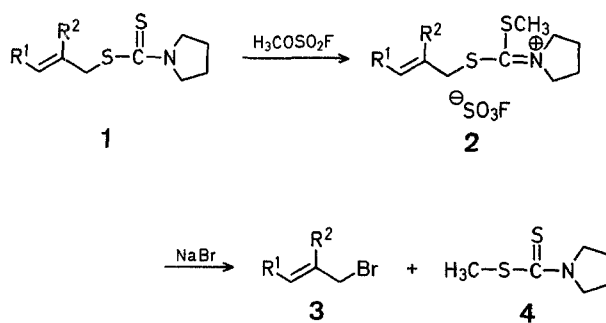


## Conversion of Dithiocarbamates to Bromides via *S*-Alkylation

Akio SAKURAI\*, Toshio HAYASHI, Takeshi OISHI

The Institute of Physical and Chemical Research, Wako-shi, Saitama 351, Japan

We have already reported<sup>1</sup> that allylic dithiocarbamates can easily be converted via *S*-alkylation by methyl iodide into the corresponding allylic iodides. However, since the allylic iodides are generally too unstable to be stored, we have designed a simple synthesis for allylic bromides, which are much more stable than the corresponding iodides. The method involves the addition of methyl fluorosulfate to an allylic dithiocarbamate **1** in dichloromethane. The precipitated *S*-methyliminium fluorosulfate derivative **2** was dissolved in dimethylformamide, and then treated with sodium bromide at room temperature to give the allylic bromide **3** (62–70% yield) and methyl 1-pyrrolidincarbodithioate (**4**). The bromide was easily separated from **4** which precipitated from the solution. The reaction, when conducted in a solvent such as acetonitrile or dichloromethane, afforded the bromides in lower yields.



### Allylic Bromides **3**; General Procedure:

To a solution of the allylic 1-pyrrolidincarbodithioate **1** (1.8 mmol) dissolved in dry dichloromethane (2 ml) is added a solution of methyl fluorosulfate (2.0 mmol) in dry dichloromethane (1 ml) under cooling in an ice-bath. After the mixture has been stirred for 5 h, it is concentrated in vacuo and sodium bromide (2.0 mmol) is added to the residue dissolved in dimethylformamide (2 ml). Af-

Table. Allylic Bromides 3

Product No.	R <sup>1</sup>	R <sup>2</sup>	Yield [%]	b.p. [°C]/torr	Molecular formula <sup>a</sup>	<sup>1</sup> H-N.M.R. (CDCl <sub>3</sub> /TMS/100 MHz) $\delta$ [ppm]
3a	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	CH <sub>3</sub>	62	63–65°/10	C <sub>7</sub> H <sub>13</sub> Br (177.1)	0.90 (t, 3 H, CH <sub>3</sub> ); 1.2–1.6 (m, 2 H, CH <sub>2</sub> ); 1.74 (s, 3 H, CH <sub>3</sub> ); 1.8–2.1 (m, 2 H, CH <sub>2</sub> ); 3.96 (s, 2 H, CH <sub>2</sub> —Br); 5.60 (t, 1 H, —CH=)
3b	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	H	64	66–68°/10	C <sub>7</sub> H <sub>13</sub> Br (177.1)	0.89 (t, 3 H, CH <sub>3</sub> ); 1.2–1.5 (m, 4 H, CH <sub>2</sub> ); 1.9–2.2 (m, 2 H, CH <sub>2</sub> ); 3.96 (d, 2 H, CH <sub>2</sub> —Br); 5.4–5.9 (m, 2 H, —CH=)
3c	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	65	68–70°/10	C <sub>8</sub> H <sub>15</sub> Br (191.1)	0.90 (t, 3 H, CH <sub>3</sub> ); 1.2–1.4 (m, 4 H, CH <sub>2</sub> ); 1.74 (s, 3 H, CH <sub>3</sub> ); 1.9–2.2 (m, 2 H, CH <sub>2</sub> ); 3.94 (s, 2 H, CH <sub>2</sub> —Br); 5.54 (t, 1 H, —CH=)
3d	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	H	67	80–81°/11	C <sub>8</sub> H <sub>15</sub> Br (191.1)	0.88 (t, 3 H, CH <sub>3</sub> ); 1.28 (s, br, 6 H, CH <sub>2</sub> ); 1.9–2.2 (m, 2 H, CH <sub>2</sub> ); 3.94 (d, 2 H, CH <sub>2</sub> —Br); 5.50–5.90 (m, 2 H, —CH=)
3e	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	H	70	82–83°/11	C <sub>9</sub> H <sub>17</sub> Br (205.1)	0.88 (t, 3 H, CH <sub>3</sub> ); 1.28 (s, br, 8 H, CH <sub>2</sub> ); 1.9–2.2 (m, 2 H, CH <sub>2</sub> ); 3.94 (d, 2 H, CH <sub>2</sub> —Br); 5.5–5.9 (m, 2 H, —CH=)
3f	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	CH <sub>3</sub>	68	83–85°/11	C <sub>10</sub> H <sub>19</sub> Br (219.2)	0.88 (t, 3 H, CH <sub>3</sub> ); 1.30 (s, br, 8 H, CH <sub>2</sub> ); 1.75 (s, 3 H, CH <sub>3</sub> ); 1.9–2.2 (m, 2 H, CH <sub>2</sub> ); 3.95 (s, 2 H, CH <sub>2</sub> —Br); 5.52 (t, 1 H, —CH=)

<sup>a</sup> All compounds gave satisfactory microanalyses (C  $\pm$  0.34%, H  $\pm$  0.26%, Br  $\pm$  0.36%) and showed characteristic CH<sub>2</sub> deformation bands near  $\nu$  = 1210 cm<sup>-1</sup> in the I.R. spectra.

er the reaction mixture has been stirred for 48 h at room temperature, the resultant precipitate is crushed in *n*-hexane (5 ml), separated by filtration, and washed with *n*-hexane (10 ml). The combined washings are concentrated in vacuo and the residue is poured into water (5 ml) and then extracted with ether (15 ml). The ethereal layer is dried with anhydrous sodium sulfate. After the evaporation of ether in vacuo, the residue is distilled under reduced pressure (Table).

Received: April 23, 1980

<sup>1</sup> A. Sakurai, T. Hayashi, I. Hori, Y. Jindo, T. Oishi, *Synthesis* **1978**, 370, and references cited therein.