

Kazuo Ichikawa

Central Research Laboratories, Meiji Seika Kaisha Ltd., Morooka, Kohoku-ku, Yokohama 222, Japan

Seiichi Inoue and Kikumasa Sato

Department of Applied Chemistry, Faculty of Engineering, Yokohama National University, Ooka, Minami-ku, Yokohama 233, Japan

Received August 6, 1979

Intramolecular cyclization of 2-(allylthio)propionyl chloride (**3a**) effected by aluminum chloride gave two dihydrothiopyran-3-ones (**5a,6a**) and 5-chloro-2-methyltetrahydrothiopyran-3-one (**7a**). Treatment of propargylthioacetyl chloride (**4a**) with aluminum chloride afforded 5-chloro-3,6-dihydro-2*H*-thiopyran-3-one (**10a**). The cyclization reactions of related compounds were also studied.

*J. Heterocyclic Chem.*, 17, 289 (1980).

In a previous paper (1) we have reported the formation of dihydrothiopyran-3-ones by the intramolecular cyclization of allylthioacetyl chlorides. This paper reports the extension of this procedure to the cyclization of substituted 2-(allylthio)propionyl chlorides and propargylthioacetyl and propionyl chlorides.

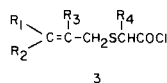
The substituted 2-(allylthio)propionic acids (**1a-d**), propargylthioacetic acids (**2a,b,d,f**), and 2-(propargylthio)propionic acids (**2c,e,g**) were obtained by the reaction of corresponding allyl or propargyl halides with mercaptoacetic or 2-mercaptopropionic acid by the method described in a previous paper (1). Their yields and properties are summarized in Table I and II. The acid chlorides (**3a-d**, **4a-g**) (Table III, IV) were prepared by treatment of acids with thionyl chloride.

Treatment of 2-(allylthio)propionyl chloride (**3a**) with aluminum chloride in 1,1,2,2-tetrachlorethane (TCE) at 50-55° for 2.5 hours afforded the mixture of three compounds in a ratio of 36.5:30.0:34.5. Each substance was isolated by preparative gas-liquid chromatography. The first and second compounds were determined to be 2-methyl-3,4-dihydro-2*H*-thiopyran-3-one (**5a**) and 2-methyl-3,6-dihydro-2*H*-thiopyran-3-one (**6a**), by the ir, uv, nmr, and mass spectrometry. The third compound was a crystalline substance, m.p. 56°. The structure was assigned as 5-chloro-2-methyltetrahydrothiopyran-3-one (**7a**) based on the mass, ir, uv, and nmr spectra. The mass spectrum showed a molecular ion peak at *m/e* 164 and ir spectrum indicated a carbonyl band at 1720 cm<sup>-1</sup>. In the uv spectrum, it showed a absorption maximum around 240 nm, suggesting the absence of  $\alpha,\beta$ -unsaturated ketone structure. The nmr spectrum agreed with the structure **7a**. One of the C-4 methylene protons exhibited a triplet at  $\delta$  2.53 ppm (*J* = 12.5 Hz), while the signals of another one was overlapped with multiplet of C-6 methylene protons at  $\delta$  3.05. This means that geminal coupling constant *J*<sub>4a,4e</sub> and vicinal coupling constant *J*<sub>4a,5</sub> have the same value

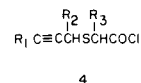
of 12.5 Hz, indicating that the proton at C-5 is an axial orientation.

Cyclization of 2-(2-butenylthio)propionyl chloride (**3a**) afforded two products, 2,4-dimethyl-3,6-dihydro-2*H*-thiopyran-3-one (**6b**) (29%) and 5-chloro-2,4-dimethyltetrahydrothiopyran-3-one (**7b**) (25%). In the nmr spectrum of **7b**, the coupling constant between H-4 and H-5 was 10.5 Hz, indicating that H-4 and H-5 are in an axial orientation. The coupling constants (10.5 Hz and 5.5 Hz) between H-5 and two protons at C-6 supported this conformation.

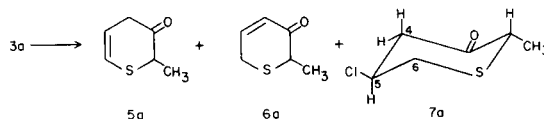
The reaction of 2-(2-methylallylthio)propionyl chloride (**3c**) with aluminum chloride gave 2,5-dimethyl-3,6-dihydro-2*H*-thiopyran-3-one (**6c**) as sole product in 76% yield. With 2-(3,3-dimethylallylthio)propionyl chloride (**3d**) this procedure resulted in formation of 2-methyl-4-isopropylidinetetrahydrothiophen-3-one (**8d**) (25%). As reported (1), the similar compound, 4-isopropylidene-tetrahydrothiophen-3-one was obtained by cyclization of 3,3-dimethylallylthioacetyl chloride.

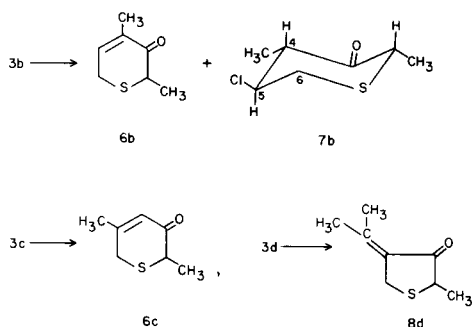


- a, R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = H, R<sub>4</sub> = Me  
 b, R<sub>1</sub> = R<sub>3</sub> = H, R<sub>2</sub> = R<sub>4</sub> = Me  
 c, R<sub>1</sub> = R<sub>2</sub> = H, R<sub>3</sub> = R<sub>4</sub> = Me  
 d, R<sub>1</sub> = R<sub>2</sub> = R<sub>4</sub> = Me, R<sub>3</sub> = H



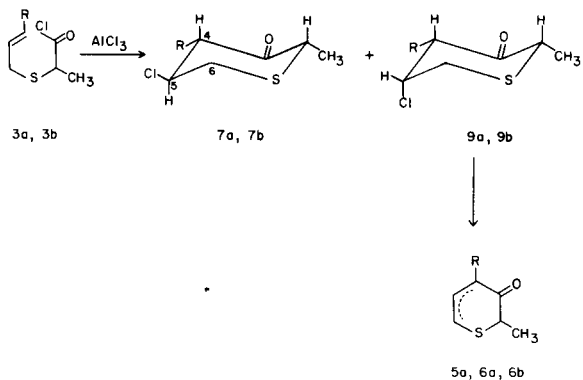
- a, R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = H  
 b, R<sub>1</sub> = Me, R<sub>2</sub> = R<sub>3</sub> = H  
 c, R<sub>1</sub> = R<sub>2</sub> = H, R<sub>3</sub> = Me  
 d, R<sub>1</sub> = R<sub>3</sub> = H, R<sub>2</sub> = Me  
 e, R<sub>1</sub> = H, R<sub>2</sub> = R<sub>3</sub> = Me  
 f, R<sub>1</sub> = R<sub>2</sub> = Me, R<sub>3</sub> = H  
 g, R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = Me



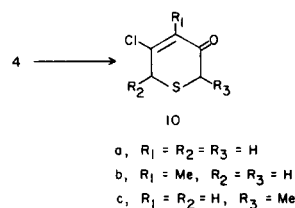


In a series of reactions described above, the formation of compounds **7a** and **7b** is interesting, because the similar compound containing chlorine was not obtained in the cyclization of allylthioacetate chlorides (1). It seems reasonable to assume that, as shown in Scheme I, cyclization of **3a** (or **3b**) forms two isomers **7a** (or **7b**) and **9a** (or **9b**), and the latter is transformed to **5a** and **6a** (or **6b**) by *trans* elimination of hydrogen chloride. The methyl group at C-2 of compound **7a** (or **7b**) may stabilize the conformation in which the chlorine group is equatorial.

Scheme I



When propargylthioacetate chloride (**4a**) was treated with aluminum chloride in TCE, 5-chloro-3,6-dihydro-2H-thiopyran-3-one (**10a**) was obtained in 64% yield. Compound **10a** was characterized by the spectral data: ir, 1658 (C=O), 1610 (C=C) and 743 cm<sup>-1</sup> (C-Cl) uv, λ max 245 nm (α,β-unsaturated ketone); nmr, two methylene groups at δ 3.63 and one olefinic proton at 6.24 ppm; mass spectrum, molecular ion peak at m/e 148. The cyclization of 3-methylpropargylthioacetate chloride (**4b**) or 2-(propargylthio)propionyl chloride (**4c**) produced 5-chloro-4-methyl-3,6-dihydro-2H-thiopyran-3-one (**10b**) (58%) or 5-chloro-2-methyl-3,6-dihydro-2H-thiopyran-3-one (**10c**) (74%), respectively. The attempted cyclization of compounds (**4d,e,f,g**) was unsuccessful.



## EXPERIMENTAL

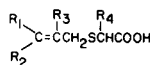
All melting points and boiling points are uncorrected. Infrared (ir) spectra were obtained with a Hitachi Model 215 spectrophotometer and uv spectra with a Hitachi Model ESP-2 spectrophotometer. Nmr spectra were recorded at 100 MHz with a JOEL JMN-4H-100 spectrometer and at 60 MHz with a Varian T-60 spectrometer, tetramethylsilane being used as an internal reference. Mass (ms) spectra were taken with JEOL-01 SG double focusing spectrometer using a direct insertion technique and the ionizing energy was 73 eV. Preparative gas chromatography was performed on a JEOL-1100 TFP Preparative gas chromatography using a 5 mm. × 200 cm. column of 25% silicone DC 200 on Celite 545 with He as the carrier gas.

## Starting Materials.

1-Chloro-3-methyl-2-butene (2), 3-bromo-1-butyne (3), 1-bromo-2-butyne (4) and 2-bromo-3-pentyne were prepared by the methods described in the literatures. The other chemicals were commercially available.

Table I.

## 2-(Allylthio)propionic Acids (I)



Compound	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	Yield (%)	B.p. (°C (mm.))	Formula	Analyses (%)			
								Found		Calcd.	
								C	H	C	H
<b>1a</b>	H	H	H	CH <sub>3</sub>	48	105-107 (0.5)	C <sub>6</sub> H <sub>10</sub> O <sub>2</sub> S	49.03	6.19	49.29	6.89
<b>1b</b>	H	H	CH <sub>3</sub>	CH <sub>3</sub>	67	104-107 (1.0)	C <sub>7</sub> H <sub>12</sub> O <sub>2</sub> S	52.18	7.67	52.47	7.55
<b>1c</b>	H	H	CH <sub>3</sub>	CH <sub>3</sub>	71	107-110 (1.8)	C <sub>7</sub> H <sub>12</sub> O <sub>2</sub> S	52.24	7.69	52.47	7.55
<b>1d</b>	CH <sub>3</sub>	CH <sub>3</sub>	H	CH <sub>3</sub>	45	111-113 (0.7)	C <sub>8</sub> H <sub>14</sub> O <sub>2</sub> S	54.91	8.06	55.12	8.10

Table II  
Propargylthioacetic and Propargylthiopropionic Acid (2)

$$R_1-C \equiv C \overset{R_2}{\underset{R_3}{CH}} S CH_2 COOH$$

Compound	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	Yield (%)	B.p. (°C (mm.))	Formula	Analyses (%)			
							Found		Calcd.	
							C	H	C	H
2a (a)	H	H	H	42	110-113 (2.0) m.p. 60-61°	C <sub>5</sub> H <sub>6</sub> O <sub>2</sub> S	46.02	4.60	46.14	4.65
2b	CH <sub>3</sub>	H	H	56	117-120 (0.4)	C <sub>6</sub> H <sub>8</sub> O <sub>2</sub> S	49.86	5.50	49.98	5.59
2c	H	H	CH <sub>3</sub>	38	113-116 (1.0) m.p. 42-43°	C <sub>5</sub> H <sub>6</sub> O <sub>2</sub> S	49.78	5.56	49.98	5.59
2d	H	CH <sub>3</sub>	H	33	101-130 (1.0)	C <sub>6</sub> H <sub>8</sub> O <sub>2</sub> S	49.80	5.51	49.98	5.59
2e	H	CH <sub>3</sub>	CH <sub>3</sub>	70	94-97 (0.3)	C <sub>7</sub> H <sub>10</sub> O <sub>2</sub> S				
2f	CH <sub>3</sub>	CH <sub>3</sub>	H	70	123-125 (0.5)	C <sub>7</sub> H <sub>10</sub> O <sub>2</sub> S	53.01	6.32	53.14	6.37
2g	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	69	124-127 (0.6)	C <sub>8</sub> H <sub>12</sub> O <sub>2</sub> S	55.88	6.85	55.79	7.02

(a) G. Pourcelot and P. Cadiot, *Bull. Soc. Chim. France*, 3016 (1966).

Table III  
2-(Allylthio)propionyl Chlorides (3)

Compound	Yield (%)	B.p. (°C (mm.))	n <sub>D</sub> <sup>20</sup>	Formula	Analyses (%)			
					Found		Calcd.	
					C	H	C	H
3a	81	38-41 (0.6)	1.4989	C <sub>6</sub> H <sub>9</sub> ClOS	43.63	5.69	43.77	5.51
3b	88	70-71 (1.4)	1.5015	C <sub>7</sub> H <sub>11</sub> ClOS	47.21	6.42	47.06	6.21
3c	75	70-72 (1.0)	1.4989	C <sub>7</sub> H <sub>11</sub> ClOS	47.27	6.03	47.06	6.21
3d	67	64-66 (0.8)	1.5019	C <sub>8</sub> H <sub>13</sub> ClOS	49.64	6.99	49.87	6.79

Table IV  
Progargylthioacetyl Chlorides (4)

Compound	Yield (%)	B.p. (°C (mm.))	n <sub>D</sub> <sup>20</sup>	Formula	Analyses (%)			
					Found		Calcd.	
					C	H	C	H
4a	74	44-46 (0.6)	1.5273	C <sub>6</sub> H <sub>9</sub> ClOS	40.18	3.20	40.41	3.29
4b	84	62-65 (0.3)	1.5258	C <sub>6</sub> H <sub>9</sub> ClOS	44.07	4.54	44.31	4.34
4c	69	51-55 (1.4)	1.5142	C <sub>6</sub> H <sub>9</sub> ClOS	44.46	4.17	44.31	4.34
4d	65	44-47 (0.9)	1.5076	C <sub>6</sub> H <sub>9</sub> ClOS	44.59	4.12	44.31	4.34
4e	84	47-49 (0.3)	1.4990	C <sub>7</sub> H <sub>9</sub> ClOS	47.41	5.08	47.59	5.13
4f	85	54-58 (0.3)	1.5132	C <sub>7</sub> H <sub>9</sub> ClOS	47.74	5.01	47.59	5.13
4g	79	66-69 (0.5)	1.5028	C <sub>8</sub> H <sub>11</sub> ClOS	50.16	5.90	50.39	5.82

#### The Reaction of 3a with Aluminum Chloride.

A solution of 3a (23 g., 0.14 mole) in dry TCE (70 ml.) was added dropwise during 2 hours to a solution of anhydrous aluminum chloride (20 g., 0.15 mole) in dry TCE (140 ml.) at 50° with stirring. The mixture was stirred for additional 1.5 hours at 50°, cooled, and poured into ice and diluted hydrochloric acid. The organic layer was separated and the aqueous layer was extracted with ether (three 40 ml. portions). The combined organic layer was washed with saturated sodium bicarbonate solution, and dried. After the solvent was removed *in vacuo*, the dark residue was distilled to give a pale yellow oil (6.7 g.; b.p. 70-73° (0.3 mm.)). The

glc analysis showed three components: 5a (35.5%), 6a (30.0%), and 7a (34.5%). Each components were separated by preparative gas chromatography using silicone DC 200 at 180°.

#### 3,4-Dihydro-2-methyl-2H-thiopyran-3-one (5a).

A colorless oil was obtained, n<sub>D</sub><sup>20</sup> 1.5402; uv λ max (95% ethanol): 219 (ε 3860) and 241 nm (3580); ir (neat): 1700 (C=O) and 1610 cm<sup>-1</sup> (C=C); nmr (carbon tetrachloride): δ 1.30 (d, 3H, J = 7.0 Hz), 2.97 (m, 2H), 3.56 (tq, 1H, J = 2.0 and 7.0 Hz), 5.82 (dt, 1H, J = 9.0 and 4.0 Hz), 6.20 (dt, 1H, J = 9.0 and 2.0 Hz); ms: m/e 128 (M<sup>+</sup>).

Anal. Calcd. for C<sub>6</sub>H<sub>8</sub>OS: C, 56.22; H, 6.29. Found: C, 55.97; H, 6.10.

3,6-Dihydro-2-methyl-2*H*-thiopyran-3-one (**6a**).

A colorless oil was obtained  $n_D^{20}$  1.5362;  $uv \lambda$  max (95% ethanol): 232 nm ( $\epsilon$  5830); ir (neat): 1680 (C=O) and 1620  $cm^{-1}$  (C=C); nmr (carbon tetrachloride):  $\delta$  1.47 (d, 3H,  $J = 7.0$  Hz), 3.25-3.60 (m, 3H), 6.02 (dt, 1H,  $J = 11.0$  and 2.0 Hz), 6.90 (ddd, 1H,  $J = 11.0$ , 5.0 and 3.0 Hz); ms:  $m/e$  128 ( $M^+$ ).

Anal. Calcd. for  $C_8H_8OS$ : C, 56.22; H, 6.29. Found: C, 56.03; H, 6.09.

5-Chloro-2-methyltetrahydrothiopyran-3-one (**7a**).

A pale yellow oil which solidified on standing at room temperature and recrystallized from petroleum ether to light yellow needles was obtained, m.p. 56°; ir (neat): 1720 (C=O), 1675 and 683  $cm^{-1}$  (C-Cl); nmr (carbon tetrachloride):  $\delta$  1.24 (d, 3H,  $J = 7.0$  Hz), 2.53 (t, 1H,  $J = 12.5$  Hz), ca. 3.1 (m, 3H), 3.45 (q, 1H,  $J = 7.0$  Hz), 4.38 (m, 1H); ms:  $m/e$  164 ( $M^+$ ).

Anal. Calcd. for  $C_8H_9ClOS$ : C, 43.77; H, 5.51. Found: C, 43.95; H, 5.52.

The Reaction of **3b** with Aluminum Chloride.

The reaction of **3b** (15.7 g., 0.008 mole) with anhydrous aluminum chloride by the same procedure as described above gave a colorless oil (9.6 g.), b.p. 75-75° (0.2 mm.). Analysis by glc showed **6b**, 54% and **7b**, 46%. These were separated by preparative gas chromatography.

2,4-Dimethyl-3,6-dihydro-2*H*-thiopyran-3-one (**6b**).

A colorless oil was obtained  $n_D^{20}$  1.5342;  $uv \lambda$  max (95% ethanol): 241 nm ( $\epsilon$  9386); ir (neat): 1670 (C=O) and 1630  $cm^{-1}$  (C=C); nmr (carbon tetrachloride):  $\delta$  1.29 (d, 3H,  $J = 7.5$  Hz), 1.75 (s, 3H), 2.9-3.7 (m, 3H), 6.62 (m, 1H); ms:  $m/e$  142 ( $M^+$ ).

Anal. Calcd. for  $C_7H_{10}OS$ : C, 59.12; H, 7.09. Found: C, 58.96; H, 6.97.

5-Chloro-2,4-dimethyltetrahydrothiopyran-3-one (**7b**).

Light yellow needles were obtained m.p. 91-91.5° (petroleum ether); ir (neat): 1727 (C=O), 1670 and 690  $cm^{-1}$  (C-Cl); nmr (carbon tetrachloride):  $\delta$  1.25 (d, 3H,  $J = 7.0$  Hz), 1.30 (d, 3H,  $J = 7.0$  Hz), 2.46 (dq, 1H,  $J = 10.5$  and 7.0 Hz), 3.07 (dd, 1H,  $J = 13.7$  and 5.5 Hz), 3.20 (dd, 1H,  $J = 13.7$  and 10.5 Hz), 3.45 (q, 1H,  $J = 7.0$  Hz), 4.01 (dt, 1H,  $J = 10.5$  and 5.5 Hz); ms:  $m/e$  178 ( $M^+$ ).

Anal. Calcd. for  $C_7H_{11}ClOS$ : C, 47.07; H, 6.21. Found: C, 47.18; H, 6.90.

2,5-Dimethyl-3,6-dihydro-2*H*-thiopyran-3-one (**6c**).

The cyclization of **3c** (15 g., 0.084 mole) was effected by the same method as described above to give a colorless oil (12 g., 76%); b.p. 55-56° (0.15 mm.),  $n_D^{20}$  1.5389;  $uv \lambda$  max (95% ethanol): 240 nm ( $\epsilon$  8240); ir (neat): 1670 (C=O) and 1620  $cm^{-1}$  (C=C); nmr (carbon tetrachloride):  $\delta$  1.30 (d, 3H,  $J = 7.5$  Hz), 1.97 (s, 3H), 3.06 (d, 1H,  $J = 17.5$  Hz), 3.29 (q, 1H,  $J = 7.5$  Hz), 3.44 (d, 1H,  $J = 17.5$  Hz), 5.23 (bs, 1H); ms:  $m/e$  142 ( $M^+$ ).

Anal. Calcd. for  $C_7H_{10}OS$ : C, 59.12; H, 7.09. Found: C, 59.02; H, 7.05.

2-Methyl-4-isopropylidenetetrahydrothiophen-3-one (**8d**).

Compound **3d** (19.3 g., 0.1 mole) was similarly treated with anhydrous aluminum chloride to give **8d** as a colorless oil (3.9 g., 25%), b.p. 57° (0.2 mm.);  $n_D^{20}$  1.5381;  $uv \lambda$  max (95% ethanol): 253 nm ( $\epsilon$  9400); ir (neat): 1682 (C=O) and 1618  $cm^{-1}$  (C=C); nmr (carbon tetrachloride):  $\delta$  1.32 (d, 3H,  $J = 7.0$  Hz), 3.57 (q, 2H,  $J = 2.0$  Hz); ms:  $m/e$  156 ( $M^+$ ).

Anal. Calcd. for  $C_8H_{12}OS$ : C, 61.50; H, 7.74. Found: C, 61.24; H, 7.67.

5-Chloro-3,6-dihydro-2*H*-thiopyran-3-one (**10a**).

From **4a** (11.8 g., 0.08 mole) was obtained **10a** as a colorless oil (7.6 g., 64%), b.p. 61-62° (0.6 mm.);  $n_D^{20}$  1.5863;  $uv \lambda$  max (95% ethanol): 243 nm ( $\epsilon$  6960); ir (neat): 1658 (C=O), 1610 (C=C) and 743  $cm^{-1}$  (C-Cl); nmr (carbon tetrachloride):  $\delta$  3.27 (s, 2H), 3.63 (s, 2H), 6.24 (s, 1H); ms:  $m/e$  150 ( $M+2$ ), 148 ( $M^+$ ).

Anal. Calcd. for  $C_8H_9ClOS$ : C, 40.41; H, 3.39. Found: C, 40.25; H, 3.21.

5-Chloro-4-methyl-3,6-dihydro-2*H*-thiopyran-3-one (**10b**).

From **4b** (8.3 g., 0.051 mole) was obtained **10b** as a colorless oil (4.8 g., 58%); b.p. 68-69° (0.2 mm.);  $n_D^{20}$  1.5696;  $uv \lambda$  max (95% ethanol): 250 nm ( $\epsilon$  7888); ir (neat): 1670 (C=O), 1624 (C=C) and 750  $cm^{-1}$  (C-Cl); nmr (carbon tetrachloride):  $\delta$  1.97 (t, 3H,  $J = 1.4$  Hz), 3.28 (s, 2H), 3.63 (q, 2H,  $J = 1.4$  Hz); ms:  $m/e$  164 ( $M+2$ ), 162 ( $M^+$ ).

Anal. Calcd. for  $C_9H_9ClOS$ : C, 44.31; H, 4.34. Found: C, 44.13; H, 4.46.

5-Chloro-2-methyl-3,6-dihydro-2*H*-thiopyran-3-one (**10c**).

From **4c** (17.5 g., 0.108 mole) was obtained **10c** as a colorless oil (12.9 g., 74%), b.p. 62-63° (0.3 mm.);  $n_D^{20}$  1.5590;  $uv \lambda$  max (95% ethanol): 242 nm ( $\epsilon$  16260); ir (neat): 1676 (C=O), 1620 (C=C) and 735  $cm^{-1}$  (C-Cl); nmr (carbon tetrachloride):  $\delta$  1.39 (d, 3H,  $J = 7.5$  Hz), 3.45 (dq, 1H,  $J = 1.4$  and 7.5 Hz), 3.47 (d, 1H,  $J = 18.7$  Hz), 3.87 (dt, 1H,  $J = 18.7$  and 1.4 Hz), 6.23 (t, 1H,  $J = 1.4$  Hz); ms:  $m/e$  164 ( $M+2$ ), 162 ( $M^+$ ).

Anal. Calcd. for  $C_8H_7ClOS$ : C, 44.31; H, 4.34. Found: C, 44.09; H, 4.20.

## Acknowledgement.

One of the authors, K. I., wishes to express his deep gratitude to Dr. T. Niida, Director of these laboratories, for his encouragement, and to Dr. T. Ito of this laboratory for his kind advice and helpful discussion.

## REFERENCES AND NOTES

- (1) K. Sato, S. Inoue, and K. Kondo, *J. Org. Chem.*, **36**, 2077 (1971).
- (2) J. Tanaka, T. Katagiri, and S. Yamada, *J. Chem. Soc. Japan*, **87**, 877 (1966).
- (3) F. Sondheimer and D. A. Ben-Efraim, *J. Am. Chem. Soc.*, **85**, 52 (1963).
- (4) K. Schulte and K. P. Reiss, *Chem. Ber.*, **87**, 964 (1954).
- (5) L. I. Smith and J. S. Swenson, *J. Am. Chem. Soc.*, **79**, 2962 (1957).