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## Addition Reactions of Diketene. IV.<sup>1)</sup> Reaction of Diketene with Thioureas, Thioamide, and Aminothiols<sup>2)</sup>

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The reaction of benzimidazoline-2-thione (**2**) with diketene (**1**) gave the oxazine derivative **3** and the thiazine derivative **4**. However, the reaction of 2-indolinethione (**6**) with diketene afforded only the thiazine derivative **7**. On the other hand, no cyclized compound was obtained from 2-indolinone (**8**) and diketene.

The reactions of *N,N'*-diphenylthiourea (**11**) and 2-aminobenzothiol (**14**) with diketene were also studied; **11** and **14** gave the thiouracil **12** and the benzothiazine **16**, respectively.

**Keywords**—diketene; thiourea; thioamide; aminothiol; cyclization; 1,3-oxazine; 1,3-thiazine; thiouracil; thiazepine

Previously, we reported that the reaction of diketene with *N'*-2-benzimidazolyl-*N,N*-dimethylformamide afforded 3-acetyl-4*H*-pyrimido[1,2-*a*]benzimidazol-4-one.<sup>1a)</sup> Similarly, Kato *et al.*<sup>3)</sup> reported the reaction of diketene with benzimidazole and its derivatives. Diketene also reacts with thiourea,<sup>4)</sup> thioamide,<sup>5)</sup> amide,<sup>6)</sup> the products depending on the reaction conditions, especially on the solvent. Although many papers have appeared on the reaction of diketene with acyclic thioureas, thioamides, and amides, relatively few reports have dealt with the reaction of diketene with cyclic compounds. In the present paper, we wish to report the reactions of diketene with benzimidazoline-2-thione, 2-indolinethione, and 2-aminobenzenethiol.

When a mixture of benzimidazoline-2-thione (**2**)<sup>7)</sup> and diketene (**1**) was refluxed without any solvent, two crystalline products, 2-methyl-4*H*-[1,3]oxazino[3,2-*a*]benzimidazol-4-one (**3**) and 2-methyl-4*H*-[1,3]thiazino[3,2-*a*]benzimidazol-4-one (**4**)<sup>8)</sup> were isolated, after purification by silica gel column chromatography, in 34 and 3% yields, respectively. The structures of **3** and **4** were confirmed by comparison of the spectral data with those of the known compound **5**<sup>9)</sup> (see Table I). In particular, the 4-one structures **3** and **4** were indicated by the <sup>1</sup>H-nuclear magnetic resonance (NMR) spectrum since the position of the C-6 benzene ring proton was shifted downfield from the other aromatic protons. Significant signals in the <sup>13</sup>C-NMR spectrum of **3** are a singlet at 165.5 ppm due to the carbonyl C-atom and a doublet at 100.2 ppm due to the carbon  $\alpha$  to carbonyl in the oxazinone ring. The <sup>13</sup>C-NMR spectrum of **4** shows a signal due to the carbonyl C-atom at 159.5 ppm (singlet) and other signals are consistent with the assigned structure.

Similarly, 2-indolinethione (**6**) reacted with diketene under the same conditions to give 2-methyl-4*H*-[1,3]thiazino[3,2-*a*]indol-4-one (**7**) in 44% yield. The structure of **7** followed from a comparison of its spectra with those of the thiazine derivatives **4** and **5** (see Table I).

Similar reaction of 2-indolinone (**8**) with diketene gave the acetoacetylated compound **9** and the pyrone derivative **10** in 10 and 9% yields, respectively. The spectral evidence for the structure of **9** includes a singlet at 2.32 ppm due to the methyl group and a singlet at 4.15 ppm due to the methylene H-atoms of the acetoacetyl group in the <sup>1</sup>H-NMR spectrum. The infrared (IR) bands at 1755, 1727, and 1704 cm<sup>-1</sup> indicate three carbonyl functions. The main

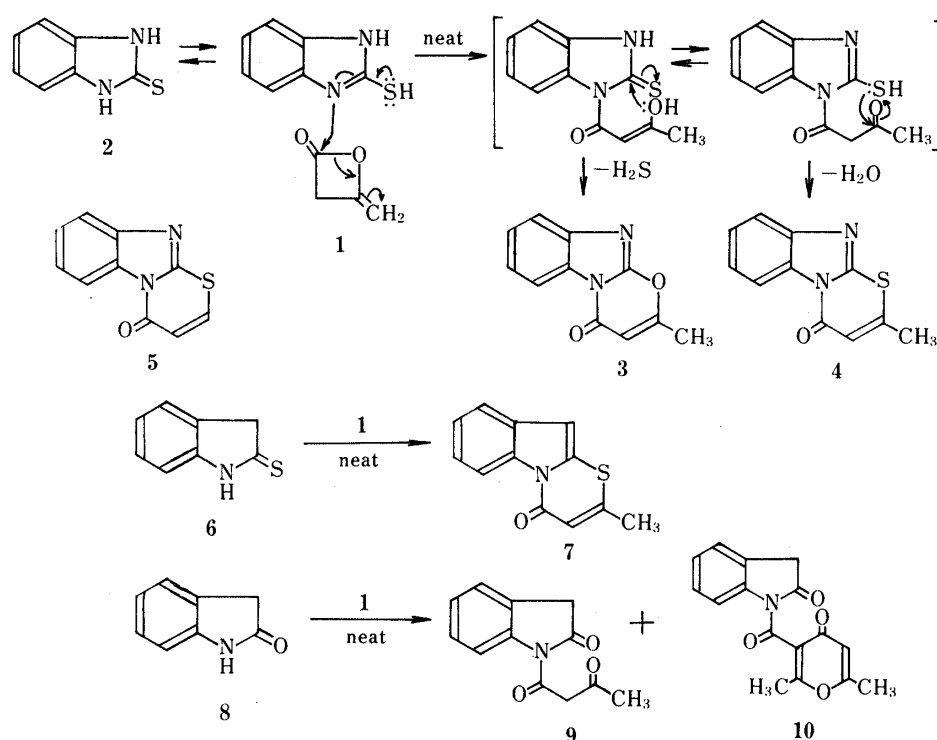


Chart 1

TABLE I. Spectral Data for 3, 4, 5, and 7

Compd. No.	IR	<sup>1</sup> H-NMR $\delta$ in DMSO- <i>d</i> <sub>6</sub>		
	$\nu_{\max}$ cm <sup>-1</sup>	CH <sub>3</sub>	H-C(3)	H-C(6)
3	1723 (Nujol)	2.21 (s)	6.20 (s)	8.04–8.22 (m)
4	1675 (KBr)	2.45 (s)	6.48 (s)	8.35–8.57 (m) <sup>b)</sup>
5 <sup>a)</sup>	1712 (Nujol)	—	6.80 (d)	8.1–8.5 (m)
7	1675 (CHCl <sub>3</sub> )	2.25 (s)	6.23 (s)	8.74 (dd) <sup>b)</sup>

a) This compound has been reported in the literature.<sup>8)</sup>

b) CDCl<sub>3</sub> was used instead of DMSO-*d*<sub>6</sub>.

structural features of **10** are also supported by spectral data. In particular, the IR spectrum shows a strong band at 1668 cm<sup>-1</sup>, and the <sup>1</sup>H-NMR spectrum includes two singlets at 2.26 and 2.34 ppm due to the two methyl groups and a singlet at 6.10 ppm due to the olefinic proton. From these data, the product **10** was concluded to have the 2,6-dimethyl-4-pyrone moiety.<sup>10)</sup>

Lacey<sup>4)</sup> reported that the reaction of diketene with *S*-methyl-*N*-phenylthiourea in ether gives 2-amino-2,3-dihydro-6-methyl-2-methylthio-4-oxo-3-phenyl-1,3-oxazine, but the reaction of diketene with *N,N'*-diphenylthiourea (**11**) in boiling acetic acid gives acetoacetanilide, phenyl isothiocyanate, and *N,N'*-diphenylurea. When a mixture of **11** and diketene was refluxed without solvent, two crystalline products, 1,3-diphenyl-6-methyl-2-thiouracil (**12**) and 3-acetyl-6-methyl-1-phenyl-2,4(1*H*,3*H*)-pyridinedione (**13**)<sup>11)</sup> were obtained in 19 and 7% yields, respectively. The structure of **12** was confirmed by comparison of its spectral data with those of 6-methyl-3-phenyl-2-thiouracil and 3,6-dimethyl-1-phenyl-2-thiouracil.<sup>12)</sup> In the IR spectrum, the bands at 1690 and 1270 cm<sup>-1</sup> arise from the carbonyl and thioxo

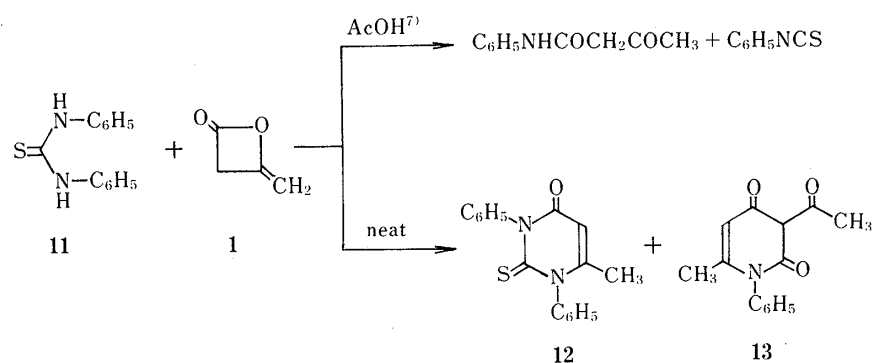


Chart 2

functions of the thiouracil ring, respectively.

Ried *et al.* reported that 2-aminobenzothiol (14) reacted with diketene in dry benzene to give 4-methyl-1,5-benzothiazepin-2(3H)-one (15), but the structure of 15 was not confirmed.<sup>13)</sup> When this reaction was re-examined, the results obtained were a little different from those reported by Ried *et al.*<sup>13)</sup> The product was obtained as a tautomeric mixture of 15a and 15b (5:4) in 58% yield. The spectral evidence for the mixture of 15a and 15b includes in the <sup>1</sup>H-NMR spectrum a singlet at 2.12 ppm due to the methyl group of 15b, a singlet at 2.34 ppm due to the methyl group of 15a, a singlet at 4.52 ppm due to the methylene H-atoms of 15a and a singlet at 6.04 ppm due to the olefinic proton of 15b. Significant signals in the <sup>13</sup>C-NMR spectrum are a triplet at 48.8 ppm due to the methylene C-atom of 15a and a doublet at 93.3 ppm due to the olefinic carbon of 15b.

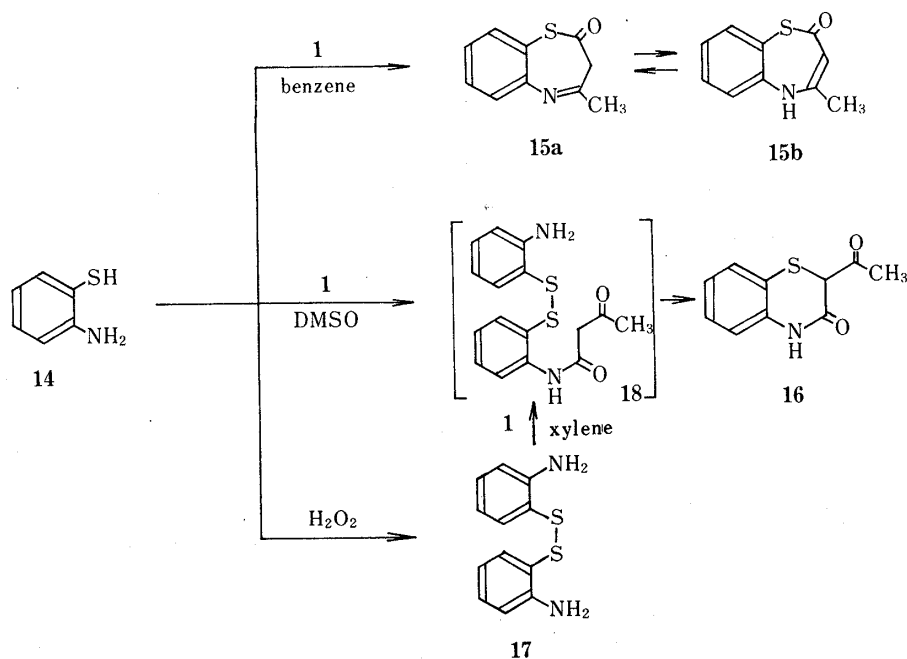


Chart 3

On the other hand, when a mixture of 14 and diketene was heated in dimethyl sulfoxide (DMSO) at 155 °C, 2-acetyl-1,4-benzothiazin-3(2H,4H)-one (16) was formed in 29% yield. Since 14 is readily oxidized to bis(2-aminophenyl) disulfide (17)<sup>14)</sup> under these conditions, and since the amide (18) is an intermediate in the reaction,<sup>15)</sup> the reaction of 17 with diketene was

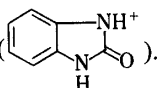
carried out in xylene. The product **16** was obtained in 18% yield. The structure of **16** was elucidated on the basis of its spectral data. In particular, the bands at 1710 and 1673  $\text{cm}^{-1}$  in the IR spectrum arise from the ketone and the amide functionalities, respectively. The  $^1\text{H-NMR}$  spectrum includes a singlet at 2.32 ppm due to the methyl group, a singlet at 4.79 ppm due to the H-atom  $\alpha$  to the both carbonyls ( $\text{D}_2\text{O}$ -erasable) and a broad signal at 10.72 ppm due to the amide ( $\text{D}_2\text{O}$ -erasable). This structure was also supported by the  $^{13}\text{C-NMR}$  spectrum, as detailed in the experimental section.

### Experimental

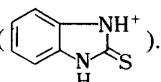
All melting points were measured in a Yanaco MP-3 apparatus and are uncorrected.  $^1\text{H-}$  and  $^{13}\text{C-NMR}$  spectra were recorded on JEOL PS-100 and JEOL FX-60 spectrometers, respectively. Chemical shifts are given in  $\delta$ -values referred to internal tetramethylsilane, and the following abbreviation is used;  $W_{1/2}$  = signal width at the half-height of the signal. IR spectra were taken on a JASCO DS-701G or Hitachi 215 instrument. A JEOL JMS-D300 spectrometer was used to obtain mass spectra (MS).

**Reaction of Benzimidazole-2-thione (2) with Diketene (1)**—A mixture of 1.50 g (10.0 mmol) and **2**<sup>7</sup> and 4.20 g (50 mmol) of **1** was refluxed for 1 h. After cooling, the solid mixture was washed with ether and with a small amount of acetone, then chromatographed on  $\text{SiO}_2$  (chloroform) to give 685 mg (34%) of **3** as colorless needles and 62 mg (3%) of **4** as yellow prisms.

2-Methyl-4H-[1,3]oxazino[3,2-*a*]benzimidazol-4-one (**3**). mp 223–224 °C. *Anal.* Calcd for  $\text{C}_{11}\text{H}_8\text{N}_2\text{O}_2$ : C, 65.99; H, 4.03; N, 13.99. Found: C, 65.46; H, 4.08; N, 13.96. IR  $\nu_{\text{max}}^{\text{Nujol}} \text{cm}^{-1}$ : 1723 (C=O).  $^1\text{H-NMR}$  (in  $\text{DMSO-}d_6$ ): 2.21 (3H, s,  $\text{H}_3\text{C-C(2)}$ ), 6.20 (1H, s, H-C(3)), 7.23–7.72 (3H, m, H-C(7), H-C(8), and H-C(9)), 8.04–8.22 (1H, m, H-C(6)).  $^{13}\text{C-NMR}$  (in  $\text{DMSO-}d_6$ ): 18.9 (q,  $\text{CH}_3$ ), 100.2 (d, C(3)), 114.2, 118.5, 123.0, and 125.2 (4d, C(6), C(7), C(8), and C(9)), 127.8 and 138.8 (2s, C(5a) and C(9a)), 151.8 and 156.9 (2s, C(2) and C(10a)), 165.5 (s, C(4)). MS  $m/z$ :

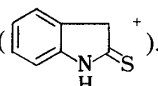
200 ( $\text{M}^+$ ), 185 ( $\text{M}^+ - \text{CH}_3$ ), 134 ().

2-Methyl-4H-[1,3]thiazino[3,2-*a*]benzimidazol-4-one (**4**). mp 176–177 °C (lit.,<sup>8</sup>) mp 167–170 °C. *Anal.* Calcd for  $\text{C}_{11}\text{H}_8\text{N}_2\text{OS}$ : C, 61.11; H, 3.73; N, 13.17. Found: C, 60.94; H, 3.78; N, 13.17. IR  $\nu_{\text{max}}^{\text{KBr}} \text{cm}^{-1}$ : 1675 (C=O).  $^1\text{H-NMR}$  (in  $\text{CDCl}_3$ ): 2.45 (1H, s,  $\text{H}_3\text{C-C(2)}$ ), 6.48 (1H, s, H-C(3)), 7.22–7.80 (3H, m, H-C(7), H-C(8), and H-C(9)), 8.35–8.57 (1H, m, H-C(6)).  $^{13}\text{C-NMR}$  (in  $\text{CDCl}_3$ ): 22.7 (q,  $\text{CH}_3$ ), 115.5, 115.9, 118.5, 124.1, and 125.8 (5d, C(3), C(6), C(7), C(8), and C(9)), 131.0 (s, C(9a)), 142.4, 146.5, and 148.6 (3s, C(2), C(5a), and C(10a)), 159.5 (s, C(4)). MS

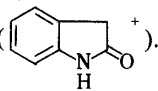
$m/z$ : 216 ( $\text{M}^+$ ), 188 ( $\text{M}^+ - \text{CO}$ ), 150 (.

**Reaction of 2-Indolinethione (6) with 1**—A mixture of 603 mg (4.0 mmol) of **6** and 1.71 g (20 mmol) of **1** was refluxed for 1.5 h. After cooling, the mixture was extracted with hexane. The extract was concentrated *in vacuo* and chromatographed twice on  $\text{SiO}_2$  (methylene chloride–acetone 1:1 and chloroform) to give a crystalline substance. Recrystallization from hexane afforded 380 mg (44%) of **7** as yellow prisms.

2-Methyl-4H-[1,3]thiazino[3,2-*a*]indol-4-one (**7**). mp 146–148 °C. *Anal.* Calcd for  $\text{C}_{12}\text{H}_9\text{NOS}$ : C, 66.97; H, 4.22; N, 6.51. Found: C, 66.82; H, 4.13; N, 6.51. IR  $\nu_{\text{max}}^{\text{CHCl}_3} \text{cm}^{-1}$ : 1675 (C=O).  $^1\text{H-NMR}$  (in  $\text{CDCl}_3$ ): 2.25 (3H, s,  $\text{H}_3\text{C-C(2)}$ ), 6.23 (1H, s, H-C(3)), 6.62 (1H, s, H-C(10)), 7.24–7.56 (3H, m, H-C(7), H-C(8), and H-C(9)), 8.74 (1H, dd,  $J_1 = 7 \text{ Hz}$ ,  $J_2 = 3 \text{ Hz}$ , H-C(6)).  $^{13}\text{C-NMR}$  (in  $\text{CDCl}_3$ ): 22.4 (q,  $\text{CH}_3$ ), 103.5 (d, C(10)), 114.6, 117.0, 119.0, 123.2, and 124.2 (5d, C(3), C(6), C(7), C(8), and C(9)), 127.0, 128.6, 134.6, and 147.6 (4s, C(2), C(5a), C(9a), and C(10a)), 160.1

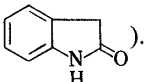
(s, C(4)). MS  $m/z$ : 215 ( $\text{M}^+$ ), 187 ( $\text{M}^+ - \text{CO}$ ), 149 (.

**Reaction of 2-Indolinone (8) with 1**—A mixture of 717 mg (5.4 mmol) of **8** and 2.28 g (27 mmol) of **1** was refluxed for 1 h. Then the reaction mixture was concentrated *in vacuo*, and the residue was chromatographed on  $\text{SiO}_2$  (chloroform–ether 3:1) to give 121 mg (10%) of **9** as colorless prisms and 133 mg (9%) of **10** as yellow prisms.

1-Acetoacetyl-2-indolinone (**9**). mp 113–116 °C (chloroform–hexane). *Anal.* Calcd for  $\text{C}_{12}\text{H}_{11}\text{NO}_3$ : C, 66.35; H, 5.10; N, 6.45. Found: C, 66.17; H, 5.10; N, 6.41. IR  $\nu_{\text{max}}^{\text{CHCl}_3} \text{cm}^{-1}$ : 1755, 1727, 1704 (C=O).  $^1\text{H-NMR}$  (in  $\text{CDCl}_3$ ): 2.32 (3H, s,  $\text{CH}_3$ ), 3.69 (2H, s,  $W_{1/2} = 3 \text{ Hz}$ , 2H-C(3)), 4.15 (2H, s,  $\text{H}_3\text{CCOCH}_2\text{CO}$ ), 7.11–7.39 (3H, m, H-C(4), H-C(5), and H-C(6)), 8.20 (1H, d,  $J = 7 \text{ Hz}$ , H-C(7)). MS  $m/z$ : 217 ( $\text{M}^+$ ), 133 (.

2,6-Dimethyl-4-pyrone-3-yl 2-oxo-1-indolinyl ketone (**10**). mp 213–215 °C (benzene–hexane). *Anal.* Calcd for  $\text{C}_{16}\text{H}_{13}\text{NO}_4$ : C, 67.84; H, 4.63; N, 4.95. Found: C, 67.87; H, 4.48; N, 4.91. IR  $\nu_{\text{max}}^{\text{CHCl}_3} \text{cm}^{-1}$ : 1763, 1668 (C=O).  $^1\text{H-}$

NMR (in  $\text{CDCl}_3$ ): 2.26 and 2.34 (6H, 2s,  $2\text{CH}_3$ ), 3.69 (2H, s,  $W_{1/2} = 3$  Hz, 2H-C(3) in indoline), 6.10 (1H, s, H-C(5) in pyrone), 7.06–7.42 (3H, m, H-C(4), H-C(5), and H-C(6) in indoline), 8.20 (1H, d,  $J = 7$  Hz, H-C(7) in indoline). MS

$m/z$ : 283 ( $\text{M}^+$ ), 151 ( $\text{M}^+ -$ ).

**Reaction of *N,N'*-Diphenylthiourea (11) with 1**—A mixture of 1.14 g (5.0 mmol) of 11 and 2.10 g (25 mmol) of 1 was refluxed for 1 h. After cooling, the reaction mixture was concentrated *in vacuo*. The residue was washed with ether and acetone, and purified by preparative thin-layer chromatography (TLC) (chloroform–acetone 20:1) to provide 280 mg (19%) of 12 as colorless needles and 80 mg (7%) of 13<sup>11</sup>) as colorless needles.

1,3-Diphenyl-6-methyl-2-thiouracil (12). mp 241–242 °C (acetone). *Anal.* Calcd for  $\text{C}_{17}\text{H}_{14}\text{N}_2\text{OS}$ : C, 69.36; H, 4.79; N, 9.52. Found: C, 69.30; H, 4.75; N, 9.68. IR  $\nu_{\text{max}}^{\text{Nujol}} \text{cm}^{-1}$ : 1690 (C=O), 1270 (C=S).  $^1\text{H-NMR}$  (in  $\text{CDCl}_3$ ): 1.94 (3H, s,  $\text{H}_3\text{C-C}(6)$ ), 6.16 (1H, s, H-C(5)), 7.20–7.60 (10H, m, phenyl groups). MS  $m/z$ : 294 ( $\text{M}^+$ ), 185 ( $\text{M}^+ - \text{S-C}_6\text{H}_5$ ).

3-Acetyl-6-methyl-1-phenyl-2,4(1*H*,3*H*)-pyridinedione (13). mp 233–234 °C (lit.,<sup>11</sup>) mp 219–220 °C. IR  $\nu_{\text{max}}^{\text{Nujol}} \text{cm}^{-1}$ : 1650 (C=O). MS  $m/z$ : 243 ( $\text{M}^+$ ), 228 ( $\text{M}^+ - \text{CH}_3$ ), 200 ( $\text{M}^+ - \text{H}_3\text{CCO}$ ).

**Reaction of 2-Aminobenzenethiol (14) with 1**—A solution of 1.25 g (10.0 mmol) of 14 and 0.84 g (10 mmol) of 1 in 40 ml of dry benzene was refluxed under  $\text{N}_2$  for 1 h. After cooling, the reaction mixture was concentrated *in vacuo*, and recrystallization of the residue from EtOH gave 1.10 g (58%) of a 5:4 mixture of 15a and 15b as pale yellow prisms.

4-Methyl-1,5-benzothiazepin-2(3*H*)-one (15a) and 4-methyl-1,5-benzothiazepin-2(5*H*)-one (15b). mp 116–118 °C (lit.,<sup>13</sup>) mp 114 °C). *Anal.* Calcd for  $\text{C}_{10}\text{H}_9\text{NOS}$ : C, 62.81; H, 4.75; N, 7.33. Found: C, 62.81; H, 4.61; N, 7.43. IR  $\nu_{\text{max}}^{\text{KBr}} \text{cm}^{-1}$ : 1608 (C=O).  $^1\text{H-NMR}$  (in  $\text{DMSO-}d_6$ ): 2.12 (3H, s,  $\text{H}_3\text{C-C}(4)$  of 15b), 2.34 (3H, s,  $\text{H}_3\text{C-C}(4)$  of 15a), 4.52 (2H, s, 2H-C(3) of 15a), 6.04 (1H, s, H-C(3) of 15b), 7.12–8.16 (m, aromatic H-atoms).  $^{13}\text{C-NMR}$  (in  $\text{DMSO-}d_6$ ): 31.3 (q,  $\text{CH}_3$ ), 48.8 (t, C(3) of 15a), 93.3 (d, C(3) of 15b), 123.5, 123.8, 126.4, 127.5, and 127.8 (5d, C(6), C(7), C(8), and C(9)), 136.8, 153.9 and 165.3 (3s, C(4), C(5a), and C(9a)), 204.4 (s, C(2)). MS  $m/z$ : 191 ( $\text{M}^+$ ), 176 ( $\text{M}^+ - \text{CH}_3$ ), 149 ( $\text{M}^+ - \text{H}_2\text{C}=\text{C}=\text{O}$ ).

**Reaction of 14 with 1 in DMSO**—A solution of 1.25 g (10 mmol) of 14 and 1.00 g (11.9 mmol) of 1 in 5 ml of DMSO was stirred for 9.5 h at 155 °C. After cooling, the reaction mixture was concentrated *in vacuo*, and the resulting precipitates were washed with ether and collected by filtration. Recrystallization from acetone gave 610 mg (29%) of 16 as colorless prisms.

2-Acetyl-1,4-benzothiazin-3(2*H*,4*H*)-one (16). mp 164–166 °C. *Anal.* Calcd for  $\text{C}_{10}\text{H}_9\text{NO}_2\text{S}$ : C, 57.97; H, 4.38; N, 6.76. Found: C, 58.12; H, 4.19; N, 6.82. IR  $\nu_{\text{max}}^{\text{KBr}} \text{cm}^{-1}$ : 3400 (br, N–H), 1710 (C=O), 1673 (C=O).  $^1\text{H-NMR}$  (in  $\text{DMSO-}d_6$ ): 2.32 (3H, s,  $\text{CH}_3$ ), 4.79 (1H, s,  $\text{D}_2\text{O-erasable}$ , H-C(2)), 6.90–7.40 (4H, m, aromatic H-atoms), 10.72 (1H, br,  $\text{D}_2\text{O-erasable}$ , NH).  $^{13}\text{C-NMR}$  (in  $\text{DMSO-}d_6$ ): 28.3 (q,  $\text{CH}_3$ ), 51.6 (d, C(2)), 117.3 (s, C(8a)), 118.4, 124.5, and 128.9 (3d, C(5), C(6), C(7), and C(8)), 138.3 (s, C(4a)), 164.8 (s, C(3)), 201.5 (s,  $\text{COCH}_3$ ). MS  $m/z$ : 207 ( $\text{M}^+$ ), 165 ( $\text{M}^+ - \text{H}_2\text{C}=\text{C}=\text{O}$ ).

**Reaction of Bis(2-aminophenyl) Disulfide (17) with 1**—A solution of 1.24 g (5.0 mmol) of 17 and 1.00 g (11.9 mmol) of 1 in 40 ml of dry xylene was refluxed for 10 h. After cooling, the reaction mixture was concentrated *in vacuo*. The residue was washed with ether, purified by preparative TLC (chloroform–acetone 20:1), and recrystallized from acetone to afford 380 mg (18%) of 16 (mp 164–166 °C). This sample was identified on the basis of the IR spectrum and mixed melting point determination with the compound obtained from 14 and 1.

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