

Conversion of Bis(o-nitrophenyl)disulfides to Heterocycles Containing Sulfur and Nitrogen by the Action of Samarium Diiodide

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ABSTRACT: Treatment of bis(o-nitrophenyl)disulfides **1** with SmI₂ led to simultaneous reduction of nitro groups and reductive cleavage of S–S bonds as well as the formation of the active intermediates **2**. The intermediates **2** reacted smoothly with aldehydes or ketones, acid chlorides or anhydrides, α -bromoketones, and α,β -unsaturated ketones at room temperature to afford the desired benzothiazolines **3**, benzothiazoles **4**, 2H-1,4-benzothiazines **5**, and 2,3-dihydro-1,5-benzothiazepines **6**, respectively, in moderate to high yields under mild and neutral conditions. © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:156–160, 2001

INTRODUCTION

Heterocycles containing sulfur and nitrogen, such as benzothiazolines and 1,5-benzothiazepines, are biologically and industrially important compounds [1]. The main method for preparing these compounds makes use of o-aminothiophenols as starting materials; however, it usually involves harsh condi-

tions such as using acid or base catalysts, moderate to high temperature, and a long reaction time [2].

The Kagan [3] reagent, samarium diiodide (SmI₂), has evolved into an exceedingly reliable, mild, neutral, selective, and versatile single-electron-reducing agent for promoting reductive reactions difficult to accomplish by other existing methodologies. Its broad application in organic synthesis during the last decade has been reviewed [4]. The reduction of nitro compounds [5] and reductive cleavage of S–S, Se–Se and Te–Te bonds by SmI₂ [6] has been investigated extensively. However, to our knowledge, the simultaneous reduction of more than one group by SmI₂ has not been reported. Here we wish to report our preliminary studies on the simultaneous reduction of nitro groups and S–S bonds in bis(o-nitrophenyl)disulfides by SmI₂ and its use in the synthesis of some heterocycles containing sulfur and nitrogen.

RESULTS AND DISCUSSION

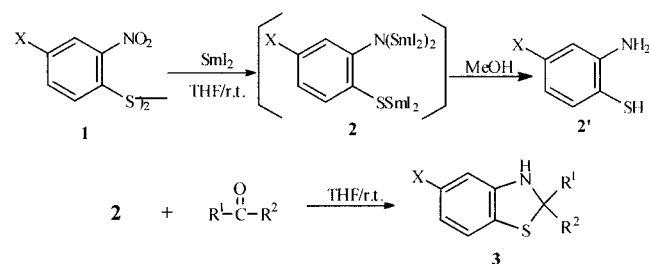
When 0.5 equivalents of a bis(o-nitrophenyl)disulfide **1** was added dropwise to 7.0 equivalents of SmI₂ at room temperature under a nitrogen atmosphere, the deep blue color of the solution gradually changed to an orange-yellow color. This observation suggested that nitro groups were reduced and S–S bonds were reductively cleaved by SmI₂. The inter-

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mediates **2**, formed at the same time, had high activity and reacted smoothly with aldehydes or ketones to give the desired benzothiazolines **3** in good yields (Scheme 1). When MeOH (0.2 mL) was added to the solution of the intermediates **2**, the orange-yellow color of the mixture turned into light yellow immediately, and *o*-aminothiophenols **2'** were formed. Table 1 shows that *o*-aminothiophenols **2'** were less reactive toward aldehydes than the intermediates **2** (entry 2). Table 1 summarizes the results of the reaction of the intermediates **2** with aldehydes or ketones. Aldehydes or aliphatic ketones gave satisfactory yields of benzothiazolines **3**. Aromatic ketones, however, gave similar products but with poor yields or did not react at all (entries 5 and 7) probably due to steric hindrance.

When acid chlorides or anhydrides were added to a solution of intermediates **2** at room temperature, benzothiazoles **4** were obtained (Scheme 2). The results are summarized in Table 2. It seems that the yield when using acid anhydrides is higher than when using acid chlorides.

α -Bromoketones underwent displacement by the active intermediates **2** successfully to give the corresponding 2*H*-1,4-benzothiazines **5** (Scheme 3). Re-



SCHEME 1

TABLE 1 Synthesis of Benzothiazolines **3** Promoted by Sml_2

Entry	X	R^1	R^2	T (h)	Product	Yield (%) ^a
1	H	<i>n</i> -Pr	H	2	3a	80
2 ^b	H	<i>n</i> -Pr	H	4	3a	25
3	H	<i>p</i> -NO ₂ C ₆ H ₅	H	2	3b	75
4	H	Me	<i>n</i> -Bu	2	3c	74
5	Cl	Me	Ph	4	3d	52
6	Cl	-(CH ₂) ₅ -	Ph	3	3e	78
7	Cl	Ph	Ph	24	3f	0 ^c

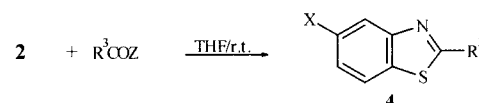
^aYields of crude product based on bis(*o*-nitrophenyl)disulfides.

^bMeOH was added to the solution of the intermediate **2**, followed by reaction with aldehyde.

^cThe reaction was studied at 0°C, 25°C, and THF-refluxing temperature.

sults are summarized in Table 3 and indicate that yields were affected by substituents on the aromatic rings of α -bromoketones (i.e., entries 13–16). The presence of electron-withdrawing groups on the aromatic ring resulted in higher yields than when electron-donating groups were present. Moreover, aromatic α -bromoketones (entry 13) are more reactive toward intermediates **2** than aliphatic α -bromoketones (entry 17).

Ring-closure reactions between α,β -unsaturated ketones and intermediates **2** took place readily to afford 2,3-dihydro-1,5-benzothiazepines **6** (Scheme 4). The results are summarized in Table 4. It was found

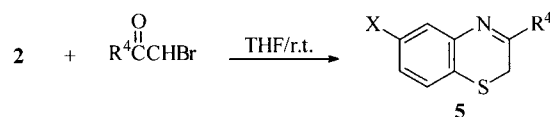


SCHEME 2

TABLE 2 Synthesis of Benzothiazoles **4** Promoted by Sml_2

Entry	X	R^3	Z	T (h)	Products	Yield (%) ^a
8	H	<i>n</i> -Pr	Cl	2	4a	65
9	H	<i>n</i> -Pr	<i>n</i> -PrCO ₂	2	4a	83
10	Cl	Et	Cl	2	4b	68
11	Cl	Et	EtCO ₂	2	4b	86
12	Cl	Ph	Cl	2	4c	72

^aYields of crude product based on bis(*o*-nitrophenyl)disulfides.

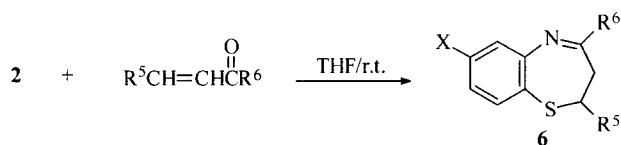


SCHEME 3

TABLE 3 Synthesis of 2*H*-1,4-Benzothiazines **5** Promoted by Sml_2

Entry	X	R^4	T (h)	Products	Yield (%) ^a
13	H	C ₆ H ₅	2	5a	62
14	H	<i>p</i> -MeC ₆ H ₄	2	5b	68
15	H	<i>p</i> -BrC ₆ H ₄	4	5c	79
16	H	<i>m</i> -NO ₂ C ₆ H ₄	8	5d	86
17	Cl	CH ₃	24	5e	40
18	Cl	2-benzofuryl	4	5f	65
19	Cl	<i>p</i> -MeOC ₆ H ₄	4	5g	64
20	Cl	<i>p</i> -ClC ₆ H ₅	4	5h	71

^aYields of crude product based on bis(*o*-nitrophenyl)disulfides.



SCHEME 4

TABLE 4 Synthesis of 2,3-Dihydro-1,5-Benzothiazepines **6** Promoted by SmI_2

Entry	X	R^5	R^6	T (h)	Products	Yield (%) ^a
21	H	C_6H_5	Ph	4	6a	86
22	Cl	C_6H_5	Ph	4	6b	83
23	Cl	$p\text{-ClC}_6\text{H}_4$	Ph	3	6c	78
24	Cl	$p\text{-CH}_3\text{C}_6\text{H}_4$	Ph	4	6d	80
25	Cl	$p\text{-CH}_3\text{OC}_6\text{H}_4$	Ph	4	6e	77
26	Cl	$3,4\text{-(OCH}_2\text{O)C}_6\text{H}_3$	Ph	4	6f	85
27	Cl	C_6H_5	$\text{PhCH}=\text{CH}$	8	6g	52
28	H	C_6H_5	CH_3	10	6h	43

^aYields of crude product based on bis(*o*-nitrophenyl)disulfides.

that chalcones are more reactive toward the new anionic species **2** than any other α,β -unsaturated ketones (entries 27 and 28).

In conclusion, the intermediates **2** derived from bis(*o*-nitrophenyl)disulfides by SmI_2 treatment were found to be more reactive than *o*-aminothiophenols. The present study provides a new, simple, and versatile synthetic method for preparing some heterocycles containing sulfur and nitrogen using bis(*o*-nitrophenyl)disulfides as synthons.

EXPERIMENTAL

Melting points were obtained on an electrothermal melting point apparatus and were uncorrected. Infrared spectra were recorded on an Shimadzu IR-408 spectrometer using KBr pellets or a thin film with maximum absorption indicated in cm^{-1} . ^1H NMR spectra were recorded on a Bruker AC-80 spectrometer using CDCl_3 solutions, J values are in Hz. Chemical shifts are expressed in ppm downfield from internal tetramethylsilane. Mass spectra were recorded on a HP 5989B MS spectrometer. Microanalyses were carried out on a Carlo Erba EA 1110 instrument.

Tetrahydrofuran (THF) was distilled from sodium-benzophenone immediately prior to use. All organic compounds, such as aldehydes, ketones, and acid chlorides or anhydrides were commercially available and were used without further purification. α -Bromoketones and α,β -unsaturated ketones were prepared by known procedures. All reactions were

performed in a Schlenk-type glass apparatus under a nitrogen atmosphere.

Formation of the Intermediates **2** Promoted by SmI_2

Samarium powder (1.05 g, 7 mmol, 99.9%) was placed in a well-dried three-necked round-bottom flask containing a magnetic stir bar. The flask was flushed with nitrogen several times. Tetrahydrofuran (30 mL) was added through a rubber septum by a syringe. Iodine (1.75 g, 7 mmol) was added to the flask, and the mixture was stirred at room temperature until the solution became deep blue and homogeneous (1–2 hours). The solution of SmI_2 was now ready for subsequent use. To the solution of SmI_2 was added bis(*o*-nitrophenyl)disulfide **1** (0.154 g, 0.5 mmol) in THF (3 mL) by syringe at room temperature under a nitrogen atmosphere. The deep-blue solution gradually became brown within 0.5 hours, which showed that the nitro groups were reduced and the S–S bond were reductively cleaved by SmI_2 ; the intermediates **2** had been generated.

Reactions of the Intermediates **2** with Aldehydes or Ketones

An aldehyde (1.1 mmol) or a ketones (1.1 mmol) in THF (1 mL) was added by syringe. After having been stirred for a given time (Table 1) (the reaction was monitored by thin-layer chromatography), the reaction was quenched with dilute hydrochloric acid (0.1 mol/L, 3 mL), and the mixture was extracted with ether (3×30 mL). The combined organic extracts were washed with saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (15 mL) and saturated aqueous NaCl (15 mL), and then dried over anhydrous MgSO_4 . After evaporating the solvent under reduced pressure, the crude product was purified by preparative thin-layer chromatography on silica gel using ethyl acetate/cyclohexane (1:5) as eluant.

Reactions of the Intermediates **2** with Acid Chlorides or Anhydrides, α -Bromoketones, and α,β -Unsaturated Ketones

The preparation of the intermediates **2** is the same as described previously. An acid chloride (or anhydride, α -bromoketone, α,β -unsaturated ketone, 1.1 mmol) in THF (1 mL) was then added by syringe, and the mixture was stirred at room temperature for a given time (Tables 2–4). The crude product was isolated as before and purified by preparative thin-

layer chromatography on silica gel using ethyl acetate/cyclohexane (1:7) as eluant.

DATA OF PRODUCTS

3a, 2-*n*-Propylbenzothiazoline: oil [7], $\nu_{\max}(\text{cm}^{-1})$ 3350 (NH); δ_{H} 7.15–6.20 (4H, m), 4.92 (1H, m), 3.07 (1H, br s), 1.78–1.22 (4H, m), 0.85 (3H, t, $J = 6$ Hz).

3b, 2-(4'-Nitrophenyl)benzothiazoline: yellow crystals, m.p. 116–118°C (lit. [8a] 117–118°C); $\nu_{\max}(\text{cm}^{-1})$ 3375 (NH), 1520, 1350 (NO₂); δ_{H} 8.21–7.48 (4H, m), 7.09–6.47 (4H, m), 6.29 (1H, s), 4.10 (1H, br s).

3c, 2-*n*-Butyl-2-methylbenzothiazoline: oil, $\nu_{\max}(\text{cm}^{-1})$ 3340 (NH); δ_{H} 6.90–6.30 (4H, m), 3.65 (1H, br s), 1.92–1.13 (9H, m), 0.85 (3H, t, $J = 6$ Hz); m/z 207 (M^+ , 1.5), 136 (25), 101 (50), 43 (100); Anal. calcd. for C₁₂H₁₇NS: C, 69.52; H, 8.26; N, 6.76%; found: C, 69.67; H, 8.13; N, 6.64.

3d, 5-Chloro-2-methyl-2-phenylbenzothiazoline: light-yellow crystals, m.p. 68–70°C (lit. [8b] 71°C); $\nu_{\max}(\text{cm}^{-1})$ 3345 (NH); δ_{H} 7.85–6.48 (8H, m), 5.65 (1H, br s), 4.75 (1H, m), 2.63 (3H, s).

3e, 5-Chloro-2,2-pentamethylenebenzothiazoline: yellow crystals, m.p. 43–45°C (lit. [8b] 47°C); $\nu_{\max}(\text{cm}^{-1})$ 3352 (NH); δ_{H} 6.76–6.24 (3H, m), 3.89 (1H, br s), 2.02–1.20 (10H, m).

4a, 2-Propylbenzothiazole: light-yellow oil [9]; $\nu_{\max}(\text{cm}^{-1})$ 1620–1580 (C=N), 760 (C–S); δ_{H} 7.80–7.30 (4H, m, ArH), 2.73 (2H, t, $J = 6$ Hz), 2.10–1.35 (2H, m), 0.95 (3H, t, $J = 6.5$ Hz);.

4b, 5-Chloro-2-ethylbenzothiazole: pale-yellow crystals, m.p. 54–56°C (lit. [10] 56–57°C); $\nu_{\max}(\text{cm}^{-1})$ 1618–1577 (C=N), 763 (C–S); δ_{H} 7.75–7.31 (3H, m, ArH), 2.80 (2H, q, $J = 6.5$ Hz), 1.18 (3H, t, $J = 6.5$ Hz).

4c, 5-Chloro-2-phenylbenzothiazole: light-yellow crystals, m.p. 136–138°C (lit. [10] 139°C); $\nu_{\max}(\text{cm}^{-1})$ 1625–1583 (C=N), 1500, 1450 (Ar), 762 (C–S); δ_{H} 7.83–7.06 (8H, m).

5a, 3-Phenyl-2H-1,4-benzothiazine: light-yellow crystals, m.p. 46–48°C (lit. [11a] 47–48°C); $\nu_{\max}(\text{cm}^{-1})$ 2930, 1475 (CH₂), 1650 (C=N), 765 (C–S); δ_{H} 7.42–6.87 (9H, m), 3.63 (2H, s).

5b, 3-(4'-Methylphenyl)-2H-1,4-benzothiazine: light-yellow crystals, m.p. 52–54°C (lit. [11b] 53–55°C); $\nu_{\max}(\text{cm}^{-1})$ 2980, 2930 (CH₂), 1475, 1380 (CH₃), 1660 (C=N), 760 (C–S); δ_{H} 8.00–6.60 (8H, m), 3.48 (2H, s), 2.32 (3H, s).

5c, 3-(4'-Bromophenyl)-2H-1,4-benzothiazine: light-yellow crystals, m.p. 60–62°C (lit. [11b] 59–61°C); $\nu_{\max}(\text{cm}^{-1})$ 2940, 1475 (CH₂), 1685 (C=N), 760 (C–S); δ_{H} 8.04–6.72 (8H, m), 3.74 (2H, s).

5d, 3-(3'-Nitrophenyl)-2H-1,4-benzothiazine: light-yellow crystals, m.p. 86–88°C; $\nu_{\max}(\text{cm}^{-1})$ 2930,

1475 (CH₂), 1675 (C=N), 1560, 1350 (NO₂), 760 (C–S); δ_{H} 8.21–6.85 (8H, m), 3.63 (2H, s); m/z (%): 270 (M^+ , 15), 256 (100), 210 (34), 134 (57); Anal. calcd. for C₁₄H₁₀N₂O₂S: C, 62.21; H, 3.73; N, 10.36; found: C, 62.08; H, 3.89; N, 10.14.

5e, 6-Chloro-3-Methyl-2H-1,4-benzothiazine: oil, $\nu_{\max}(\text{cm}^{-1})$ 2980, 2930, 1475, 1380 (CH₃, CH₂), 1650 (C=N), 760 (C–S), 742 (C–Cl); δ_{H} 7.58–6.92 (3H, m), 2.75 (2H, s), 2.13 (3H, s); m/z (%): 199 (M^+ , 2, 3.2), 197 (M^+ , 8.7), 184 (32.7), 182 (100); Anal. calcd. for C₉H₈ClNS: C, 54.68; H, 4.08; N, 7.09; found: C, 54.77; H, 3.89; N, 6.83.

5f, 6-Chloro-3-(2'-benzofuryl)-2H-1,4-benzothiazine: light-yellow crystals, m.p. 125–127°C; $\nu_{\max}(\text{cm}^{-1})$ 2940, 1465 (CH₂), 1645 (C=N), 1250 (C–O–C), 763 (C–S), 740 (C–Cl); δ_{H} 7.63–6.83 (8H, m), 3.53 (2H, s); m/z (%): 301 (M^+ , 2, 1.2), 299 (M^+ , 3.5), 286 (32.4), 284 (100). Anal. calcd. for C₁₆H₁₀ClNOS: C, 64.11; H, 3.36; N, 4.67; found: C, 64.27; H, 3.29; N, 4.49.

5g, 6-Chloro-3-(4'-methoxyphenyl)-2H-1,4-benzothiazine: light-yellow crystals, m.p. 117–119°C; $\nu_{\max}(\text{cm}^{-1})$ 2980, 2925, 1475, 1380 (CH₃, CH₂), 1650 (C=N), 1250 (C–O–C), 760 (C–S), 740 (C–Cl); δ_{H} 7.85–6.70 (7H, m), 3.86 (3H, s), 3.68 (2H, s); m/z (%): 291 (M^+ , 2, 4.8), 289 (M^+ , 14.9), 276 (31.7), 274 (100); Anal. calcd. for C₁₅H₁₂ClNOS: C, 62.17; H, 4.17; N, 4.83; found: C, 62.02; H, 4.22; N, 4.99.

5h, 6-Chloro-3-(4'-chlorophenyl)-2H-1,4-benzothiazine: light-yellow crystals, m.p. 119–121°C; $\nu_{\max}(\text{cm}^{-1})$ 2935, 1470 (CH₂), 1660 (C=N), 760 (C–S), 742 (C–Cl); δ_{H} 8.01–7.05 (7H, m), 3.82 (2H, s); m/z 294 (M^+ , 12.7), 279 (100). Anal. Calcd. for C₁₄H₉Cl₂NS: C, 57.16; H, 3.08; N, 4.76; found: C, 56.97; H, 3.14; N, 4.56.

6a, 2,3-Dihydro-2,4-diphenyl-1,5-benzothiazepine: pale-yellow crystals, m.p. 112–114°C (lit. [12] 114–115°C); $\nu_{\max}(\text{cm}^{-1})$ 1610–1590 (C=N), 758 (C–S); δ_{H} 8.06–6.76 (14H, m), 4.90–4.45 (1H, m), 3.10–2.45 (2H, m).

6b, 7-Chloro-2,3-dihydro-2,4-diphenyl-1,5-benzothiazepine: light-yellow crystals, m.p. 132–134°C; $\nu_{\max}(\text{cm}^{-1})$ 1610–1580 (C=N), 755 (C–S); δ_{H} 8.07–6.57 (13H, m), 4.87–4.57 (1H, m), 3.47–2.77 (2H, m); m/z 349 (M^+ , 2.0), 248 (36), 246 (100), 105 (67), 77 (36); Anal. calcd. for C₂₁H₁₆ClNS: C, 72.09; H, 4.61; N, 4.00%; found: C, 72.20; H, 4.53; N, 3.78.

6c, 7-Chloro-2-(4'-chlorophenyl)-2,3-dihydro-4-phenyl-1,5-benzothiazepine: yellow crystals, m.p. 145–147°C; $\nu_{\max}(\text{cm}^{-1})$ 1610–1580 (C=N), 760 (C–S); δ_{H} 8.00–6.40 (12H, m), 5.90–5.67 (1H, m), 2.62–2.34 (2H, m); m/z 383 (M^+ , 1.6), 279 (38), 248 (36), 246 (100); Anal. calcd. for C₂₁H₁₅Cl₂NS: C, 65.63; H, 3.93; N, 3.64%; found: C, 65.39; H, 4.04; N, 3.78.

6d, 7-Chloro-2,3-dihydro-2-(4'-methylphenyl)-4-

phenyl-1,5-benzothiazepine: light-yellow crystals, m.p. 165–167°C; $\nu_{\max}(\text{cm}^{-1})$ 1610–1578 (C=N), 760 (C–S); δ_{H} 8.04–6.92 (8H, m, ArH), 4.90–4.62 (1H, m), 3.14–2.74 (2H, m), 2.24 (3H, s); m/z 363 (M^+ , 1.9), 259 (19), 245 (14), 221 (39), 207 (100), 105 (35), 77 (37); Anal. calcd. for $\text{C}_{22}\text{H}_{18}\text{ClNS}$: C, 72.61; H, 4.99; N, 3.85%; found: C, 72.47; H, 5.10; N, 3.62.

6e, 7-Chloro-2,3-dihydro-2-(4'-methoxyphenyl)-4-phenyl-1,5-benzothiazepine: light-yellow crystals, m.p. 148–150°C; $\nu_{\max}(\text{cm}^{-1})$ 1613–1585 (C=N), 1250 (=C–OMe), 755 (C–S); δ_{H} 8.02–6.40 (12H, m), 4.25–4.05 (1H, m), 3.51 (3H, s), 3.25–2.85 (2H, m); m/z 379 (M^+ , 1.2), 248 (19), 246 (49), 134 (100); Anal. calcd. for $\text{C}_{22}\text{H}_{18}\text{ClNOS}$: C, 69.56; H, 4.78; N, 3.69%; found: C, 69.44; H, 4.52; N, 3.51.

6f, 7-Chloro-2,3-dihydro-2-(3',4'-dioxomethylenephényl)-4-phenyl-1,5-benzothiazepine: light-yellow crystals, m.p. 178–180°C; $\nu_{\max}(\text{cm}^{-1})$ 2780, 925, 720 (OCH_2O), 1615–1580 (C=N), 760 (C–S); δ_{H} 8.00–6.42 (11H, m), 5.77 (2H, s), 4.96–4.62 (1H, m), 3.36–2.80 (2H, m); m/z 393 (M^+ , 4.2), 289 (23.3), 246 (24.8), 149 (100); Anal. calcd. for $\text{C}_{22}\text{H}_{16}\text{ClNO}_2\text{S}$: C, 67.09; H, 4.09; N, 3.56%; found: C, 67.20; H, 3.92; N, 3.43.

6g, 7-Chloro-2,3-dihydro-2-phenyl-4-styryl-1,5-benzothiazepine: light-yellow crystals, m.p. 102–104°C; $\nu_{\max}(\text{cm}^{-1})$ 1650, 965 (C=C), 1615–1582 (C=N), 760 (C–S); δ_{H} 8.10–6.70 (13H, m), 6.23–5.76 (2H, m), 4.53–4.23 (1H, m), 3.10–2.53 (2H, m); m/z 375 (M^+ , 1.2), 272 (16), 270 (33), 247 (38.6), 245 (100); Anal. calcd. for $\text{C}_{23}\text{H}_{18}\text{ClNS}$: C, 73.49; H, 4.83; N, 3.73%; found: C, 73.33; H, 4.76; N, 3.57.

6h, 2,3-Dihydro-4-methyl-2-phenyl-1,5-benzothiazepine: yellow crystals, m.p. 123–124°C (lit. [13], 121–123°C); $\nu_{\max}(\text{cm}^{-1})$ 2980, 1380 (CH_3), 1610–1590 (C=N), 758 (C–S); δ_{H} 7.82–6.74 (9H, m), 4.70–4.35 (1H, m), 3.10–2.75 (2H, m), 2.03 (3H, s).

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