided by INEPT also showed that (6) had seven quaternary C atoms whereas (5) had only six. That the benzoyl group in (6) is ortho to the -NH- group is evidenced by the fact that no doublet or doublet of doublets occurred in the 1H nmr and the ^{13}C spectrum showed a total of 18 signals which are too many for para orientation.

The ir spectrum of (7) displayed a strong nu C=O stretching at $1680 - 1670\text{ cm}^{-1}$ characteristic of an amide group and a moderate absorption band at 3370 cm^{-1} characteristic of a secondary cyclic amine. Further evidence for the presence of this cyclic amino functionality is a 1H singlet at δ 9.85 in the 1H spectrum. The liberation of benzoic acid from (7) upon acid hydrolysis confirmed the presence of the N-phenylbenzamido group and assignment of its para

orientation on the phenyl attached to C₄ of the thiazole-2-thione ring explained the two sets of doublets at delta 7.96 and at delta 8.62 with J values of 7.8 and 8.3 Hz respectively in the ¹H spectrum. ¹³C nmr showed a total of 16 signals, seven of which corresponded to quaternary C atoms, and also confirmed the presence of C=S (delta 185.54 ppm) and C=O (delta 165.40 ppm) functional groups. The mass spectrum of (7) showed a molecular ion (base peak) at 388, and also a significant fragment (% Int. Base 8.41) peak at 196 that corresponds to the N-phenylbenzamido group. This fragment also appeared but with lower intensity (4.64%) in the mass spectrum of (5) but was entirely missing from the spectrum of (6). Elemental analysis also supported the assigned structure of compound (7).

EXPERIMENTAL

Mps are uncorrected and were determined on a Bristoline hot stage microscope. Ir spectra were recorded (in CHBr₃ solution) on a Perkin-Elmer 283 B grating spectrophotometer and calibrated with polystyrene. ¹H nmr spectra were obtained on a Varian EM-360L (60 MHz) spectrometer using tetramethylsilane as internal standard and ¹³C nmr spectra were obtained on a JEOL FX-100 FT spectrometer operating at 25.00 MHz with tetramethylsilane as internal standard. Samples were run in deuteriochloroform unless stated otherwise. Mass spectra were measured at 70 eV using A.E.I. MS-30 mass spectrometer operating with a Kratos DS-55 data system. Column chromatographic separations were achieved using M.C.B. Silica Gel (230-400 mesh) under slight positive pressure.

Potassium (N'-Phenylhydrazino)dithioformate (1).- To phenylhydrazine (86.4 g, 0.80 mol) in absolute ethanol (800 ml) at 0 °C, ice-cold carbon disulphide (60.8 g, 0.80 mol) was added gradually with stirring. After 1 min, a white crystalline precipitate started to form, and potassium hydroxide (44.8 g, 0.80 mol) in absolute ethanol (200 ml) previously cooled to 0 °C was added gradually with stirring. After 4 h at 4 °C, the potassium (N'-phenylhydrazino)dithioformate was washed with ether and dried (153 g, 86%). The colourless rod-shaped prisms had mp 144-145 °C (decomp.) (from methanol).^{11,12}

Phenacyl (N'-Phenylhydrazino)dithioformate (2).- Phenacyl bromide (119.4 g, 0.60 mol) in ethanol (900 ml) was added dropwise over 5 h with stirring at 0 °C to potassium (N'-phenylhydrazino)dithioformate (1) (133.2 g, 0.60 mol) in water (360 ml). A yellow oil separated and crystallized, water (1200 ml) was added, and the mixture was left for 16 h at 4 °C. The product was collected and washed with water. Phenacyl (N'-phenylhydrazino)dithioformate (168.6 g, 93%) formed needles, mp 151 °C (from benzene) [Lit. mp 152 °C]³; ν_{max} . 3300, 3020, 1675, 1595, 1490, 1360, 1300, 1135, 1040, 738 and 680 cm⁻¹.

3-Phenylamino-4-phenyl-1,3-thiazole-2-thione (3).- Phenacyl (N'-phenylhydrazino)dithioformate (2) (3.02 g, 10 mmol) was refluxed in methanol (75 ml) with HCl/MeOH (5 ml of 5% solution) for 15 min. To the hot solution, water was gradually added until turbidity was induced. The mixture was cooled at 4 °C for 8 h, and the product collected and dried (2.04 g,

72%). The thione crystallized from methanol in prisms, mp 69-70 °C [Lit. mp 116-117°C]³; ν_{\max} . 3290-3220, 3100, 3060, 3020, 1600, 1492, 1447, 1310, 1280, 1232, 1180, 1142, 1080, 1060, 1030, 1000, 975, 890, 860, 840, 770, 750, 728, 690 and 660-640 cm^{-1} ; ^1H nmr (CDCl_3) delta: 6.69 (1 H, s, thiazole ring 5-H), and 6.93-7.93 (11 H, m, Ar-H and N-H); ^{13}C nmr (CDCl_3) delta: 105.61 (thiazole ring C-4), 114.79, 122.46, 128.31 and 129.01 (Ar-CH), 129.48 (thiazole ring C-5), 144.10 and 144.80 (Ar-C), 186.05 (C=S); m/z 284 (M^+ , 29.16%), 251 (12.94), 193 (13.59), 134 (100.00), 93 (22.59), 77 (12.18), 65 (23.53), 51 (10.83) and 39 (18.58); Anal. Calcd. for $\text{C}_{15}\text{H}_{12}\text{N}_2\text{S}_2$: C 63.35, H 4.25, N 9.85. Found: C 62.98, H 4.11, N 9.85.

2-Methylthio-3-phenylamino-4-phenyl-1,3-thiazolium Iodide (4).- 3-Phenylamino-4-phenyl-1,3-thiazole-2-thione (3) (4.26 g, 15 mmol), CH_2Cl_2 (20 ml), C_6H_6 (30 ml) and methyl iodide (6.39 g, 45 mmol) were kept at 20 °C for 30 h. The mixture was evaporated at 50 °C/20mm to give the iodide (5.56 g, 87%) which formed pale yellow prismatic plates (from ethanol), mp 97-98 °C; ν_{\max} . 3120-3050, 3015, 2970-2920, 1598, 1485, 1440, 1420, 1380, 1340, 1310, 1282-1275, 1230, 1175, 1160, 1145, 1135, 1078-1070, 1058, 1022, 995, 970-960, 915, 875, 855, 835, 810, 750-743, 685, 660 and 636 cm^{-1} ; ^1H nmr (CDCl_3) delta: 2.77 (3 H, s, S- CH_3), 6.53-7.97 (10 H, m, Ar-H), 8.27 (1 H, s, thiazole ring 5-H) and 9.80 (1 H, s, N-H).

3-(N-Phenylbenzamido)-4-phenyl-1,3-thiazole-2-thione (5).- 3-Phenylamino-4-phenyl-1,3-thiazole-2-thione (3) (5.32 g, 18.7 mmol), methylene chloride (24 ml), benzoyl chloride (3.59 g, 25.6 mmol), *p*-dimethylaminopyridine (DMAP) (0.015 g) and triethylamine (15 ml), were stirred at 20 °C for 15 h. The mixture was evaporated at 40 °C/20 mm, and was washed well with water to remove DMAP. The thione (5) crystallized from ethanol as creamy prisms (5.67 g, 78%), mp 172-173 °C; ν_{\max} . 3105, 3060, 3020, 2253, 1690-1675, 1585, 1480, 1440, 1315, 1300-1280, 1255, 1228, 1140-1135, 1113, 1050, 1020, 980, 917, 840, 730, 690 and 660-635 cm^{-1} ; ^1H nmr [$\text{CDCl}_3/(\text{CD}_3)_2\text{SO}$] delta: 6.53-7.77 (m); ^{13}C nmr [$\text{CDCl}_3/(\text{CD}_3)_2\text{SO}$] delta: 106.08 (thiazole ring C-4), 123.22, 125.56, 126.38, 126.90, 127.20, 128.48, 129.65, 131.47, 138.54 and 141.41 (Ar-Cs + thiazole ring C-5), 165.92 (C=O), and 185.64 (C=S); m/z 388 (M^+ , 7.67%), 279 (5.09), 196 (4.64), 180 (9.58), 134 (23.88), 105 (100.00), 89 (5.06), 77 (61.25), 65 (5.03), 51 (18.44) and 28 (43.48); Anal. Calcd. for $\text{C}_{22}\text{H}_{16}\text{N}_2\text{OS}_2$: C 68.02, H 4.15, N 7.21. Found: C 67.98, H 4.07, N 7.03.

Thermal Rearrangement of 3-(N-Phenylbenzamido)-4-phenyl-1,3-thiazole-2-thione.- Compound (5) (2.065 g, 5.3 mmol) was heated at 183 °C for 35 min. TLC examination of the resulting brown sticky mass revealed six spots (A-F) of the following R_f values (in $\text{CHCl}_3/\text{C}_6\text{H}_{14}$; 40/60 V/V): 0.13, 0.20, 0.33, 0.54, 0.75 and 0.84 respectively. In addition, a dark immobile spot remained at the origin. Components A (R_f 0.13) and D (R_f 0.54), the major products, were isolated by column chromatography (using silica gel and gradient elution with $\text{CHCl}_3/\text{C}_6\text{H}_{14}$) and recrystallized yielding chromatographically pure crystalline products.

Product A was 3-(2-benzoylphenylamino)-4-phenyl-1,3-thiazole-2-thione (6) (0.192 g, 9%), it formed prisms, mp 204-205 °C (from CHCl_3); ν_{\max} . 3290-3280, 3163, 3100, 3020, 1650-1635, 1600, 1590, 1578, 1527, 1497, 1480, 1446, 1423, 1400, 1363, 1337, 1327, 1315, 1290, 1257, 1240, 1180, 1142, 1115, 1097, 1070, 1042, 1010, 992, 950, 935, 912, 890, 832, 802, 775, 730, 713, 705, 685 and 655 cm^{-1} ; ^1H nmr [$(\text{CD}_3)_2\text{SO}$] delta: 7.38-8.03 (m); ^{13}C nmr [$(\text{CD}_3)_2\text{SO}$] delta: 115.14, 121.36, 121.64, 123.92, 125.74, 126.03, 127.60, 127.84, 128.37, 128.60, 128.95, 131.99, 133.69, 134.68, 135.50 and 141.35 (Ar-Cs + thiazole ring C-4 and C-5), 166.16 (C=O) and 185.72 (C=S); m/z 388

(M⁺, 17.79%), 134 (4.48), 105 (100), 77 (44.88), 63 (1.99) and 51 (7.08); Anal. Calcd. for C₂₂H₁₆N₂OS₂: C 68.02, H 4.15, N 7.21. Found: C 67.73, H 4.10, N 7.01.

Product D was 4-[4-(N-phenylbenzamido)phenyl]-1,3-thiazole-2-thione (7) (0.507 g, 25%), it formed prismatic needles, mp 125-126 °C (from ethanol); ν_{\max} . 3370, 3108, 3020, 2250, 1680-1670, 1600, 1575, 1510, 1490, 1472, 1440, 1430, 1300, 1250, 1145-1135, 1070, 1023, 890, 835, 790, 770, 753, 738, 725, 690 and 675-630 cm⁻¹; ¹H nmr (300 MHz; CDCl₃) delta: 7.17-7.80 (11 H, m), 7.96 (2 H, d, J = 7.8 Hz), 8.62 (2 H, d, J = 8.3 Hz) and 9.85 (1 H, s, N-H); ¹³C nmr (CDCl₃) delta: 114.97, 120.47, 122.22, 124.68, 126.14, 127.31, 128.31, 128.66, 131.88, 132.05, 133.34, 134.45, 136.26, 140.59 (Ar-Cs + thiazole ring C-4 and C-5), 165.42 (C=O) and 185.54 (C=S); m/z 388 (M⁺, 11.42%), 355 (2.47), 283 (28.16), 251 (91.68), 222 (33.60), 196 (8.41), 134 (8.16), 105 (100), 77 (42.81) and 51 (5.25); Anal. Calcd. for C₂₂H₁₆N₂OS₂: C 68.02, H 4.15, N 7.21. Found: C 67.68, H 3.98, N 6.98.

Acid Hydrolysis of 4-[4-(N-Phenylbenzamido)phenyl]-1,3-thiazole-2-thione (7).- Compound (7) (0.120 g, 0.3 mmol) was heated at gentle boiling with 70% H₂SO₄ (5 ml) under reflux condenser for 15 min. The colourless needle-shaped crystals that sublimed were collected from the condenser and dried (0.031 g, 82%), mp 122 °C; m/z 122 (M⁺, 82.09%), 105 (100.00), 77 (80.30), 51 (43.53) and 45 (3.62); Anal. Calcd. for C₇H₆O₂: C 68.85, H 4.95. Found: C 68.99, H 4.92.

Upon treatment of (6) under the same conditions but for 1 h, the liberation of benzoic acid could not be detected.

Potassium hydrazinodithioformate (8).- To anhydrous hydrazine (25.6 g, 0.8 mol) in absolute ethanol (800 ml) at 0 °C carbon disulphide (60.8 g, 0.8 mol) was added gradually with shaking followed by ice-cold potassium hydroxide (44.8 g, 0.8 mol) in absolute ethanol (200 ml). After standing at 4 °C for 3 h more, potassium hydrazinodithioformate (56.98 g, 49%) was collected and washed with ice cold methanol. The salt was recrystallized from methanol yielding prisms; mp 112-113 °C (decomp.)¹³; Anal. Calcd. for CH₃N₂KS₂: C 8.21, N 19.15. Found: C 8.45, N 19.15. Found: C 8.45, N 19.15.

Phenacyl Hydrazinodithioformate (9).- To potassium hydrazinodithioformate (8) (29.2 g, 0.2 mol) in water (120 ml), phenacyl bromide (39.8 g, 0.2 mol) in absolute ethanol (300 ml) was added dropwise at 4 °C over 4 h with stirring, followed by water (400 ml). The mixture was held at 4 °C for 16 h, and the thioformate was collected, washed with water and dried (40.9 g, 90%). Recrystallization from benzene gave rod-shaped prisms, mp 124 - 125 °C [Lit. mp 126-127 °C]⁴; ν_{\max} . 3360, 3295, 3180, 3020, 2250, 1600, 1440, 1390-1375, 1327, 1305, 1245, 1208, 1040, 960, 910, 855, 800, 760, 725 and 665-625 cm⁻¹.

3-Amino-4-phenyl-1,3-thiazole-2-thione (10) and 5-Phenyl-3,6-dihydro-1,3,4-thiadiazine-2-thione (11).- Phenacyl hydrazinodithioformate (9) (9.27 g, 41 mmol) was refluxed for 30 min with aqueous hydrochloric acid (15N, 10 ml) in absolute ethanol (100 ml). The clear yellow solution was cooled to 20 °C, and poured gradually with stirring into water (400 ml) at 0 °C. A yellow oil separated, which upon continued cooling and scratching, solidified to a mixture (8.0 g) of (10) and (11). The crude product was ground with 1N NaOH (40 ml). The yellow insoluble fraction was filtered off, washed well with water and dried to give 3-amino-4-phenyl-1,3-

thiazole-2-thione (4.13 g, 48%), which crystallized as creamy flakes, mp 146-147 °C (from ethanol) [Lit. mp 146-147 °C]⁴; ν_{\max} . 3340, 3180-3130, 3010, 2248, 1600, 1570, 1430, 1405, 1300, 1280, 1260, 1200, 1140-1125, 1070, 1050, 895, 830, 750 and 650-620 cm^{-1} ; ¹H nmr [(CD₃)₂SO] delta: 6.15 (2 H, s, NH₂), 7.20 (1 H, s, thiazole ring 5-H) and 7.43-7.93 (5 H, m, Ar-H); ¹³C nmr [(CD₃)₂SO] delta: 106.54 (thiazole C-4), 128.19, 128.89 and 129.18 (Ar-CH), 130.00 (thiazole C-5), 143.23 (Ar-C) and 181.66 (C=S).

The clear alkaline yellow filtrate was acidified with dilute HCl to precipitate the dihydrothiadiazine-2-thione (11) that was collected, washed with water and dried (2.45 g, 29%). Recrystallization of (11) from ethanol afforded yellow flakes; mp 135-136 °C [Lit. mp 136-137 °C]⁴; ν_{\max} . 3280-3250, 3020, 2250, 1610, 1483, 1440, 1270, 1215, 1175, 1140-1130, 1060, 985, 930, 840, 760, 720 and 650-625 cm^{-1} ; ¹H nmr[(CD₃)₂SO] delta: 4.10 (2 H, s, CH₂) and 7.47-7.93 (5 H, m, Ar-H); ¹³C nmr [(CD₃)₂SO] delta: 24.76 (C₆ of thiadiazine-2-thione ring), 126.67 (m-C atoms of phenyl group), 128.78 (o-C atoms of phenyl group), 130.65 (p-C atom of phenyl group), 133.81 (C₁ of phenyl group), 147.85 (C₅ of thiadiazine-2-thione ring), 187.69 (C₂ of thiadiazine-2-thione ring); m/z 208 (M⁺, 66.77%), 176 (2.83), 132 (6.64), 103 (100.00), 77 (40.83), 59 (5.29) and 51 (22.83); Anal. Calcd. for C₉H₈N₂S₂: C 51.90, H 3.87, N 13.45. Found: C 52.01, H 3.93, N 13.34.

3-Benzylideneamino-4-phenyl-1,3-thiazole-2-thione (12).- To 3-amino-4-phenyl-1,3-thiazole-2-thione (10) (3.0 g, 14.4 mmol) in absolute ethanol (75 ml) at 60 °C, sodium acetate (0.6 g) in EtOH/H₂O (3 ml) and benzaldehyde (3.0 g, 28.8 mmol) were added. The reaction mixture was acidified with aqueous hydrochloric acid (15N, 4 ml) and heated at 60 - 70 °C for 2 h. After cooling at 4 °C for 3 h, the yellow thione separated, it was washed with ice-cold ethanol (10 ml) and dried (3.82 g, 90%). Recrystallization from ethanol gave yellow rod-shaped prisms, mp 114-115 °C [Lit. mp 115-116 °C]⁴; ν_{\max} . 3020, 2335, 2245, 1600, 1570, 1440, 1275, 1245, 1220, 1132, 1050, 935, 750, 720, 680 and 640-635 cm^{-1} ; ¹H nmr (CDCl₃) delta: 6.63 (1 H, s, thiazole 5-H), 7.33-8.03 (10 H, m, Ar-H) and 9.58 (1 H, s, =CH-).

3-Benzylamino-4-phenyl-1,3-thiazole-2-thione (13).- 3-Benzylideneamino-4-phenyl-1,3-thiazole-2-thione (12) (1.6 g, 5.4 mmol) in methanol (50 ml) was stirred at 25 °C for 2 h with sodium borohydride (3.8 g) added at intervals. The solvent was then removed at 40 °C under vacuum, the solid residue was broken up with water (30 ml) and the mixture was extracted with CH₂Cl₂. After drying (MgSO₄), solvent was removed at 30 °C under vacuum and the benzylaminothione recrystallized from ethanol to give prismatic rods (1.03 g, 81%); mp 141-142 °C; ν_{\max} . 3220, 3105, 3020, 2870, 2255, 1600, 1583, 1560, 1495, 1488, 1450, 1442, 1345, 1290-1270, 1200, 1170, 1140, 1060, 1025, 1000, 980, 960, 915, 855, 810, 795, 760, 750, 725, 690 and 665-635 cm^{-1} ; ¹H nmr (CDCl₃) delta: 3.87 (2 H, s, CH₂), 5.97 (1 H, s, N-H), 6.55 (1 H, s, thiazole 5-H) and 7.27-7.80 (10 H, m, Ar-H); m/z 298 (M⁺, 0.29%), 193 (100), 134 (40.97), 106 (69.94), 91 (25.56), 77 (18.36), 65 (5.15) and 51 (7.78); Anal. Calcd. for C₁₆H₁₄N₂S₂: C 64.40, H 4.73, N 9.31. Found: C 64.17, H 4.72, N 9.21.

2-Methylthio-3-benzylamino-4-phenyl-1,3-thiazolium Iodide (14).- 3-Benzylamino-4-phenyl-1,3-thiazole-2-thione (13) (4.03 g, 13.5 mmol) in CH₂Cl₂ (20 ml) and C₆H₆ (30 ml) was treated at 25 °C with methyl iodide (5.75 g, 40.5 mmol). After standing for 15 h, the colourless crystalline iodide (14) was recrystallized from ethanol to give prisms (4.87 g, 82%), mp 137-138

$^{\circ}\text{C}$ (decomp.); ν_{max} . 3100, 3020, 2930, 2285, 2255, 1600, 1580, 1560, 1490, 1443, 1420, 1380, 1315, 1295, 1212, 1205, 1140, 1075, 1035, 1000, 970, 958, 865, 742, 690 and 660-635 cm^{-1} ; ^1H nmr [$\text{CDCl}_3/(\text{CD}_3)_2\text{SO}$] δ : 2.90 (3 H, s, CH_3) 3.81 (2 H, d, $J=5.1$ Hz, CH_2), 7.03-7.85 (11 H, m), and 8.13 (1 H, s); Anal. Calcd. for $\text{C}_{17}\text{H}_{17}\text{N}_2\text{S}_2$: C 46.37, H 3.89, N 6.36. Found: C 46.32, H 3.88, N 6.20.

3-(N-Benzylbenzamido)-4-phenyl-1,3-thiazole-2-thione (15). - To 3-benzylamino-4-phenyl-1,3-thiazole-2-thione (13) (1.13 g, 3.8 mmol) and DMAP (15 mg) in CH_2Cl_2 (8 ml), triethylamine (6 ml) and benzoyl chloride (0.74 g, 5.2 mmol) were added and the mixture was stirred at 40°C for 24 h. Solvent and excess triethylamine were removed under vacuum at 40°C and the solid product was well washed with water to remove DMAP. Compound (15) was recrystallized from ethanol in creamy rod-shaped prisms, mp $197 - 198^{\circ}\text{C}$; ν_{max} . 3115, 3060, 3020, 2780, 2580, 2440, 2250, 1955, 1890, 1685-1675, 1600, 1575, 1480, 1440, 1360, 1330, 1313, 1270, 1230, 1170, 1140, 1065, 1055, 1022, 997, 970, 950, 930, 920, 870, 845, 805, 760, 730, 690, 655-630 and 605 cm^{-1} ; ^1H nmr [$\text{CDCl}_3/(\text{CD}_3)_2\text{SO}$] δ : 4.00 (2 H, s, CH_2), 7.10 (1 H, s, thiazole 5-H) and 7.18-7.97 (15 H, m).

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