(m, 2 H, chain 4-CH_2), 1.51 (m, 2 H, chain 4-CH_2), 1.11 (m, 2 H, chain 3-CH_2), 0.95 (m, 2 H, chain 3-CH_2), 0.27 (m, 2 H, chain 1-CH_2), +0.05 to −0.15 (m, 4 H, chain 2-CH_2), −0.72 (m, 2 H, chain 1-CH_2), −4.00 (br s, 2 H, NH). Anal. Calcd for $C_{46}H_{54}N_4O_2$: C, 79.50; H, 7.83; N, 8.06; O, 4.60. Found: C, 79.24; H, 8.00; N, 7.94; O, 4.80.

7,17-Diethyl-2,8,12,18-tetramethyl-3,13-[(2,5-dioxo-1,4-phenylene)bis(pentamethylene)]porphyrin (1b). **1b** was prepared from **40b** (61.6 mg, 0.09 mmol) as described above (41.2 mg, 69.9%): mp >270 °C dec; exact mass calcd for $C_{44}H_{50}N_4O_2$ 666.3934, found 666.3984; visible spectrum (CH_2Cl_2) [λ_{max}, nm (log ϵ)] 260.0 (4.47), 396.8 (95.21), 498.0 (4.07), 534.8 (3.98), 567.2 (3.82), 620.8 (3.58); ^{13}C NMR (10% TFA/$CDCl_3$) δ 186.33 (2 C, quinone 2,5-C), 147.05 (2 C, quinone 1,4-C), 146.15, 142.99, 142.81, 142.05, 141.92, 140.86, 140.17, 139.62 (16 C, α- and β-pyrrolic C), 131.45 (2 C, quinone 3,6-C), 99.85, 98.72 (4 C, meso C), 28.66, 27.00, 26.86, 25.99, 25.92 (10 C, chain C), 20.43 (2 C, CH_2CH_3), 16.54 (2 C, CH_2CH_3), 12.20, 11.80 (4 C, CH_3); ^1H NMR ($CDCl_3$) δ 9.47 (s, 4 H, methine 5,10,15,20-H), 4.30 (m, 2 H, chain 5-CH_2), 4.08–4.25 (m, 4 H, CH_2CH_3), 3.97 (m, 4 H, chain 5-CH_2), 3.70, 3.57 (s, 12 H, 4 CH_3), 2.94 (s, 2 H, quinone 3,6-H), 2.33 (m, 2 H, chain 4-CH_2) 1.93 (t, m, 8 H, CH_2CH_3, chain 4-CH_2), 1.25 (m, 2 H, chain 3-CH_2), 1.14 (m, 2 H, chain 3-CH_2), 0.65 (m, 2 H, chain 1-CH_2), −0.02 (m, 2 H, chain 1-CH_2), −0.32 (m, 2 H, chain 2-CH_2), −1.29 (m, 2 H, chain 2-CH_2), −3.91 (br s, 2 H, NH). Anal. Calcd for $C_{44}H_{50}N_4O_2$: C, 79.24; H, 7.56; N, 8.40; O, 4.80. Found: C, 77.00; H, 7.44; N, 8.00; O, 6.77. Calcd for $C_{44}H_{50}N_4O_2 \cdot 1H_2O$: C, 77.16; H, 7.65; N, 8.18; O, 7.01.

Acknowledgment. This work was supported by the U.S. National Institutes of Health (Grant AM 17989) and the Natural Sciences and Engineering Research Council of Canada.

Registry No. **1a**, 98977-32-3; **1b**, 98977-31-2; **2a**, 110569-90-9; **2b**, 110569-91-0; **9**, 2199-44-2; **10b**, 14794-31-1; **11a**, 68500-90-3; **11b**, 68500-89-0; **12a**, 98977-05-0; **12b**, 98977-04-9; **13a**, 98977-07-2; **13b**, 98977-06-1; **14a**, 98977-09-4; **14b**, 98977-08-3; **15a**, 98977-11-8; **15b**, 98977-10-7; **16a**, 110569-80-7; **16b**, 110569-81-8; **17a**, 98977-13-0; **17b**, 98977-12-9; **18a**, 98977-15-2; **18b**, 98977-14-1; **19a**, 98977-17-4; **19b**, 98977-16-3; **20**, 37945-37-2; **21**, 110569-92-1; **22**, 110569-93-2; **25**, 71128-83-1; **28a**, 110569-82-9; **28b**, 110569-83-0; **29a**, 110569-84-1; **29b**, 110589-04-3; **30**, 7310-97-6; **31a**, 98977-20-9; **31b**, 98977-19-6; **32**, 37789-74-5; **33a**, 110569-85-2; **33b**, 110569-86-3; **34a**, 98977-22-1; **34b**, 98977-21-0; **35a**, 110569-87-4; **37a**, 110589-05-4; **39a**, 110569-88-5; **39b**, 110569-89-6; **40a**, 98977-28-7; **40b**, 98977-27-6; **42a**, 98977-30-1; $CH_3CH_2OCO(CH_2)_3COOH$, 1070-62-8; $CH_3CH_2OCO(CH_2)_3COCl$, 5205-39-0; 2,6-bis(hydroxymethyl)-4-methylanisole, 6327-85-1; 2,5-bis(hydroxymethyl)-1,4-dimethoxybenzene, 51829-43-7; 1,4-bis[6-[2-(ethoxycarbonyl)-3-methylpyrrol-4-yl]hex-1-enyl]-2,5-dimethoxybenzene, 98990-28-4.

Synthesis of Dihydro-1,4-oxathiins by Action of Chlorine on 1,3-Oxathiolanes[1]

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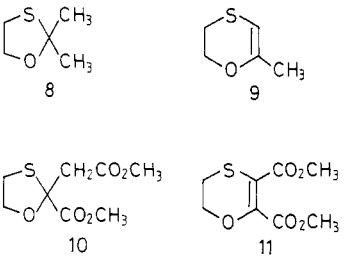
A new convenient synthesis of 5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxylic acid derivatives **1** has been achieved by using the action of chlorine on 2-methyl-*N*-phenyl-1,3-oxathiolane-2-acetamide (**4a**) and 2-methyl-1,3-oxathiolane-2-acetic acid methyl ester (**4b**). From the initially formed chlorosulfonium salts **16** unobserved transient sulfenyl chlorides **5** were generated, followed by cyclization to probable oxonium ion **18** to produce dihydrooxathiins **1**. In the chlorinolysis reactions of **4a** and **4b** minor byproducts were formed: respectively 2,3-dichloro-2-methyl-1,4-oxathiin-3-carboxanilide **12a** and its methyl ester analogue **12b**. While **12b** was stable, **12a** was unstable, transforming to the corresponding 2-chloromethyl compound **13**. The mechanism of formation of **13** as well as relative stability of dichlorides **12a**, **12b**, and related compounds is also discussed.

Introduction

In our previous paper[2] we reported a new synthesis of dihydro-1,4-oxathiins **1** by rearrangement of 1,3-oxathiolane *S*-oxides **2** involving sulfenic acid **3** (Scheme I, path a). As an inevitable extension of this work we now report a possibly simpler synthesis of **1** by chlorinolysis of readily available 1,3-oxathiolanes **4** involving sulfenyl chlorides **5** (Scheme I, path b).

Wilson[3] previously reported the chlorinolysis of 2,2-dimethyloxathiolane (**8**) in refluxing methylene chloride–carbon tetrachloride to obtain 5,6-dihydro-2-methyl-1,4-oxathiin (**9**) in fair yield. Another paper by ten Haken[4] described ring expansion of 2-carbomethoxy-1,3-oxathiolane-2-acetic acid methyl ester (**10**) by action of chlorine to 5,6-dihydro-1,4-oxathiin-2,3-dicarboxylic acid, bis(methyl ester) (**11**) in low yield. The reaction was carried out initially at −20 °C to ambient temperature and at 120 °C in the last stage. No mechanistic considerations were given in this report.



A salient feature of the 1,3-oxathiolanes **4** is the presence of both carbonyl-activated methylene and unactivated methyl hydrogens β to the C–S bond being ruptured.

(1) A part of this work was presented (a) at the 28th International Union of Pure and Applied Chemistry Congress, Vancouver, Canada, August 16–21, 1981, and (b) in Lee, W. S.; U.S. Pat. 4 230 871, 1980; Can. Pat. 1 035 778, 1978; *Chem. Abstr.* **1979**, *90*, 102970d.

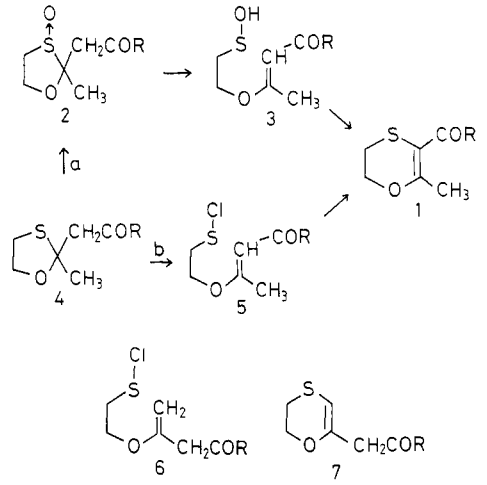
(2) Lee, W. S.; Hahn, H. G.; Nam, K. D. *J. Org. Chem.* **1986**, *51*, 2789–2795.

(3) Wilson, G. E., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 3785–3786.

(4) ten Haken, P. *J. Heterocycl. Chem.* **1970**, *7*, 1211–1213.

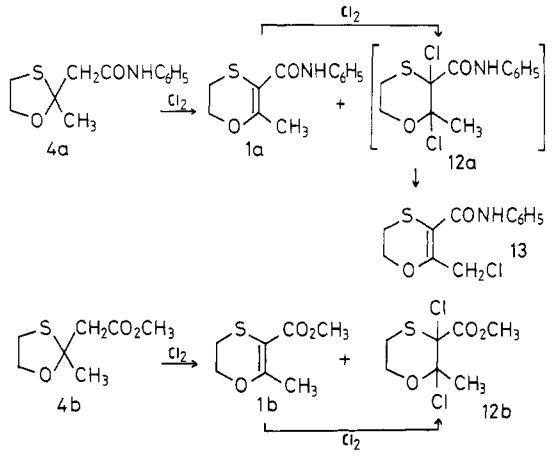
0022-3263/87/1952-5374$01.50/0

Scheme I[a]



[a] R = (a) NHC_6H_5; (b) OCH_3.

Scheme II



Thus, in considering the chlorinolysis approach, it was essential that only the methylene carbon be involved in the ring expansion, since methyl group involvement could give the undesired isomeric oxathiin **7** via sulfenyl chloride **6**.

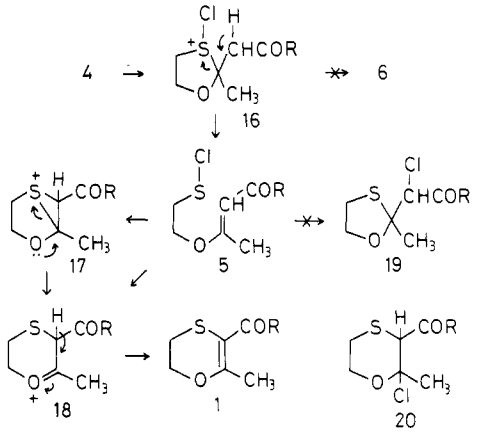
Results

The starting oxathiolanes **4** were prepared by the previous method.[2] The chlorinolysis reactions were carried out in methylene chloride solution at −20 °C to ambient temperature. When the oxathiolane **4a** was allowed to react with 1 equiv of chlorine, there was obtained a 75:10:10:5 mixture of dihydrooxathiin **1a**, chloromethyl compound **13**, starting material **4a**, and acetoacetanilide,[5] respectively. These were separated by preparative TLC. The same reaction for the oxathiolane **4b** gave a 70:13:12:5 mixture of **1b**, dichloro compound **12b**, starting material **4b**, and methyl acetoacetate.[5] The results are summarized in Scheme II.

It appeared likely that the chloromethyl compound **13** arose by further chlorination of the dihydrooxathiin **1a**. This was made plausible by the conversion of **1a** to **13** by the action of chlorine. Interestingly, the chloromethyl compound was also obtained when the sulfide **4a** was treated with 2 equiv of chlorine. The compound **13** was also prepared by *N*-chlorosuccimide chlorination of the 2-methyl group of **1a**. We were unable to isolate the probable intermediate dichloride amide **12a** as a pure compound but immediately after workup there were present in the ^1H NMR spectrum of the crude reaction mixture a methyl signal, NH, and four methylene hydrogens assignable to the structure of this compound.[6]

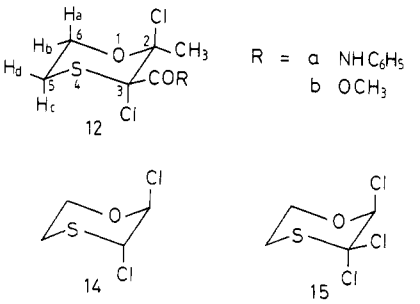
(5) Small amounts of these parent β-keto acid derivatives may have been produced from the decomposition of the chlorosulfonium salts **16** (Scheme III) by action of hydrogen chloride and/or water present in the reaction mixture.

Scheme III[a]



[a] R = (a) NHC_6H_5; (b) OCH_3.

At room temperature, the dichloride amide **12a** was gradually ($t_{1/2} \cong 3$ h) converted to the chloromethyl compound **13**. However, in the case of chlorinolysis of the sulfide ester **4b** or addition of chlorine to the corresponding dihydrooxathiin ester **1b**, dichloro compound **12b** was isolated as a stable crystalline solid. Its structure follows from elemental analysis and the ^1H NMR spectrum, which was similar to that of the dichloride amide (see Experimental Section). The structure was further confirmed by its conversion to the dihydrooxathiin **1b** on elimination of chlorines in refluxing ether with magnesium–iodine. On the basis of the chemical shifts and coupling constants of dichlorides **12a** and **12b** which were similar to those of previously reported[8] *trans*-2,3-dichloro-1,4-oxathiane (**14**) and *trans*-2,3,3-trichloro-1,4-oxathiane (**15**), both **12a** and **12b** were assigned trans dichlorides in which the two chlorine atoms are axial.



Discussion

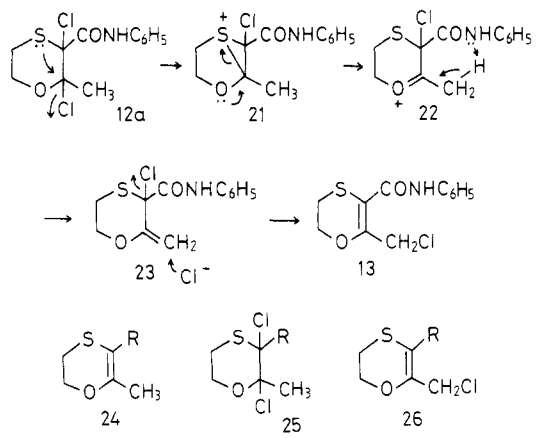
Dihydrooxathiins. The mechanism for formation of dihydro-1,4-oxathiin **1** is summarized in Scheme III. The ring expansion reaction undoubtedly proceeds via unisolable transient sulfenyl chlorides **5** as generated from the initially formed chlorosulfonium salt **16**.[3,9] The ring

(6) This chloromethyl compound had previously been prepared by Knight et al.[7] from the reaction of the parent dihydrooxathiin with sulfuryl chloride in boiling benzene. No mechanism of formation nor any intermediate was mentioned in this report.

(7) Knight, B. I.; Curcumelli-Rodostamo, M.; Kulka, M.; Schmeling, B. V. U.S. Pat. 3728357, 1973.

(8) De Wolf, N.; Henniger, P. W.; Havinga, E. *Recl.: J. Roy. Neth. Chem. Soc.* **1967**, *86*, 1227–1236.

Scheme IV[a]



[a] R = (a) $CON(CH_3)C_6H_5$; (b) CH_3.

opening of **16** occurred probably by a concerted β-elimination[10] involving the carbonyl-activated methylene hydrogens to produce **5** and alternative sulfenyl chlorides **6** were not formed. The internal substrate of the sulfenyl chloride **5** may be viewed as a combined enol ether and a α,β-unsaturated carbonyl system. The addition reactions of sulfenyl chlorides for α,β-unsaturated amides or esters[11] and for enol ether[3] or dihydropyran[12] have been studied previously.

In view of the well-established thiiranium ion intermediacy in the above-mentioned reactions, thiiranium ion **17** may be a possible intermediate, but this would open in only one direction to form the low energy oxonium ion **18**. It is also possible that **18** was formed directly from **5**. These views are supported by the fact that no anti-Markovnikov adduct **19**[13] was formed. The oxonium ion involvement is also suggested by the previously known open ion involvement in the addition of sulfenyl chloride to dihydropyran.[12] The oxonium ion could then lose the acidic proton adjacent to the carbonyl group to give the dihydrooxathiins **1**.[2] Although the Markovnikov adduct **20** could not be observed, it may not be ruled out that this intermediate was formed by the chloride attack on the oxonium ion, followed by spontaneous dehydrohalogenation.[14]

Dichlorides and Chloromethyl Compounds. As indicated earlier dichloro compounds **12** were most likely formed by addition of chlorine to dihydrooxathiins produced in the chlorinolysis reaction of oxathiolanes **4**. A proposed mechanism for the formation of the chloromethyl compound **13** from the unstable dichloride **12a** is shown in Scheme IV. The sulfur is postulated to attack the anomeric carbon of the halo ether to give a thiiranium ion **21** which would open to more stable oxonium ion **22**. The removal of a methyl proton is now effected by the amide nitrogen to form exocyclic methylene compound **23**, followed by allylic chlorination to give the observed product **13**.

The stability of dichloride ester **12b** is attributable to the stronger electron withdrawal by the ester carbonyl group compared with the amide carbonyl. This would result in a lower electron density on the sulfur atom in the ester, reducing its ability to form a thiiranium ion like **21**. By contrast a relatively stronger nucleophilicity of the sulfur atom in the amide could afford displacement of C-2 chlorine. Besides, the ideally located amide nitrogen is effecting removal of a methyl proton.[15] Support for this idea is the fact that dichloro compound **25a** (Scheme IV), prepared from *N*-methylamide **24a**, was transformed to chloromethyl compound **26a** much faster ($t_{1/2} \cong {}^1/_3$ h) than the dichloride **12a** ($t_{1/2} \cong 3$ h) was to **13** at room temperature. The N-methyl group not only gave rise to a more reactive sulfur by decreasing the carbonyl inductive effect but made the nitrogen more basic to facilitate the elimination.

On the other hand it was found that 2,3-dichloro-2,3-dimethyloxathiane (**25b**), obtained from **24b**, was converted slowly ($t_{1/2} \cong 24$ h) to chloromethyl compound **26b**. As would be expected, dichloride **25b** disappeared at a faster rate in the presence of triethylamine. However, dichloride ester **12b** remained unchanged even with a large excess of this base in methylene chloride solution at room temperature. In brief, these results suggest that the presence of an amide nitrogen is not required but it can speed up conversion of the dichloride to chloromethyl compound and that the dichloride ester **12b** very likely did not form a thiiranium ion or an oxonium ion.

A more systematic study on the relative stabilities of various 2,3-dichlorooxathianes is in progress in our laboratory.

Experimental Section

General Procedures. All melting points were obtained with an Electrothermal melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Perkin-Elmer 736B spectrophotometer. All ^{1}H NMR spectra were recorded on Varian Model EM 360 (60 MHz) or Bruker AM-system (200 MHz) using Me_4Si as an internal standard and all are reported in δ. All chromatographic isolations were accomplished by preparative thin-layer chromatography (TLC), using Kieselgel GF 254 silica gel. Microanalyses were performed either in the Microanalytical Laboratory at the Korea Advanced Institute of Science and Technology or at the National Research Council of Canada.

Synthesis of Methyl 2,3-Dichloro-2-methyl-1,4-oxathiane-3-carboxylate (12b). Method A. To a stirred solution of 5,6-dihydro-1,4-oxathiin **1b** (2.175 g, 12.5 mmol) in methylene chloride (40 mL) cooled in a salt–ice bath at −5 °C was added dropwise a solution of chlorine (0.885 g, 12.5 mmol) in methylene chloride (28 mL) over 10 min. After the reaction mixture was stirred at −5 °C for 10 min, the solvent was removed under reduced pressure to obtain white crystalline solid **12b** (3.06 g, 100%), mp 59–63 °C: IR (KBr) 1745 (s, C=O cm^{-1}); ^{1}H NMR (200 MHz) $CDCl_3$) δ 2.20 (s, 3 H, 2-CH_3), 2.51 (m, J_{ad} = 2.3 Hz, J_{bd} = 2.1, J_{cd} = 14.1, 1 H, 5-CH (equatorial)), 3.41 (m, J_{ac} = 12.4, J_{bc} = 3.6, 1 H, 5-CH (axial)), 4.14 (m, J_{ab} = 12.2, 1 H, 6-CH (equatorial)), 4.35 (m, 1 H, 6-CH (axial)). Anal. Calcd for $C_7H_{10}O_3SCl_2$: C, 34.30; H, 4.11; S, 13.08; Cl, 28.93. Found: C, 34.15; H, 4.09.

Method B. The reaction was carried out by using oxathiolane **4a** as starting material and 2 mol of chlorine to obtain the same results as in method A.

Synthesis of 2-(Chloromethyl)-5,6-dihydro-*N*-phenyl-1,4-oxathiin-3-carboxamide (13). Method A. To a stirred

(9) (a) Wilson, G. E. *Tetrahedron* **1982**, *38*, 2597–2625. (b) Wilson, G. E.; Huang, M.-G. *J. Org. Chem.* **1976**, *41*, 966–968.

(10) Caputo, R.; Ferreri, C.; Palumbo, G. *Tetrahedron* **1986**, *42*, 2369–2376.

(11) Rasteikiene, L.; Greiciute, D.; Lin'kova, G.; Knunyants, I. L. *Russ. Chem. Rev.* **1977**, *46*, 548–564; *Usp. Khim.* **1977**, *46*, 1041–1073.

(12) Baldwin, M. J.; Brown, R. K. *Can. J. Chem.* **1968**, *46*, 1093–1099.

(13) The compound **19** was obtained as a stable crystalline solid by treating a mixture of 2-chloroacetoacetanilide and 2-mercaptoethanol with titanium tetrachloride. Therefore, this compound would have been isolated from the chlorinolysis reaction mixture were it formed.

(14) Mueller, W. H.; Butler, P. E. *J. Am. Chem. Soc.* **1968**, *90*, 2075–2081.

(15) The alternative mechanism involving the carbonyl oxygen may not be ruled out. However, aside from the ambiguous relative basicity[16] of the amino nitrogen and carbonyl oxygen, the nitrogen atom involvement seems more probable on the grounds that with the C(O)–N bond length greater than C–O,[16] the nitrogen atom has better proximity to the methyl proton than the oxygen (Dreiding models).

(16) Zabicky, J., Ed. *The Chemistry of Amides*; Interscience Publishers: New York, 1970; pp 188–189, pp 2–5.

solution of 5,6-dihydro-1,4-oxathiin **1a** (1.00 g, 4.25 mmol) in methylene chloride (20 mL) cooled in an acetone–dry ice bath at −20 °C was added dropwise a solution of chlorine (0.30 g, 4.25 mmol) in methylene chloride (9.8 mL) over 5 min. When the addition was complete the solvent was removed under reduced pressure at 0 °C to obtain an oily residue (1.3 g), which was initially a 91:9 mixture of dichloro compound **12a** and chloromethyl compound **13**, respectively as determined by ^{1}H NMR spectroscopy. On standing, compound **12a** ($t_{1/2} \cong 3$ h) in this mixture was transformed to **13**. The oily residue was allowed to stand for 19 h at room temperature until all of **12a** was converted to **13** and then dissolved in methylene chloride, washed with saturated sodium bicarbonate solution and water, and dried (Na_2SO_4). The solvent was removed to give a yellow crystalline solid (1.03 g). Recrystallization from methylene chloride–cyclohexane gave white needles **13** (0.91 g, 80%).

For **12a**: ^{1}H NMR (200 MHz) ($CDCl_3$) δ 2.14 (s, 3 H, CH_3), 2.61 (m, 1 H, 5-CH (equatorial)), 3.51 (m, 1 H, 5-CH (axial), 4.15 (m, 1 H, 6-CH (equatorial)), 4.45 (m, 1 H, 6-CH (axial)), 7.13–7.56 (m, 5 H, Ar H), 8.17 (s, 1 H, NH).

For **13**: mp 104–106 °C (lit.[4] mp 103–106 °C); IR (KBr) 3270 (m, NH), 1640 (s, C=O) cm^{-1}; ^{1}H NMR (60 MHz) ($CDCl_3$) δ 2.97–3.13 (m, 2 H, 5-CH_2), 4.37–4.53 (m, 2 H, 6-CH_2), 4.57 (s, 2 H, CH_2Cl), 7.20–7.70 (m, 5 H, Ar H), 8.00 (s, 1 H, NH). Anal. Calcd for $C_{12}H_{12}NSClO_2$: C, 53.48; H, 4.49; N, 5.19; Cl, 13.6; S, 12.28. Found: C, 53.50; H, 4.46; N, 5.03; Cl, 13.31; S, 11.78.

Method B. The reaction was carried out by using oxathiolane **4b** as starting material and 2 mol of chlorine to obtain the same results as in method A.

Synthesis of 2-(Chloromethyl)-5,6-dihydro-*N*-methyl-*N*-phenyl-1,4-oxathiin-3-carboxamide (26a). To a stirred solution of 5,6-dihydro-1,4-oxathiin **24a**[17] (250 mg, 1 mmol) in methylene chloride (5 mL) at −20 °C was added dropwise a solution of chlorine (71 mg, 1 mmol) in methylene chloride (2.3 mL) over 1 min. As soon as the addition was complete, the solvent was removed under reduced pressure at −20 to 0 °C to obtain an oily residue (285 mg) as a 1:1 mixture of **25** and **26** as shown by ^{1}H NMR spectroscopy (workup time $\cong$ 20 min, therefore $t_{1/2}$ for **25** $\cong {}^1/_3$ h). The NMR pattern for **25a** was similar to that for **12a** in the preceding reaction. After all of **25a** was converted to **26a**, it was crystallized from benzene–petroleum ether, giving white needles **26** (117 mg, 41%), mp 130–133 °C (lit.[4] mp 131–133 °C); IR (KBr) 1640 (s, C=O) cm^{-1}; ^{1}H NMR (60 MHz) ($CDCl_3$) δ 2.69–2.80 (m, 2 H, 5-CH_2), 3.36 (s, 3 H, NCH_3), 4.10–4.21 (m, 2 H, 6-CH_2), 4.21 (s, 2 H, CH_2Cl), 7.20–7.70 (m, 5 H, Ar H). Anal. Calcd for $C_{13}H_{14}NSClO_2$: C, 55.02; H, 4.97; N, 4.94; S, 11.30; Cl, 12.49. Found: C, 55.17; H, 4.99; N, 4.77.

Reaction of 1,3-Oxathiolane 4a with Chlorine. To a stirred solution of 1,3-oxathiolane **4a** (1.0 g, 4.2 mmol) in dry methylene chloride (20 mL) cooled in an acetone–dry ice bath at −20 °C was added dropwise a solution of chlorine (0.3 g 4.2 mmol) in methylene chloride (9.6 mL) over 10 min. The cooling bath was then removed and the reaction mixture allowed to reach ambient temperature, 18 °C) while being stirred for about 30 min. Triethylamine (1.18 mL, 8.4 mmol) in methylene chloride (5.9 mL) was added dropwise over 10 min, after the reaction mixture was placed in the ice bath. The mixture was washed with ice-cold water and dried ($MgSO_4$). Evaporation of solvent gave an oily residue (0.93 g) as a mixture of dihydrooxathiin **1a**, dichloro compound **12a**, chloromethyl compound **13**, oxathiolane **4a**, and acetoacetanilide (AAA) as shown by ^{1}H NMR spectroscopy and TLC. On standing, dichloro compound **12a** ($t_{1/2} \cong 3$ h) gradually transformed to chloromethyl compound **13**, resulting in approximately a 75:10:10:5 mixture of **1a**, **13**, **4a**, and AAA, respectively (^{1}H NMR spectrum and TLC). From this mixture were removed **4a** and AAA by preparative TLC using 7:3 (v/v) benzene–ethyl acetate as eluant. The remaining **1a** and **13** were separated by preparative TLC, eluting with benzene to obtain dihydrooxathiin **1a** (0.54 g) and chloromethyl compound **13** (8 mg). These compounds have identical ^{1}H NMR and IR spectra with those of the compounds prepared by the previously known method[2] and preceding experiment.

The above reaction was carried out at −20 °C by addition of chlorine solution over $1^1/_2$ min, immediately followed by evaporation of the solvent at below 0 °C to obtain almost the same results as above.

Reaction of 1,3-Oxathiolane 4b with Chlorine. To a stirred solution of 1,3-oxathiolane **4b** (1.0 g, 5.7 mmol) in dry methylene chloride (20 mL) cooled in an acetone–dry ice bath at −20 °C was added dropwise a solution of chlorine (0.4 g, 5.7 mmol) in dry methylene chloride (12.9 mL) over 10 min. The cooling bath was removed and the reaction mixture allowed to reach ambient temperature (20 °C) while being stirred for about 30 min. The reaction mixture was washed with ice-cold water and dried (Na_2SO_4). Evaporation of solvent gave an oily residue (0.98 g), which was a 70:13:12:5 mixture of dihydrooxathiin **1b**, dichloro compound **12b**, oxathiolane **4b**, and methyl acetoacetate (MAA), respectively, as determined by ^{1}H NMR spectroscopy. To a mixture of dry ether (20 mL) and magnesium turnings (170 mg) at reflux was added slowly a solution of iodine (190 mg) in dry ether (10 mL), followed by addition of the above residue (0.98 g) in a dry ether solution (10 mL). The reaction mixture was allowed to reflux for 18 h and cooled to room temperature, and the solid material was filtered off. The filtrate was washed with water twice and dried (Na_2SO_4). The solvent was evaporated to give a solid residue (0.843 g) as a 9:1 mixture of dihydrooxathiin **1b** and oxathiolane **4b** (^{1}H NMR spectrum). Crystallization from benzene–petroleum ether gave colorless crystalline solid **1b** (0.691 g, 70% based on the starting **4b**). This compound has an identical ^{1}H NMR spectrum with that of the compound prepared by the previous method.[1]

Reaction of 5,6-Dihydro-2,3-dimethyl-1,4-oxathiin (24b) with Chlorine. To a stirred solution of 5,6-dihydro-2,3-dimethyl-1,4-oxathiin (**24b**)[18] (0.500 g, 3.82 mmol) in methylene chloride (10 mL) at −20 °C was added a solution of chlorine (0.271 g, 3.82 mmol) in methylene chloride (8.7 mL) in 3 min. The solvent was then evaporated at 0 °C to obtain dichloride **25b** as an oily residue (0.81 g, 100%), which on standing in chloroform solution was slowly transformed ($t_{1/2} \cong 24$ h at 25 °C) to 2-chloromethyl compound **26b**, as determined by ^{1}H NMR spectroscopy.

For **25b**: ^{1}H NMR (60 MHz) ($CDCl_3$) δ 2.00 (s, 6 H, 2-CH_3 and 3-CH_3), 2.44 (m, J_{ad} = 2.3 Hz, J_{bd} = 2.1, J_{cd} = 14.1, 1 H, 5-CH (equatorial), 3.53 (m, J_{ac} = 12.4, J_{bc} = 3.6, 1 H, 5-CH (axial), 4.14 (m, J_{ab} = 12.2, 1 H, 6-CH (equatorial)), 4.40 (m, 1 H, 6-CH (axial)) (refer to the structure **12** for C-5 and C-6 protons).

For **26b**: ^{1}H NMR (60 MHz) ($CDCl_3$) δ 1.93 (s, 3 H, 2-CH_3), 2.87–3.02 (m, 2 H, 5-CH_2), 4.08–4.23 (m, 2 H, 6-CH_2), 4.17 (s, 2 H, C-2-CH_2).

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Registry No. **1a**, 5234-68-4; **1b**, 102437-87-6; **4a**, 67980-06-7; **4b**, 80563-95-7; **12a**, 110512-33-9; **12b**, 110512-34-0; **13**, 42825-78-5; **19a**, 110512-38-4; **24a**, 6577-40-8; **24b**, 107954-65-4; **25a**, 110512-35-1; **25b**, 110512-36-2; **26a**, 42826-01-7; **26b**, 110512-37-3; MAA, 105-45-3; 2-chloroacetoacetanilide, 31844-92-5; 2-mercaptoethanol, 60-24-2.

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