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Photoirradiation of acetone solutions of 2,3-diallyl-6,7-dihydro-5*H*-2*a*-thia(2*a*-S<sup>IV</sup>)-2,3,4*a*,7*a*-tetraazacyclopent[*cd*]indene-1,4(2*H*,3*H*)-dithione (**1**) in the presence of excess thioacetic acid and thiobenzoic acid afforded addition products, 2,3-bis(3-acetylthiopropyl)- and 2,3-bis(3-benzoylthiopropyl)-6,7-dihydro-5*H*-2*a*-thia(2*a*-S<sup>IV</sup>)-2,3,4*a*,7*a*-tetraazacyclopent[*cd*]indene-1,4(2*H*,3*H*)-dithiones, respectively, in good yields. These photoaddition reactions were facilitated by the addition of oxygen.

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The chemistry of  $\pi$ -hypervalent heterocyclic systems, including 6*a*-thia(S<sup>IV</sup>)-pentalenes, has currently received considerable attention [1*a*-j]. Recently, we have reported the synthesis and reactivity of 2,3-disubstituted 6,7-dihydro-5*H*-2*a*-thia(2*a*-S<sup>IV</sup>)-2,3,4*a*,7*a*-tetraazacyclopent[*cd*]indene-1,4(2*H*,3*H*)-dithiones that have a 10-S-3 type structure [2*a*-g]. In the course of these studies, we found that thiocarboxylic acids add to 2,3-diallyl-6,7-dihydro-5*H*-2*a*-thia(2*a*-S<sup>IV</sup>)-2,3,4*a*,7*a*-tetraazacyclopent[*cd*]indene-1,4(2*H*,3*H*)-dithione (**1**) under irradiation with a high pressure Hg-lamp to give addition products **3** in good yields [3]. We now report the reactivity features of tetraazathiapentalene derivatives in these photoaddition reactions.

The photoreactions were performed in the following manner. A mixture of **1** and 10 molar equivalents of thioacetic acid **2a** in acetone in a Pyrex tube was irradiated with a 300 W high-pressure mercury lamp at room temperature for 6 h. Evaporation of the solvent and purification of the residue by column chromatography on silica gel gave 2,3-bis(3-acetylthiopropyl)-6,7-dihydro-5*H*-2*a*-thia(2*a*-S<sup>IV</sup>)-2,3,4*a*,7*a*-tetraazacyclopent[*cd*]indene-1,4(2*H*,3*H*)-dithione (**3a**) in 72% yield. The structure of **3a** was established from its IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and mass spectra, and elemental analysis.

Table 1 shows the yields of products obtained by the photoreaction of **1** with thiocarboxylic acids **2a** and **2b** under various reaction conditions. When the solvent was

Table 1  
Photoreaction of **1** with Thiocarboxylic Acids [a]

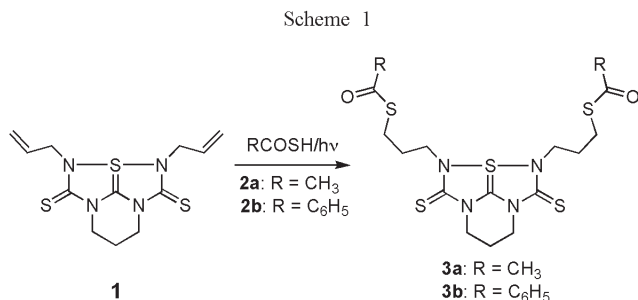
| entry | RCOSH     | solvent | additive           | irrad. time / h | product   | yield / % [b] |
|-------|-----------|---------|--------------------|-----------------|-----------|---------------|
| 1     | <b>2a</b> | acetone |                    | 6               | <b>3a</b> | 72            |
| 2     | <b>2a</b> | benzene |                    | 6               | <b>3a</b> | 70            |
| 3     | <b>2a</b> | acetone | benzo-phenone [c]  | 1               | <b>3a</b> | 88            |
| 4     | <b>2a</b> | acetone | aceto-phenone [c]  | 1               | <b>3a</b> | quant.        |
| 5     | <b>2a</b> | acetone |                    | 1               | <b>3a</b> | quant.        |
| 6     | <b>2b</b> | acetone | O <sub>2</sub> [d] | 48              | <b>3b</b> | 92            |
| 7     | <b>2b</b> | acetone | O <sub>2</sub> [d] | 3               | <b>3b</b> | quant.        |
| 8     | <b>2b</b> | acetone | O <sub>2</sub> [d] | 3 [e]           | <b>3b</b> | 11            |
| 9     | <b>2b</b> | acetone | O <sub>2</sub> [d] | 15 [e]          | <b>3b</b> | 72            |

[a] Reaction was carried out at room temperature; [b] Isolated yields based on **1**; [c] These additives were used as sensitizing agents; [d] Oxygen-bubbled acetone was used as solvent; [e] Reaction was performed in the dark.

changed from acetone to benzene in the photoreaction of **1** with **2a**, no change in the yield of **3a** was observed (entry 2). However, this photoaddition reaction was found to proceed smoothly in a short period of time by the addition of benzophenone and acetophenone as a photosensitizer, giving **3a** in high yields (entries 3 and 4). We also found that this photoreaction proceeds efficiently in the presence of oxygen even in the absence of the photosensitizer (entry 5).

The photoaddition reaction of **2b** to **1** also occurred in a similar fashion to that of the photoreaction of **2a** with **1**, to give 2,3-bis(3-benzoylthiopropyl)-6,7-dihydro-5*H*-2*a*-thia(2*a*-S<sup>IV</sup>)-2,3,4*a*,7*a*-tetraazacyclopent[*cd*]indene-1,4(2*H*,3*H*)-dithione (**3b**) as product (entries 6-7). It may be important to note here that the addition reaction of **2b** to **1** also occurs efficiently in the presence of oxygen even in the dark (entries 8 and 9).

A plausible mechanism of these photoreactions is shown in Scheme 2. The free radical R-CO-S•, which is supposed to be a key reactive species of the photoreaction, is gener-

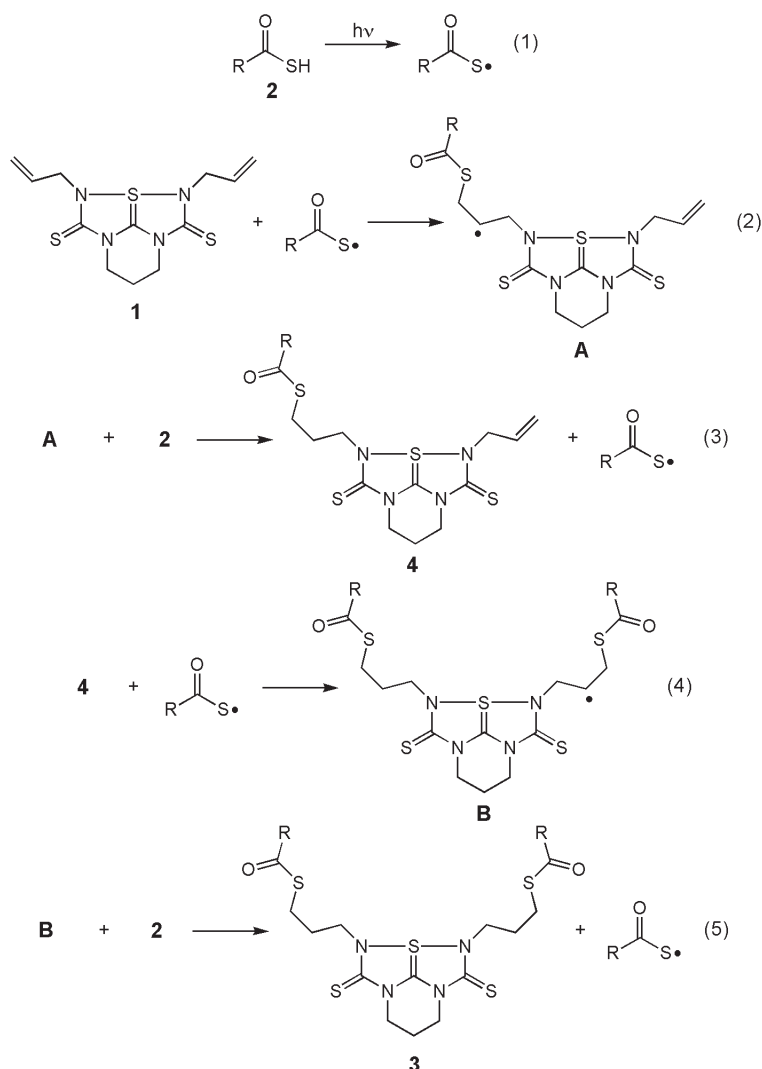


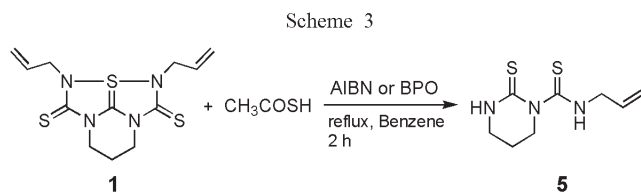
ated by homolysis of the RCOS-H bond from a photoexcited state of the thiocarboxylic acids, or *via* the hydrogen abstraction from the RCOS-H bond by excited triplet states of the sensitizers. However, the results of the entries 8 and 9 in Table 1 suggest that the R-CO-S• radical can also be produced by the attack of oxygen to thiocarboxylic acids and this radical is stable under oxygen atmosphere. The addition of the R-CO-S• radical to **1** occurs in an anti-Markovnikov fashion to give intermediate **A**. Intermediate **A** is converted to **3** *via* the consecutive reactions involving a chain reaction as the R-CO-S• as a chain carrier as shown in Scheme 2. In the absence of **2**, **1** was stable to light. When ethylmercaptane and benzenethiol were used in place of thiocarboxylic acids, the photoaddition reaction of these thiols to **1** did not occur. These results demonstrate that the RS• radicals generated from ethylmercaptane and benzenethiol are unstable under oxygen atmosphere.

When the reaction of **2a** with **1** was conducted in the presence of 2,2'-azobisisobutyronitrile (AIBN) or benzoyl peroxide (BPO) in refluxing benzene in the dark, the adduct **3a** was not formed, but the decomposition product, 1-(allylthiocarbonyl)-perhydropyrimidine-2-thione (**5**), was produced in 70 and 73% yields, respectively (Scheme 3). Furthermore, it was found that the reactions of **1** with **2a** and **2b** are carried out in refluxing benzene in the dark in the absence of AIBN and BPO, **5** was also obtained in 72 and 85% yields, respectively, without the formation of **3a** and **3b**.

These results indicate that **1** undergoes a thermal decomposition in refluxing benzene to give **5** *via* the S<sup>IV</sup>-N bond fission, although **1** is stable at room temperature even under photoirradiation. We believe that the photoaddition reactions described in this paper provide a potential and valuable method for the chemical modification of thermally unstable compounds such as **1**.

Scheme 2





## EXPERIMENTAL

All the solvents were purified by usual procedures. Column chromatography was performed on silica gel (Merck, 70-230 mesh). NMR spectra were obtained with a Varian Mucury 300 NMR spectrometer. Chemical shifts are expressed in ppm with TMS as an internal standard. Melting points were determined with a Yanako MP-500 and are uncorrected. Infrared spectra were recorded by a JASCO Herschel FTIR 230 and a PERKIN ERMER 1600. MS spectra were determined on a JEOL-DX 303 HF. Elemental analyses were performed on a YANAGIMOTO CHN corder MT-3. Photoirradiation was carried out with an Elkosha PIH-300.

### Materials.

Tetraazathiapentalene derivative (**1**) was prepared according to the procedure described in the literature [2]. All other reagents were commercially available.

### Spectral Data of Compound **1**.

Spectral properties for compound **1** are as follows: ir (potassium bromide): 2960, 1580, 1530, 1470, 1180, and 1160 cm<sup>-1</sup>; <sup>1</sup>H nmr (deuteriochloroform): δ 2.37 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 4.36 (t of d, 4H, J = 1.5 and 6.0 Hz, 2 x CH<sub>2</sub> = CHCH<sub>2</sub>N), 4.37 (t, 4H, J = 6.0 Hz, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 5.20-5.28 (m, 4H, 2 x CH<sub>2</sub> = CHCH<sub>2</sub>N), and 5.88 - 6.02 (m, 2H, 2 x CH<sub>2</sub> = CHCH<sub>2</sub>N); <sup>13</sup>C nmr (deuteriochloroform): δ 19.99, 44.84, 47.79, 118.10, 132.20, 156.66, and 169.57; uv (acetonitrile): λ max 260 nm (log ε 4.52); ms: m/z (rel intensity) 213 (M<sup>+</sup> -CH<sub>2</sub> = CHCH<sub>2</sub>NCS; 30), 99 (83); 72 (39), and 41(100).

*Anal.* Calcd. For C<sub>12</sub>H<sub>16</sub>N<sub>4</sub>S<sub>3</sub>: C, 46.12; H, 5.16; N, 17.93. Found: C, 46.02; H, 5.11; N, 17.91.

### General Procedure for the Photoreaction of **1** with **2**.

A solution of **1** (115 mg, 0.368 mmol) and thiocarboxylic acid **2a** or **2b** (3.68 mmol) in degassed acetone (20 mL) in a Pyrex tube was irradiated with a 300 W high-pressure mercury lamp at room temperature for 3-48 h. After the solvent was evaporated, the residue was purified by preparative TLC (silica gel) using CH<sub>2</sub>Cl<sub>2</sub> as an eluent or column chromatography on silica gel using CH<sub>2</sub>Cl<sub>2</sub>/AcOEt = 4/1 as an eluent. The yields of products **3a** and **3b** depended on the reaction conditions (Table 1).

### General Procedure for the Photoreaction of **1** with **2** Under Oxygen Atmosphere.

A solution of **1** (115 mg, 0.368 mmol) and thiocarboxylic acid **2a** or **2b** (3.68 mmol) in oxygen-bubbled acetone (20 mL) in a Pyrex tube was irradiated with a 300 W high-pressure mercury lamp at room temperature for 1-3 h. Products **3a** and **3b** were isolated in a similar manner to that described above.

### Photoreaction of **1** with **2**; Sensitized Irradiation.

An argon-purged solution of **1** (115 mg, 0.368 mmol), **2** (3.68 mmol), and benzophenone or acetophenone (3.68 mmol) in degassed acetone (20 mL) in a Pyrex tube was irradiated with a 300 W high-pressure mercury lamp at room temperature for 1 h. Sensitizers, benzophenone and acetophenone, were found to absorb 82 and 60% of the irradiated light at 365 nm, respectively. Products **3a** and **3b** were isolated in a similar manner to that described above.

### 2,3-Bis(3-acetylthiopropyl)-6,7-dihydro-5H-2a-thia(2a-S<sup>IV</sup>)-2,3,4a,7a-tetraazacyclopent[cd]indene-1,4(2H,3H)-dithione (**3a**).

This compound was isolated in a 72% (123 mg) yield from **1** and **2a** as a colorless solid; mp 129-132 °C; ir (potassium bromide): 2917, 1684, 1577, 1528, 1420, and 1136 cm<sup>-1</sup>; <sup>1</sup>H nmr (deuteriochloroform): δ 2.00 (m, 4H, 2 x NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>S), 2.35 (m, 8H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N, 2 x CH<sub>3</sub>CO), 2.93 (t, 4H, J=7.0 Hz, 2 x NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>S), 3.78 (t, 4H, J=7.0 Hz, 2 x NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>S), 4.40(t, 4H, J= 7.0 Hz, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N); <sup>13</sup>C nmr (deuteriochloroform): δ 19.96, 26.62, 28.03, 30.66, 43.71, 43.74, 156.20, 169.56, and 195.41; ms: m/z 289 (M<sup>+</sup>-CH<sub>3</sub>COSCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NCS).

*Anal.* Calcd. For C<sub>16</sub>H<sub>24</sub>N<sub>4</sub>O<sub>2</sub>S<sub>4</sub>: C, 41.35; H, 5.21; N, 12.06. Found: C, 41.62; H, 5.22; N, 12.02.

### 2,3-Bis[3-benzoylthiopropyl]-6,7-dihydro-5H-2a-thia(2a-S<sup>IV</sup>)-2,3,4a,7a-tetraazacyclopent[cd]indene-1,4(2H,3H)-dithione (**3b**).

This compound was isolated in a 72% (156 mg) yield from **1** and **2b** as a colorless solid; mp 49-50.5 °C; ir (potassium bromide): 1652, 1577, 1525, 1473, 1310, 1203, 1140, 908, 772, and 689 cm<sup>-1</sup>; <sup>1</sup>H nmr (deuteriochloroform): δ 2.15 (m, 4H, 2xNCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>S), 2.37 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 3.12 (t, 4H, J=7.0 Hz, 2xNCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>S), 3.86 (t, 4H, J=7.0 Hz, 2xNCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>S), 4.40 (t, 4H, J=7.0 Hz, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 7.4-7.6 (m, 6H), 7.9-8.0 (m, 4H); ms: m/z 335 (M<sup>+</sup>-C<sub>6</sub>H<sub>5</sub>COSCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NCS).

*Anal.* Calcd. For C<sub>26</sub>H<sub>28</sub>N<sub>4</sub>O<sub>2</sub>S<sub>5</sub>: C, 53.03; H, 4.79; N, 9.52. Found: C, 52.98; H, 4.60; N, 9.80.

### General Procedure for the Reaction of **1** with **2b** in the Dark Under Oxygen Atmosphere.

A solution of **1** (115 mg, 0.368 mmol) and **2b** (3.68 mmol) in oxygen-bubbled acetone (20 mL) in a Pyrex tube was stirred in the dark for 3 h and 15 h. Compound **3b** was isolated in 11% (24.0 mg) and 72% (156 mg) yields, respectively, in a similar manner to that described above.

### General Procedure for the Thermal Reaction of **1** with **2** in the Presence of AIBN or BPO.

The mixture of **1** (115 mg, 0.368 mmol) and thiocarboxylic acid **2a** or **2b** (3.68 mmol) in the presence of a catalytic amount of AIBN or BPO in benzene (15 mL) was refluxed under argon for 2 hours in the dark. After the solvent was evaporated, the residue was purified by column chromatography on silica gel using CH<sub>2</sub>Cl<sub>2</sub>/AcOEt = 9/1 as eluent to give **5** as a colorless solid. When the reaction of **1** with **2a** or **2b** in benzene was conducted in the absence of AIBN and BPO under similar conditions as above, compound **5** was also obtained in 70% (55.55 mg) and 85% (67.4 mg) yields, respectively.

### 1-(Allylthiocarbamoyl)perhydro-2-pyrimidin-2-thione (**5**).

This compound was isolated as a colorless solid, mp 167-168

°C; ir (potassium bromide): 3204, 1558, 1432, 1276, 1191, 1048, 927, 719, and 667  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  2.11 (m, 2H), 3.33-3.38 (m, 2H), 4.3-4.34 (m, 2H), 4.47 (t, 2H,  $J = 6.5$  Hz), 5.21-5.41 (m, 2H), 5.91-6.03 (m, 1H), 6.74 (brs, 1H), 11.8 (brs, 1H); ms:  $m/z$  217 ( $\text{M}^+ - \text{C}_6\text{H}_5\text{COSCH}_2\text{-CH}_2\text{CH}_2\text{NCS}$ ).

*Anal.* Calcd. For  $\text{C}_8\text{H}_{13}\text{N}_3\text{S}_2$ : C, 44.62; H, 6.08; N, 19.51. Found: C, 44.36; H, 6.04; N, 19.97.

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