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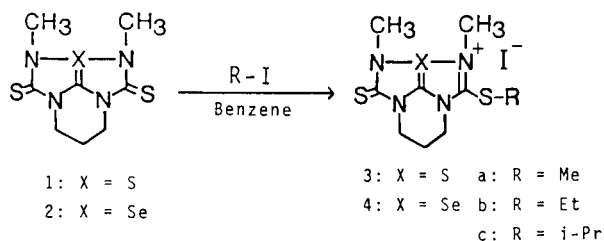
Alkylation of 2,3,4a,7a-tetraazapentalene derivatives having a hypervalent sulfur or selenium using alkyl iodide in benzene under reflux afforded the *S*-monoalkylated tetraazapentalene derivatives **3** and **4** in good yields.

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Chemistry of  $\pi$ -hypervalent heterocyclic systems related to 6a-thia( $S^{IV}$ )pentalene has been of considerable current interest. Several 10 $\pi$ -electrons systems containing the  $S-S^{IV}$ -S,  $O-S^{IV}$ -O, or  $N-S^{IV}$ -N bond in the framework have been synthesized [1a-c]. Recently, we have reported the synthesis [2] and the reactivity [3a-c] of 6,7-dihydro-2,3-dimethyl-5*H*-2a-thia(2a- $S^{IV}$ )-2,3,4a,7a-tetraazacyclopent[*cd*]indene-1,4(2*H*,3*H*)-dithione (**1**) which has 10- $S-3$  type structure. In the course of further studies on the reactivity of tetraazapentalenes, we have found that the tetraazapentalene derivatives **1** and **2** with a hypervalent sulfur or selenium and thiocarbonyl groups react with alkyl iodides to give regioselectively the *S*-monoalkylated products in good yields, although tetraazapentalene **5** with the carbonyl group brings about the *N*-methylation at 4a-position. We now report these results giving information on the reactivity of the tetraazapentalene derivatives.

The reactions are shown in Scheme 1. The procedure for the reaction of **1** with methyl iodide is described as a typical example. The tetraazapentalene **1** was treated with 100 molar equivalents of methyl iodide in benzene under reflux for 24 hours. The resulting precipitate was filtered off and recrystallized from methanol to yield 79% of 6,7-dihydro-1-methylthio-2,3-dimethyl-5*H*-2a-thia(2a- $S^{IV}$ )-3,4a,7a-triaza-2-azoniacyclopent[*cd*]indene-4(3*H*)-thione iodide (**3a**) as a colorless solid. Table 1 shows the yields of the alkylated products in the reaction of **1** or **2** with alkyl iodides. The  $^1H$  nmr spectral data of the *S*-monoalkylated products **3** and **4** are shown in Table 2.

Scheme 1



When methyl or ethyl iodide was used in this reaction, the *S*-monoalkylated product was obtained in a good yield. However, in the case of isopropyl iodide, the yield of the

Table 1

Alkylation of Tetraazapentalene Derivatives with Alkyl Iodides [a]

Tetraazapentalene	Alkyl Iodide	Product	Yield (%) [b]
<b>1</b>	CH <sub>3</sub> I	<b>3a</b>	79
<b>1</b>	CH <sub>3</sub> CH <sub>2</sub> I	<b>3b</b>	69
<b>1</b>	(CH <sub>3</sub> ) <sub>2</sub> CHI	<b>3c</b>	30
<b>2</b>	CH <sub>3</sub> I	<b>4a</b>	83
<b>2</b>	CH <sub>3</sub> CH <sub>2</sub> I	<b>4b</b>	86
<b>2</b>	(CH <sub>3</sub> ) <sub>2</sub> CHI	<b>4c</b>	15

[a] Reactions were carried out under reflux in benzene for 24 hours.

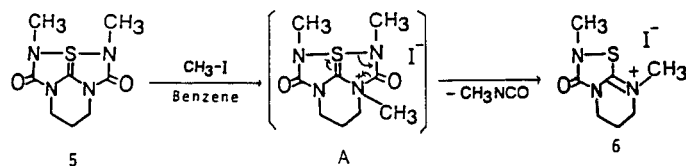
[b] The isolated yield was based on tetraazapentalene derivatives.

alkylated product became considerably lower. The low yields of **3c** and **4c** are considered to be due to the bulkiness of the isopropyl group.

Although further alkylation of **3a** with methyl iodide was examined, the *S*-dialkylated product was not obtained.

Next, we have investigated the reactivity of 6,7-dihydro-2,3-dimethyl-5*H*-2a-thia(2a- $S^{IV}$ )-2,3,4a-7a-tetraazacyclopent[*cd*]indene-1,4(2*H*,3*H*)-dione (**5**) [3c] related to **1**. The reaction of **5** with methyl iodide under similar conditions described above did not give the *O*-monoalkylated product, but 6,7-dihydro-2,4-dimethyl-5*H*-4-azonia-1,2,4-thiadiazolo[4,5-*a*]pyrimidin-1(2*H*)-one iodide (**6**) was obtained in 65% yield. Scheme 2 shows a possible pathway for the formation of **6**. The reaction would be initiated by the

Scheme 2



alkylation of the nitrogen atom at 4a-position of **5** to form an intermediate **A**, followed by the elimination of methyl isocyanate from the intermediate **A** to give the product **6**.

Table 2

<sup>1</sup>H NMR Spectral Data of Compounds 3a-c and 4a-c

Compound	<sup>1</sup> H NMR Solvent, δ (ppm)
3a	Deuteriochloroform 2.62 (m, 2H, NCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> N), 2.91 (s, 3H, SCH <sub>3</sub> ), 3.41 (s, 3H, NCH <sub>3</sub> ), 3.62 (s, 3H, NCH <sub>3</sub> ), 4.55 (t, 2H, NCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> N, J = 5.5 Hz), 4.79 (t, 2H, NCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> N, J = 5.5 Hz)
3b	Deuteriochloroform 1.41 (t, 3H, SCH <sub>2</sub> CH <sub>3</sub> , J = 8.0 Hz), 2.60 (m, 2H, NCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> N), 3.41 (s, 3H, NCH <sub>3</sub> ), 3.42 (q, 2H, SCH <sub>2</sub> CH <sub>3</sub> , J = 8.0 Hz), 3.62 (s, 3H, NCH <sub>3</sub> ), 4.56 (t, 2H, NCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> N, J = 6.1 Hz), 4.81 (t, 2H, NCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> N, J = 6.1 Hz)
3c	Deuteriochloroform 1.48 (d, 6H, SCH(CH <sub>3</sub> ) <sub>2</sub> , J = 6.8 Hz), 2.57 (m, 2H, NCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> N), 3.42 (s, 3H, NCH <sub>3</sub> ), 3.64 (s, 3H, NCH <sub>3</sub> ), 4.01 (sept, 1H, SCH(CH <sub>3</sub> ) <sub>2</sub> , J = 6.8 Hz), 4.61 (t, 2H, NCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> N, J = 6.1 Hz), 4.87 (t, 2H, NCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> N, J = 6.1 Hz)
4a	DMSO-d <sub>6</sub> 2.39 (m, 2H, NCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> N), 2.66 (s, 3H, SCH <sub>3</sub> ), 3.37 (s, 3H, NCH <sub>3</sub> ), 3.67 (s, 3H, NCH <sub>3</sub> ), 4.30 (t, 2H, NCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> N, J = 6.0 Hz), 4.40 (t, 2H, NCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> N, J = 6.0 Hz)
4b	DMSO-d <sub>6</sub> 1.25 (t, 3H, SCH <sub>2</sub> CH <sub>3</sub> , J = 8.0 Hz), 2.39 (m, 2H, NCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> N), 3.18 (q, 2H, SCH <sub>2</sub> CH <sub>3</sub> , J = 8.0 Hz), 3.39 (s, 3H, NCH <sub>3</sub> ), 3.69 (s, 3H, NCH <sub>3</sub> ), 4.30 (t, 2H, NCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> N, J = 5.0 Hz), 4.42 (t, 2H, NCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> N, J = 5.0 Hz)
4c	DMSO-d <sub>6</sub> 1.32 (d, 6H, SCH(CH <sub>3</sub> ) <sub>2</sub> , J = 7.0 Hz), 2.39 (m, 2H, NCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> N), 3.39 (s, 3H, NCH <sub>3</sub> ), 3.71 (s, 3H, NCH <sub>3</sub> ), 3.79 (sept, 1H, SCH(CH <sub>3</sub> ) <sub>2</sub> , J = 7.0 Hz), 4.30 (t, 2H, NCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> N, J = 6.0 Hz), 4.44 (t, 2H, NCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> N, J = 6.0 Hz)

The structure of all products described above was determined by ir, <sup>1</sup>H nmr spectra, and elemental analyses.

## EXPERIMENTAL

Melting points were determined on a Yanagimoto MP-S3 melting point apparatus and were uncorrected. The <sup>1</sup>H nmr spectra were obtained using a JEOL JNM-GX270 spectrometer. Chemical shifts are reported in ppm from TMS as an internal standard and are given in δ units. The ir spectra were determined on a Hitachi 215 Grating infrared spectrometer. Elemental analyses were recorded on a Yanaco CHN recorder MT-2. Purification of products was achieved by recrystallization from methanol or ethanol.

## Typical Procedure for the Formation of 3 and 4.

To a solution of 1 (100 mg, 0.38 mmole) in benzene (10 ml) was added methyl iodide (5.4 g, 38 mmoles) with stirring under argon at room temperature, and the reaction mixture was refluxed under argon for 24 hours. The resulting precipitate was corrected and recrystallized from methanol to give 6,7-dihydro-1-methylthio-2,3-dimethyl-5H-2a-thia(2a-S<sup>IV</sup>)-3,4a,7a-triaza-2-azoniacyclopent[cd]indene-4(3H)-thione iodide (3a) in 79% yield, mp 205-208° dec; ir (potassium bromide): 2920, 1615, 1565, 1485, 1410, 1370, 1310, 1265, 1205, 1135, 940 cm<sup>-1</sup>.

*Anal.* Calcd. for C<sub>9</sub>H<sub>15</sub>N<sub>4</sub>S<sub>3</sub>I: C, 26.87; H, 3.76; N, 13.93. Found: C, 26.87; H, 3.85; N, 14.05.

6,7-Dihydro-1-ethylthio-2,3-dimethyl-5H-2a-thia(2a-S<sup>IV</sup>)-3,4a,7a-triaza-2-azoniacyclopent[cd]indene-4(3H)-thione Iodide (3b).

This compound was obtained from 1 and ethyl iodide in 69% yield as a white solid, mp 204-207° dec; ir (potassium bromide): 2970, 2930, 1595, 1555, 1495, 1410, 1380, 1320, 1250, 1195, 1125, 1085, 1030, 975, 940 cm<sup>-1</sup>.

*Anal.* Calcd. for C<sub>10</sub>H<sub>17</sub>N<sub>4</sub>S<sub>3</sub>I: C, 28.85; H, 4.12; N, 13.46. Found: C, 28.66; H, 4.03; N, 13.31.

6,7-Dihydro-1-isopropylthio-2,3-dimethyl-5H-2a-thia(2a-S<sup>IV</sup>)-3,4a,7a-triaza-2-azoniacyclopent[cd]indene-4(3H)-thione Iodide (3c).

This compound was obtained from 1 and isopropyl iodide in 30% yield as a white solid, mp 195-197° dec; ir (potassium bromide): 2960, 2920, 1615, 1565, 1490, 1410, 1370, 1310, 1265, 1200, 1135, 1050, 940 cm<sup>-1</sup>.

*Anal.* Calcd. for C<sub>11</sub>H<sub>19</sub>N<sub>4</sub>S<sub>3</sub>I: C, 30.70; H, 4.45; N, 13.02. Found: C, 30.50; H, 4.47; N, 13.01.

6,7-Dihydro-1-methylthio-2,3-dimethyl-5H-2a-seleno(2a-Se<sup>IV</sup>)-3,4a,7a-triaza-2-azoniacyclopent[cd]indene-4(3H)-thione Iodide (4a).

This compound was obtained from 2 and methyl iodide in 83% yield as a white solid, mp 215-218° dec; ir (potassium bromide): 2920, 1600, 1560, 1485, 1310, 1240, 1195, 1130, 940, 730 cm<sup>-1</sup>.

*Anal.* Calcd. for C<sub>9</sub>H<sub>15</sub>N<sub>4</sub>S<sub>2</sub>SeI: C, 24.06; H, 3.37; N, 12.47. Found: C, 24.54; H, 3.41; N, 12.81.

6,7-Dihydro-1-ethylthio-2,3-dimethyl-5H-2a-seleno(2a-Se<sup>IV</sup>)-3,4a,7a-triaza-2-azoniacyclopent[cd]indene-4(3H)-thione Iodide (4b).

This compound was obtained from 2 and ethyl iodide in 86% yield as a white solid, mp 211-214° dec; ir (potassium bromide): 2970, 2930, 1595, 1555, 1495, 1320, 1250, 1195, 1125, 940 cm<sup>-1</sup>.

*Anal.* Calcd. for C<sub>10</sub>H<sub>17</sub>N<sub>4</sub>S<sub>2</sub>SeI: C, 25.93; H, 3.70; N, 12.09. Found: C, 25.98; H, 3.73; N, 11.97.

6,7-Dihydro-1-isopropylthio-2,3-dimethyl-5H-2a-seleno(2a-Se<sup>IV</sup>)-3,4a,7a-triaza-2-azoniacyclopent[cd]indene-4(3H)-thione Iodide (4c).

This compound was obtained from 2 and isopropyl iodide in 15% yield as a white solid, mp 214-217° dec; ir (potassium bro-

mide): 2920, 1595, 1555, 1495, 1315, 1245, 1195, 1125, 940  $\text{cm}^{-1}$ .

*Anal.* Calcd. for  $\text{C}_{11}\text{H}_{19}\text{N}_4\text{S}_2\text{SeI}$ : C, 27.68; H, 4.01; N, 11.74.

Found: C, 27.66; H, 4.03; N, 11.91.

6,7-Dihydro-2,4-dimethyl-5*H*-4-azonia-1,2,4-thiadiazolo[4,5-*a*]-pyrimidin-1(2*H*)-one Iodide (**6**).

This compound was obtained from **5** and methyl iodide in 65% yield as a white solid, mp 219-222° dec; ir (potassium bromide): 2940, 1730, 1640, 1490, 1410, 1375, 1310, 1290, 1230, 1155, 1140, 880, 715  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  2.44 (m, 2H,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$ ), 3.32 (s, 3H,  $\text{NCH}_3$ ), 3.39 (s, 3H,  $\text{NCH}_3$ ), 3.99 (t, 2H,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$ ,  $J = 5.0$  Hz), 4.09 (t, 2H,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$ ,  $J = 5.0$  Hz).

*Anal.* Calcd. for  $\text{C}_7\text{H}_{12}\text{N}_3\text{OSI}$ : C, 26.85; H, 3.86; N, 13.42.

Found: C, 26.79; H, 3.99; N, 13.01.

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