at 50 °C with 30 mL of 5 M HCl for 3 h. The cooled reaction was neutralized with saturated K_2CO_3 solution and extracted with EtOAc (5 × 25 mL). After drying (Na_2SO_4) and concentrating, 0.22 g (96%) of yellow solid 2,2′-bi-1*H*-imidazole-4-carboxaldehyde (**15**, R = CHO) was obtained. TLC (30% MeOH/CH_2Cl_2) showed one spot. The solid was warmed with ethanolic HCl to prepare the dihydrochloride salt (EtOH), mp 229–231 °C: ^{1}H NMR (D_2O/DSS) δ 7.62 (s, 2 H), 8.30 (s, 1 H), 9.81 (s, 1 H); MS (CI/CH_4), *m/z* 163 (M^+ + 1), 191 (M^+ + 29), 203 (M^+ + 41). Anal. Calcd for $C_7H_6N_4O$·2HCl·EtOH: C, 40.16; H, 4.87; N, 20.82. Found: C, 39.97; H, 4.90; N, 20.50.

2,2′-Bi-1*H*-imidazole-4,4′-dicarboxaldehyde (14, R = CHO). Aldehyde **12** (R = CHO) (0.7 g, 1.56 mmol) was refluxed with 30 mL of 5 N HCl for 1.5 h. The cooled reaction was neutralized with aqueous K_2CO_3 and then concentrated to dryness. The solid residue was slurried with 25 mL of H_2O, collected by vacuum filtration, and washed with 50 mL of cold H_2O. After drying, 0.2 g (67.5%) of 2,2′-bi-1*H*-imidazole-4,4′-dicarboxaldehyde (**14**, R = CHO) was obtained as a tan solid, mp >255 °C: NMR (Me_2SO-d_6) δ 7.90 (s, 2 H), 9.66 (s, 2 H); MS (CI/CH_4), *m/z* 191 (M^+ + 1, base peak), 219 (M^+ + 41), 163 (M^+ + 1 − CHO); HRMS calcd for $C_8H_6N_4O_2$ 190.0492, found 190.0502.

1,1′-Bis[[2-(trimethylsilyl)ethoxy]methyl]-4,4′-bis(methylthio)-2,2′-bi-1*H*-imidazole (12, R = SCH_3) and 1,1′-Bis-[[2-(trimethylsilyl)ethoxy]methyl]-4-(methylthio)-2,2′-bi-1*H*-imidazole (13, R = SCH_3). Under nitrogen, a mechanically stirred solution of 18.3 g (0.046 mmol) of **7**, 7.0 mL (0.046 mmol) of TMEDA, and 150 mL of THF was cooled to −40 °C, and 37.6 mL (0.116 mmol) of 3.1 M *n*-butyllithium in hexane was added. The thick slurry was stirred for 15 min and 10.2 mL (0.113 mmol) of methyl disulfide was added. The solid immediately dissolved. The reaction was allowed to warm to room temperature overnight. The reaction was diluted with H_2O and extracted into EtOAc (3 × 125 mL). The EtOAc layers washed with H_2O (3 × 50 mL), dried (Na_2SO_4), and concentrated to give 17.9 g of crude product. Flash chromatography (800 g of silica gel, 30% EtOAc/hexane) gave 4.2 g (20.8%) of **13** and 3.8 g (17%) of **12**.

13 (R = SMe): ^{1}H NMR ($CDCl_3$) δ 0.08 (s, 18 H), 0.81–1.14 (m, 4 H), 2.48 (s, 3 H), 3.46–3.79 (m, 4 H), 5.98 (s, 2 H), 6.17 (s, 2 H), 7.27 (s, br, 2 H), 7.36 (s, 1 H); MS (CI/CH_4), *m/z* 441 (M^+ + 1).

12 (R = SMe): ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 18 H), 0.95 (t, 4 H, *J* = 7 Hz), 2.49 (s, 6 H), 3.63 (t, 4 H, *J* = 7 Hz), 6.15 (s, 4 H), 7.35 (s, 2 H); MS (CI/CH_4), *m/z* 487 (M^+ + 1), 515 (M^+ + 29), 527 (M^+ + 41).

4-(Methylthio)-2,2′-bi-1*H*-imidazole (15, R = SCH_3). A mixture of 1.5 g (3.4 mmol) of **13** (R = SCH_3), 50 mL of EtOH, and 100 mL of 5 N HCl was refluxed for 3 h. The EtOH was removed in vacuo and the remaining aqueous solution neutralized with K_2CO_3 solution. The white solid which formed was collected and dried to give 0.77 g of crude product. Recrystallization (isopropyl alcohol) gave 0.3 g (49%) of 4-(methylthio)-2,2′-bi-1*H*-imidazole (**15**, R = SMe), mp >250 °C; ^{1}H NMR (Me_2SO-d_6) δ 2.68 (s, 3 H), 7.08 (s, 2 H), 7.11 (s, 1 H); MS (CI/CH_4), *m/z* 181 (MH^+), 209 (M^+ + 29), 221 (M^+ + 41); HRMS calcd for $C_7H_8N_4S$ 180.0471, found 180.0457.

4,4′-Bis(methylthio)-2,2′-bi-1*H*-imidazole (14, R = SCH_3). Using a procedure identical with that for the preparation of **15** (R = SMe), 4,4′-bis(methylthio)-2,2′-bi-1*H*-imidazole (**14**, R = SMe) was prepared in 86.3% (IPA) yield; mp >260 °C: NMR (Me_2SO-d_6) δ 2.39 (s, 6 H), 7.18 (s, 2 H); MS (EI), *m/z* 226 (M^+), 221 (M^+ − CH_3), 193 (M^+ − SH). HRMS calcd for $C_8H_{10}N_4S_2$ 226.0349, found 226.0348. Anal. Calcd for $C_8H_{10}N_4S_2$: C, 42.48; H, 4.47; N, 24.77. Found: C, 42.83; H, 4.32; N, 22.52.

4(5)-(Methylsulfinyl)-2,2′-bi-1*H*-imidazole (17). A mixture of 2.1 g of **13** (R = SMe) (0.0048 mmol) in 100 mL of CH_2Cl_2 was cooled to 0 °C. Solid 80% *m*-chloroperbenzoic acid (1.08 g, 0.0050 mmol) was added in small portions. The progress of the reaction was followed by TLC (10% hexane/EtOAc) and after 1 h the reaction was quenched with aqueous K_2CO_3 and extracted with EtOAc (2 × 100 mL). The organic layer was shaken with aqueous K_2CO_3 a second time. Drying (Na_2SO_4) and concentration gave 1.95 g (89%) of crude product. Flash chromatography (500 g of silica gel, 10% hexane/EtOAc) gave 1.3 g (59%) of 5-(methylsulfinyl)-1,1′-bis[[2-(trimethylsilyl)ethoxy]methyl]-2,2′-bi-1*H*-imidazole (**16**) as a pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 0.03 (s, 18 H), 0.98 (t, 4 H, *J* = 7 Hz), 3.14 (s, 3 H), 3.48–3.85 (m, 4 H), 5.93 (s, 2 H), 6.26 (q, 2 H, J_{gem} = 12 Hz), 7.26 (m, 2 H), 7.63 (s, 1 H); MS (CI/CH_4), *m/z* 457 (MH^+). A mixture of 1.25 g (2.74 mmol) of **16**, 50 mL of EtOH, and 100 mL of 5 N HCl was refluxed for 2.5 h. The EtOH was removed in vacuo and the aqueous solution carefully neutralized with K_2CO_3 solution. The resultng solid (**9**) was collected and the filtrate concentrated to dryness. Flash chromatography (2:18:80 concentrated NH_4OH/MeOH/$CHCl_3$) of the EtOH-soluble material gave 0.15 g (28%) of **17**, mp 87–90 °C: ^{1}H NMR (Me_2SO-d_6) δ 2.90 (s, 3 H), 7.31 (s, 2 H), 7.87 (s, 1 H); MS (EI), *m/z* 196 (M^+), 181 (M^+ − CH_3, base peak); HRMS calcd for $C_7H_8N_4OS$ 196.042, found 196.0411.

Registry No. **1**, 101226-33-9; **2** (5-isomer), 101226-34-0; **2** (4-isomer), 101226-54-4; **3** (5-isomer), 101226-35-1; **3** (4-isomer), 101226-55-5; **4** (5-isomer), 101226-36-2; **4** (4-isomer), 101226-56-6; **5**, 101226-37-3; **6**, 101226-38-4; **7**, 101226-39-5; **8**, 101226-40-8; **9**, 31722-49-3; **10** (R = Me), 101226-41-9; **10** (R = H), 101226-42-0; **11**, 101226-43-1; **12** (R = CHO), 101226-45-3; **12** (R = SMe), 101226-48-6; **13** (R = CHO), 101226-44-2; **13** (R = SMe), 101226-49-7; **14** (R = CHO), 101226-47-5; **14** (R = SMe), 101226-51-1; **15** (R = CHO), 101226-46-4; **15** (R = SMe), 101226-50-0; **16**, 101226-53-3; **17**, 101226-52-2; $Me_3Si(CH_2)_2OCH_2Cl$, 76513-69-4; imidazole, 288-32-4; 5-methylimidazole, 822-36-6; 5-methoxyimidazole, 88945-43-1; 5-(trifluoromethyl)imidazole, 33468-69-8; 1*H*-benzimidazole, 51-17-2; 1*H*-imidazo[4,5-*b*]pyridine, 273-21-2; 2,2′-bi-1*H*-imidazole, 492-98-8.

Synthesis of 1,4-Oxathiins and 5,6-Dihydro-1,4-oxathiins

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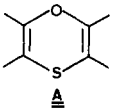
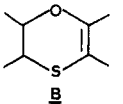
Various 1,4-oxathiin derivatives possess significant systemic fungicidal properties.[1] Whereas considerable interest has focused on the syntheses of 5,6-dihydro-1,4-oxathiins B,[2,3] only occasional reports have been published concerning 1,4-oxathiins A themselves.[3a,4-6] Most of these


A


B

examples have dealt with benzoannelated 1,4-oxathiins A. Only two monocyclic derivatives or A have been syn-

(1) (a) Grewe, F. *Chemie der Pflanzenschutz- und Schädlingsbekämpfungsmittel*; Wegler, R., Ed.; Springer: Berlin, 1970; Vol. 2, pp 104–105. (b) Melnikow, N. N. *Chemistry of Pesticides*; Springer: New York, 1971; pp 423–424. (c) Krämer, W. *Pflanzenschutz und Schädlingsbekämpfung*; Büchel, K.-H., Ed.; Thieme: Stuttgart, 1977; p 147.

(2) For reviews, see: (a) Asinger, F.; Saus, A. "Oxathiine, Dithiine und Thiomorpholine auf Basis billiger Rohstoffe; *Forschungsberichte des Landes Nordrhein-Westfalen*; Westdeutscher Verlag: Oplanden, 1978; No. 2757. (b) Ejmocki, Z.; Eckstein, Z. *Przem. Chem.* **1981**, *60*, 82; *Chem. Abstr.* **1981**, *95*, 24861.

(3) (a) Verheijen, J. H.; Klosterziel, H. *Synthesis* **1975**, 451. (b) Mühlstädt, M.; Kuhl, P. *J. Prakt. Chem.* **1978**, *320*, 873. (c) Trost, B. M.; Vladuchick, W. C.; Bridges, A. J. *J. Am. Chem. Soc.* **1980**, *102*, 3548. (d) Rooney, R. P.; Dyer, J. C.; Evans, S. A. *Org. Magn. Reson.* **1981**, *16*, 266. (e) Tegeler, J. J.; Ong, H. H.; Profitt, J. A. *J. Heterocycl. Chem.* **1983**, *20*, 867.

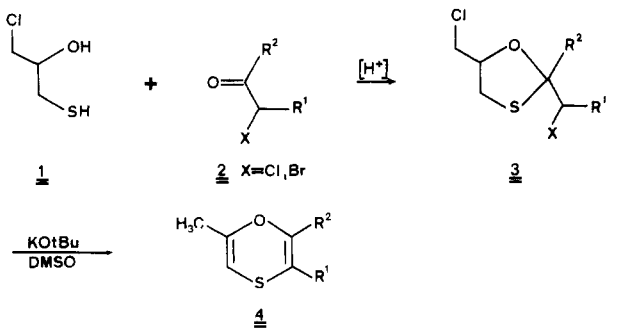
(4) Schoufs, M.; Meijer, J.; Brandsma, L. *Recl. Trav. Chim. Pay-Bas* **1980**, *99*, 12.

(5) Puig-Torres, S.; Womack, C. H.; Martin, G. E.; Smith, K. *J. Heterocycl. Chem.* **1982**, *19*, 1561 and earlier reports.

(6) For a sulfone derivative of 1, see: Baliah, V.; Ganapathy, K.; Ananthapadmanabhan, S. *Indian J. Chem., Sect. B* **1981**, *20B*, 334.

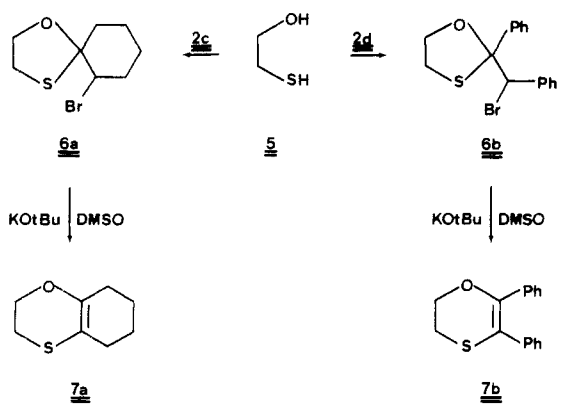
0022-3263/86/1951-1894$01.50/0

Scheme I



2–4	R^1	R^2
a	CH_3	CH_3
b	$-(CH_2)_3-$	
c	$-(CH_2)_4-$	
d	Ph	Ph

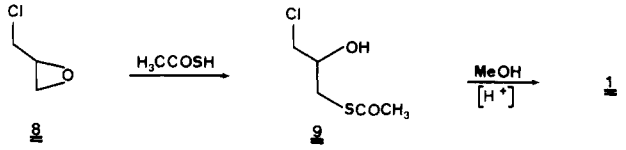
Scheme II



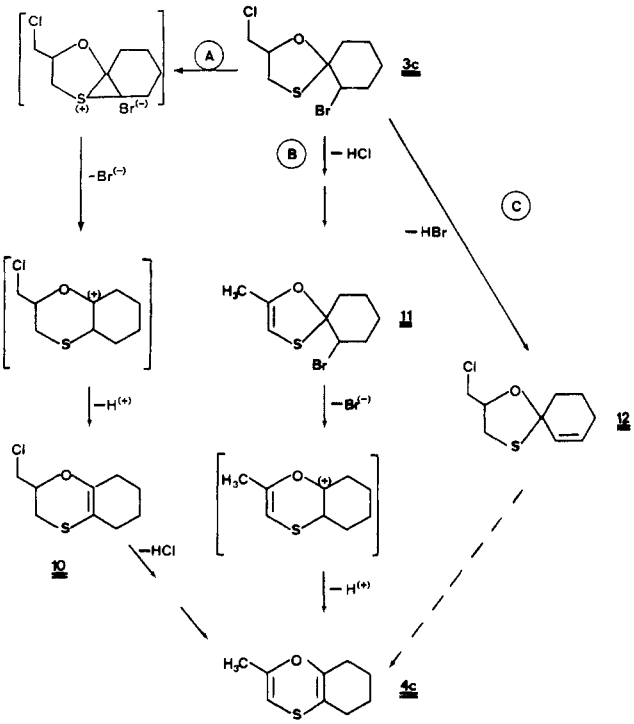
thesized by using the reaction of divinyl ethers and sulfur dichloride.[4] This latter method is obviously limited both by the accessibility of the starting materials and by low yields of even simple substituted derivatives of A. We now wish to report a new and straightforward synthesis of A and B by ring expansion of 1,3-oxathiolanes **3** and **6**, respectively.

Compounds **3** and **6** have been obtained from 1-mercapto-3-chloro-2-propanol (**1**) or 2-mercaptoethanol (**5**), respectively, and the appropriate α-halogen ketone **2** in 61–90% yield according to a method reported by Wilson.[7] In all cases these halogenated 1,3-oxathiolanes partly decompose upon distillation; in some cases, rearrangement and elimination occur to give the 1,4-oxathiin derivatives **4** or **7**.[8] Elimination and rearrangement of the 1,3-oxathiolanes by means of potassium *tert*-butoxide in dimethyl sulfoxide[9] (KO-*t*-Bu in Me_2SO) at room temperature yields 1,4-oxathiins **4** and 5,6-dihydro-1,4-oxathiins **7** in at least 80% yield, provided bromide is the leaving group (Schemes I–III). The yields decrease markedly if chloro counterparts are used.

Scheme III



Scheme IV



Compound **1** has been synthesized according to Sjöberg[10] in 80% overall yield starting from epichlorohydrin **8** (ref 10, 54% yield). The structure of **1** has been proven for the first time on the basis of ^1H and ^{13}C NMR spectroscopy.

In Scheme IV various pathways for the formation of 1,4-oxathiins **4** from 1,3-oxathiolanes **3** are shown with **3c** → **4c** as an example.

The following arguments favor mechanism A: (i) Path B is less likely than A or C because B involves loss of the poorer leaving group, Cl^-, first. (ii) Similar neighboring-group participations concerning substitution and elimination reactions have been observed with other sulfur compounds[11–13]—even with 1.3-dioxolanes.[14] Episulfonium ions may be involved as intermediates.[11–13] (iii) A sulfide is sufficiently nucleophilic for an intramolecular substitution such as **3c** → **10** as shown with **6a** (Scheme II).

Further support was obtained when a deficiency of base was used. Only **4c** was isolated along with starting material **3c**. Therefore, the rearrangement with formation of 5,6-dihydro-1,4-oxathiin **10** seems to be favored over the elimination to **12**. It should be noted that a fragmentation of the 1,3-oxathiolanes with formation of β-thia γ,δ-enones[9] has not been observed in these cases.

At present, this synthesis of 1,4-oxathiins **4** by an eliminating ring expansion from 1,3-oxathiolanes **3** is the most

(7) Wilson, G. E.; Huang, M. G.; Schlorman, W. W. *J. Org. Chem.* **1968**, *33*, 2133.

(8) The yields have not been optimized with regard to a more favorable pressure for distillation. In all cases the microanalytical data are between those of **3** (**6**) and those of **4** (**7**) indicating an easily occuring elimination of HX. These effects are favored from X = Cl < Br < CF_3COO. Therefore **3** and **6** can be used for syntheses of **4** and **7** without purification. in these cases the overall yields exceed those which are given in the Experimental Section for preparations using pure 1,3-oxathiolanes.

(9) Mattay, J.; Scharf, H.-D. *Tetrahedron Lett.* **1982**, 47.

(10) Sjöberg, B. *Chem. Ber.* **1941**, *74*, 64.

(11) Gundermann, K.-D. *Angew. Chem.* **1963**, *75*, 1194.

(12) Matlack, A. S.; Chien, J. C. W.; Breslow, D. S. *J. Org. Chem.* **1961**, *26*, 1455.

(13) Block, E. *Reactions of Organosulfur Compounds*; Academic: New York, 1978; pp 141–145.

(14) Mookherjee, B. D.; Patel, R. R.; Ledig, W. O. *J. Org. Chem.* **1971**, *36*, 4124.

versatile method with regard to the easily accessible starting materials. Moreover, this procedure can be applied also for the synthesis of 5,6-dihydro-1,4-oxathiins **7**, which in the past were mainly prepared from tetrahydro-1,4-oxathiin derivatives by elimination reaction.[2,3]

Experimental Section

For analytical procedures see ref 15.

Commercially available potassium *tert*-butoxide was purified by sublimation. Solvents were purified according to usual methods and were stored over molecular sieves. The ketones were synthesized as reported in the literature: **2a** X = Cl),[16] **2b** X = Cl),[17] **2c** X = Cl),[18] **2c** X = Br),[19] and **2d**.[20]

α-[(Trifluoroacetyl)oxy]cyclohexanone (2c, X = CF_3COO). This ketone was prepared according to a method described by Sevin[21] for α-acetoxycyclohexanone: yield, 48%; bp 53–56 °C/(2.5 torr); IR (neat) 1790 (CF_3C=O), 1730 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.50–2.70 (m, 8 H), 5.10–5.50 (m, 1 H). Anal. Calcd for $C_8H_9F_3O_3$ (210.15): C, 45.72; H, 4.32. Found: C, 45.39; H, 4.08.

1-(Acetylthio)-3-chloro-2-propanol (9):[10] yield 86%; bp 83 °C (0.3 torr); IR (neat) 3430 (OH), 1680 (SC(=O)CH_3) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.37 (s, 3 H, CH_3COS), 3.10 (br d, 2 H, CH_2S), 3.58 (br d, 2 H, CH_2Cl), 3.80–4.00 (m, 2 H, CHOH). Anal. Calcd. for $C_5H_9ClO_2S$ (152.65): C, 39.34; H, 5.94. Found: C, 39.10; H 5.73. A forerun of the distillation [bp 70 °C (0.3 torr)] consists mainly of **1-mercapto-3-chloro-2-propyl acetate**: IR (neat) 2560 (SH), 1730 (CH_3COO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.60 (t, J = 9 Hz, 3 H, SH), 2.10 (s, 3 H, CH_3COO), 2.80 (dd, J = 9, 6 Hz, 2 H, CH_2S), 3.76 (d, J = 4.8 Hz, 2 H, CH_2Cl), 5.00 (m, q, 1 H, CHO). This isomer may be formed from **9** by an "acetate rearrangement" as proposed by Sjöberg.[10] However, both isomers yield **1** upon methanolysis.

1-Mercapto-3-chloro-2-propanol (1):[10] yield, 93% (the overall yield is even higher if crude **9** is converted to **1** without purification by transesterification using methanol); bp 90 °C (13 torr); IR (neat) 3420 (OH), 2570 (SH) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.60 (t, J = 7 Hz, 1 H, SH), 2.77 (dd, J = 7, 5 Hz, 2 H, CH_2S), 3.40 (s, 1 H, OH), 3.70 (d, J = 5.5 Hz), 2 H, CH_2Cl), 3.60–4.15 (tt, 1 H, CHO); ^{13}C NMR ($CDCl_3$) δ 28.29 (CH_2S), 47.31 (CH_2Cl), 71.97 (CHO). Anal. Calcd for C_3H_7ClOS (126.61): C, 28.46; H, 5.57. Found: C, 28.22; H, 5.59.

In general the 1,3-oxathiolanes **3** and **6** were synthesized according to Wilson.[7] However, the alternative formation by continuously azeotropic distillation of water from the reaction mixture in presence of *p*-toluenesulfonic acid yielded **3** and **6** with nearly the same results. The microanalytical data are only sufficiently reproducable in the case of the chlorinated products (see also ref 8).

The ^1H NMR data are often very complex due to stereoisomeric 1,3-oxathiolanes which have not been separated.

2-(1-Chloroethyl)-2-methyl-5-(chloromethyl)-1,3-oxathiolane (3a): yield, 68%; bp 95–100 °C (13 torr); ^1H NMR ($CDCl_3$) δ 1.50–1.90 (m, 6 H, CH_3) 2.90–3.20 (m, 2 H, CH_2S), 3.60–3.70 (m, 2 H, CH_2Cl), 4.00–4.50 (m, 2 H, CHO and CHCl). Anal. Calcd for $C_7H_{12}Cl_2OS$ (215.15): C, 39.08; H, 5.62. Found: C, 39.39; H, 5.87.

2-Chloro-5′-(chloromethyl)spiro[cyclopentane-1,2′-[1,3]-oxathiolane] (3b): yield, 62%; bp 98–103 (0.3 torr); ^1H NMR ($CDCl_3$) δ 1.70–2.60 (m, 6 H, CH_2), 2.80–3.20 (m, CH_2S, 2 H), 3.55–3.80 (m, 2 H, CH_2Cl), 4.10–4.70 (m, 2 H, CHO and CHCl). Anal. Calcd for $C_8H_{12}Cl_2OS$ (227.16): C, 42.30; H, 5.33. Found: C, 42.51; H, 5.60.

2-Chloro-5′-(chloromethyl)spiro[cyclohexane-1,2′-[1,3]oxathiolane] (3c, X = Cl): yield, 79%; bp 115–117 °C (1 torr); ^1H NMR ($CDCl_3$) δ 1.30–2.30 (m, 8 H, CH_2), 2.90–3.30 (m, 2 H, CH_2S), 3.55–3.80 (m, 2 H, CH_2Cl), 3.95–4.90 (m, 2 H, CHO and CHCl). Anal. Calcd for $C_9H_{14}Cl_2OS$ (241.18): C, 44.82; H, 5.85. Found: C, 44.56; H, 5.99.

2-Bromo-5′-(chloromethyl)spiro[cyclohexane-1,2′-[1,3]oxathiolane] (3c, X = Br): yield, 75%; bp 120–132 °C (1 torr); ^1H NMR ($CDCl_3$) δ 1.30–2.30 (m, 8 H, CH_2), 2.90–3.30 (m, 2 H, CH_2S), 3.55–3.75 (m, 2 H, CH_2Cl), 4.10–4.60 (m, 2 H, CHO and CHBr).

2-[(Trifluoroacetyl)oxy]-5′-(chloromethyl)spiro[cyclohexane-1,2′-[1,3]oxathiolane] 3c, (X = CF_3COO): yield, 62%; bp 100–120 °C (0.3 torr); IR (neat) 1782 (C=O) cm^{-1}, ^1H NMR ($CDCl_3$) δ 1.30–2.30 (m, 8 H, CH_2), 2.90–3.30 (m, 2 H, CH_2S), 3.45–380 (m, 2 H, CH_2Cl), 3.90–4.70 (m, 2 H, CHO).

2-(Phenylbromomethyl)-2-phenyl-5-(chloromethyl)-1,3-oxathiolane (3d): yield, 90% of crude product (purity 95%, distillation resulted in decomposition); ^1H NMR ($CDCl_3$) δ 2.80–3.00 (m, 2 H, CH_2S), 3.35–3.70 (m, 2 H, CH_2Cl), 3.70–4.70 (m, 2 H, CHO and CHBr), 7.10–7.50 and 7.80–8.10 (m, 10 H, Ph).

2-Bromospiro[cyclohexane-1,2′-[1,3]oxathiolane (6a): yield, 82% of crude product; distillation at 90–100 °C (0.5 torr) yielded a mixture of **6a** (30%) and **7a** (10%).

2-(Phenylbromomethyl)-2-phenyl-1,3-oxathiolane (6b): **5** and **2d** already gave **7b** besides **6b** (ca. 10%).

General Procedure for the Preparation of 1,4-Oxathiins 4 and 5,6-Dihydro-1,4-oxathiins 7. To a water-cooled solution of the 1,3-oxathiolane (0.15 mol) in Me_2SO (50 mL) was added dropwise a solution of potassium *tert*-butoxide (40.4 g, 0.36 mol; in the case of **6**, 20.2 g, 0.18 mol) in Me_2SO (250 mL) under nitrogen atmosphere. After at least 30 min the conversion was complete (GC analysis). The dark colored mixture was added to 500 mL ice/water, and the products were extracted with ether (5 × 100 mL). The combined ether layers were washed with saturated NaCl/water solutions (5 × 30 mL), dried over potassium carbonate, and concentrated. The residues were either distilled or chromatographed. All products have been stored without decomposition at 0 °C for several years.

2,3,6-Trimethyl-1,4-oxathiin (4a): yield, 59%, bp 108–109 °C (760 torr); IR (neat) 3070 (=CH), 1652 and 1692 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.80 (3 × s, 9 H, CH_3), 4.85 (m, 1 H, =CH). Anal. Calcd for $C_7H_{10}OS$ (142.2): C, 59.12; H, 7.09. Found: C, 59.01; H, 7.15.

2,3-Trimethylene-6-methyl-1,4-oxathiin (4b): yield, 42%; bp 95 °C (9 torr); IR (neat) 3060 (=CH), 1640 and 1690 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.67 (d, J = 1.5 Hz, 3 H, CH_3), 1.85–2.50 (m, 6 H, CH_2), 4.50 (d, J = 1.5 Hz, 1 H, =CH); ^{13}C NMR ($CDCl_3$) δ 18.89 (CH_3), 19.87 (CH_2), 30.65 and 31.35 (allyl CH_2), 87.35 (=CHS), 98.63 (=CRS), 145.79 and 146.57 (=CO). Anal. Calcd for $C_8H_{10}OS$ (154.2): C, 62.30; H, 6.54. Found: C, 62.19; H, 6.61.

2,3-Tetramethylene-6-methyl-1,4-oxathiin (4c): yield, 46% [from **3c** (X = Cl)], 91% [from **3c** (X = Br)], 63% [from **3c** (X = CF_3COO)]; bp 63–64 (0.1 torr); IR (neat) 3070 (=CH), 1650 and 1692 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.70 (d, J = 1.5 Hz, 3 H, CH_3), 1.50–2.10 (m, 8 H, CH_2), 4.73 (d, J = 1.5 Hz, 1 H, =CH); ^{13}C NMR ($CDCl_3$) δ 19.81 (CH_3), 22.75 and 22.95 (CH_2), 27.91 and 28.09 (allyl CH_2), 90.36 (=CHS), 101.28 (=CRS), 143.77 and 147.58 (C=CO); MS (70 eV), m/e (relative intensity) 168 (100, M^+), 140 (6.6, $M^+ - C_2H_4$), 135 (32.1, M^+ - SH), 127 (31.5, $M^+ - C_3H_5$), 125 (13.9, $M^+ - CH_3CO$), 97 (22.5), 91 (16.2), 79 (13.9), 71 (16.4), 67 (16.1), 43 (34.7, CH_3CO). Anal. Calcd for $C_9H_{12}OS$ (168.3): C, 64.25; H, 7.19. Found: C, 64.40; H, 7.14.

2,3-Diphenyl-6-methyl-1,4-oxathiin (4d). **4d** was isolated as a viscous oil either by liquid chromatography (silica gel 32-100; toluene, R_f = 0.33) or by HPLC (Si 60; 15% ethyl acetate in hexane): yield, 82%, ^1H NMR ($CDCl_3$) δ 2.35 (s, 3 H, CH_3), 4.25 (br s, 1 H, =CH), 7.17 and 7.26 (m, 10 H, Ph). Anal. Calcd for $C_{17}H_{14}OS$ (266.4): C, 76.66; H, 5.30. Found: C, 76.89; H, 5.48.

2,3-Tetramethylene-5,6-dihydro-1,4-oxathiin (7a): yield, 88%; bp 47–48 °C (0.3 torr); IR (neat) 1660 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.50–1.85 (m, 4 H, CH_2), 1.85–2.10 (m, 4 H, CH_2),

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2.85–3.10 (m, 2 H, CH_2S), 4.10–4.30 (m, 2 H, CH_2O). Anal. Calcd for $C_8H_{12}OS$ (156.3): C, 61.49; H, 7.74. Found: C, 61.10; H, 7.88.

2,3-Diphenyl-5,6-dihydro-1,4-oxathiin (7b). **7b** was isolated by liquid chromatography (silica gel 32-100, toluene): yield, 85% (from the **6b**/**7b** mixture, see above); mp 59–60 °C; IR (KBr) 3020, 3060, 3080 (=CH), 1595 and 1570 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.04 (td, $\sum J$ = 9 Hz, 2 H, CH_2S), 7.08 (m, 10 H, Ph); ^{13}C NMR ($CDCl_3$) δ 27.76 (CH_2S), 65.50 (CH_2O), 107.54 (=CRS), 127.03 and 127.30 (para C of Ph), 127.44 and 128.07 (meta C of Ph), 129.05 and 130.21 (ortho C of Ph), 136.31 and 138.68 (C_1 of Ph), 145.83 (=CRO); MS (70 eV), *m/e* (relative intensity) 254 (61.9, M^+), 226 (4.5, $M^+ - C_2H_4$), 121 (100, $PhCS^+$), 105 (70.0, $PhCO^+$), 77 (28.3, $C_6H_5^+$), 51 (7.0, $C_4H_3^+$). Anal. Calcd for $C_{16}H_{14}OS$ (254.4): C, 75.55; H, 5.55. Found: C, 75.36; H, 5.42.

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Registry No. 1, 6478-04-2; **2a** (X = Cl), 4091-39-8; **2b** (X = Cl), 694-28-0; **2c** (X = Cl), 822-87-7; **2c** (X = Br), 822-85-5; **2c** (X = CF_3CO_2), 66197-69-1; **2d** (X = Br), 1484-50-0; **3a** (X = Cl), 101249-19-8; **3b** (X = Cl), 101249-20-1; **3c** (X = Cl), 101249-21-2; **3c** (X = Br), 101249-22-3; **3c** (X = CF_3CO_2), 101249-23-4; **3d** (X = Br), 101249-24-5; **4a**, 101249-27-8; **4b**, 101315-92-8; **4c**, 101249-28-9; **4d**, 101249-29-0; **5**, 60-24-2; **6a**, 101249-25-6; **6b**, 101249-26-7; **7a**, 35755-85-2; **7b**, 58041-19-3; **9**, 26226-64-2; 1-mercapto-3-chloro-2-propanol, 6478-05-3.

Syntheses of New Substituted Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanes: A Novel Synthesis of Hexacyclo[6.2.1.1^{3,6}.0^{2,7}.0^{4,10}.0^{5,9}]dodecane (1,3-Bishomopentaprismane)

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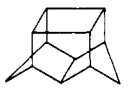
Recently, substituted 1,3-bishomopentaprismanes have attracted attention as intermediates in the synthesis of [4]peristylane and related compounds.[1-3] As part of a program that is involved with the synthesis and chemistry of new, substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanes,[4-10] we now report several new derivatives of this system that lead to a novel synthesis of the parent 1,3-bishomopentaprismane (**1**).



1

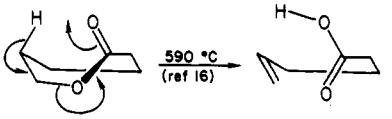
Compound **1** has been synthesized previously: (i) via [2 + 2] photocylization of isodrin followed by dechlorination of the resulting photoadduct,[11] and (ii) as a by-product that accompanies the solvolysis of any of several octahydrodimethanonaphthyl brosylates.[12] In all such cases, Diels–Alder cycloadditions of substituted cyclopentadienes with appropriately substituted norbornenes and/or norbornadienes furnish the required dimethanonaphthalene skeleton. The present synthesis of **1** is novel in that the hexacyclic ring system is formed from an appropriately substituted pentacyclic precursor (i.e., **6**).

Our approach to the synthesis of **1** is shown in Scheme I. The readily available[4] pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]-undecane-8,11-dione (**2**) was chosen as starting material for this study. Symmetrical diketone **2** could be converted into unsymmetrical enone **3** in two ways. First, **3** could be synthesized directly via Wadsworth–Emmons reaction of **2** with the ylide derived from ethyl (diethoxyphosphinyl)acetate.[13,14] Alternatively, Reformatsky reaction[15] of **2** with $BrZnCH_2CO_2Et$ afforded **4**, which was then converted to the corresponding mesylate; subsequent DBU-promoted elimination of methanesulfonic acid from this intermediate afforded **3**.

Interestingly, reduction of **3** with sodium borohydride in methanol at 0 °C resulted in regiospecific reduction via exclusive attack at the exo face of the ketone carbonyl group. Subsequent transannular Michael addition of the resulting endo alcohol to the proximate α,β-unsaturated ester moiety then afforded the observed product, **5**. Alternatively, catalytic hydrogenation of **3** simply resulted in reduction of its carbon–carbon double bond, thereby affording **6**.

Reaction of **6** with sodium borohydride in methanol at 0 °C resulted again in regiospecific reduction via exclusive exo attack at the ketone carbonyl group. Subsequent transannular transesterification between the resulting endo alcohol and the proximate ester moiety afforded one of the observed reaction products, lactone **7**. Lactol **8** was also produced in this reaction, presumably via further reaction of **7** with excess sodium borohydride. The structure of **8** was established via dehydration to the corresponding vinyl ether **9**.

Flash vacuum pyrolysis of **7** at 700 °C resulted in elimination of carbon dioxide with concomitant formation of 1,3-bishomopentaprismane (**1**). It should be noted that **7** contains a substituted ϵ-caprolactone moiety. Flash vacuum pyrolysis of the parent, unsubstituted ϵ-caprolactone has been studied by Bailey and Bird;[16] pyrolysis of this compound at 590 °C was observed to afford 5-hexenoic acid in 53% yield. Presumably, ϵ-caprolactone is sufficiently flexible that normal ester pyrolysis occurs, resulting in β-elimination via a quasi-six-membered ring transition state[16] (eq 1). Such flexibility is not present



(1)

in **7**, nor is alkene formation (via β-elemination) likely to occur in this strained cage system (Scheme II). To our knowledge, the formation of **1** from **7** represents the first example wherein pyrolysis of a substituted ϵ-caprolactone results in fragmentation with elimination of carbon dioxide

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