Ring Expansions of 4-(2,6-Dithiacyclohexyl)- and 4-Oxiranylcyclobuten-1-ones

Kwan Hee Lee and Harold W. Moore*

Department of Chemistry, University of California, Irvine, California 92717

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Reported here are a number of unusual rearrangements of 4-alkyl-4-hydroxycyclobutenones in which the alkyl group bears a heteroatom at its 2-position, e.g., compound **1** in Scheme 1. Thermolysis of such compounds was envisaged to result in ring-expanded medium-sized heterocyclic compounds. That is, stereospecific electrocyclic ring opening of **1** to the *cis*-vinylketene **2** followed by intramolecular attack of the heteroatom on the ketene moiety would give **3**, and this leads directly to the macrocycle **4**.[1] In fact, some of the transformations reported herein involve this sequence but proceed further to ring-contracted products since the initially formed macrocycles are not stable under the reaction conditions.

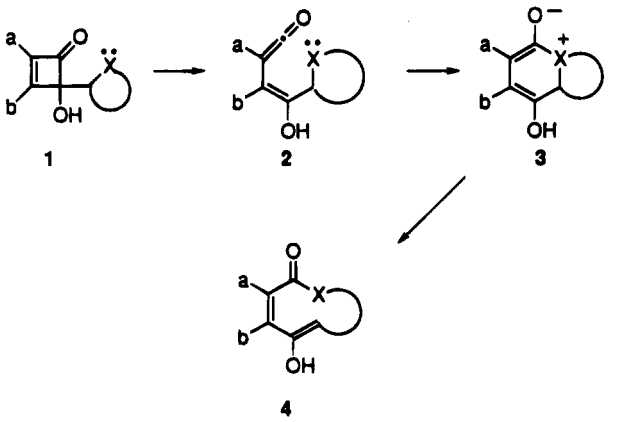
The most unusual examples were observed for the thermolyses of selected 4-(2,6-dithiacycloalkyl)cyclobutenones. Specifically, when a *p*-xylene solution containing 0.2 mmol of **5** was refluxed for 3 h a good to excellent yield (70–90%) of the spirobutenolide **11** was realized (Scheme 2). In reference to the mechanistic postulate presented above, this rearrangement is envisaged to involve formation of the thiolactone **8** via the ketene **6** and the zwitterion **7**. The thiolactone then undergoes further intramolecular transannular ring closure leading to the zwitterion **9** which leads to **10** upon heterolytic cleavage and ultimately to the observed product **11**.

In an analogous fashion, the spirobutenolides **13a** (70%) and **13b** (50%) were obtained from the respective cyclobutenones **12a** and **12b**. The structures of **13a,b** as well as **11** are based upon their spectral properties. They show carbonyl stretching at, respectively, 1756, 1760, and 1771 cm^{-1} in their IR spectra, and an AB pattern for the methylene flanked by the quaternary carbon and the sulfur is apparent in their ^1H NMR spectra. Confirmation of their structures was unambiguously established by a complete X-ray analysis for **13b**.

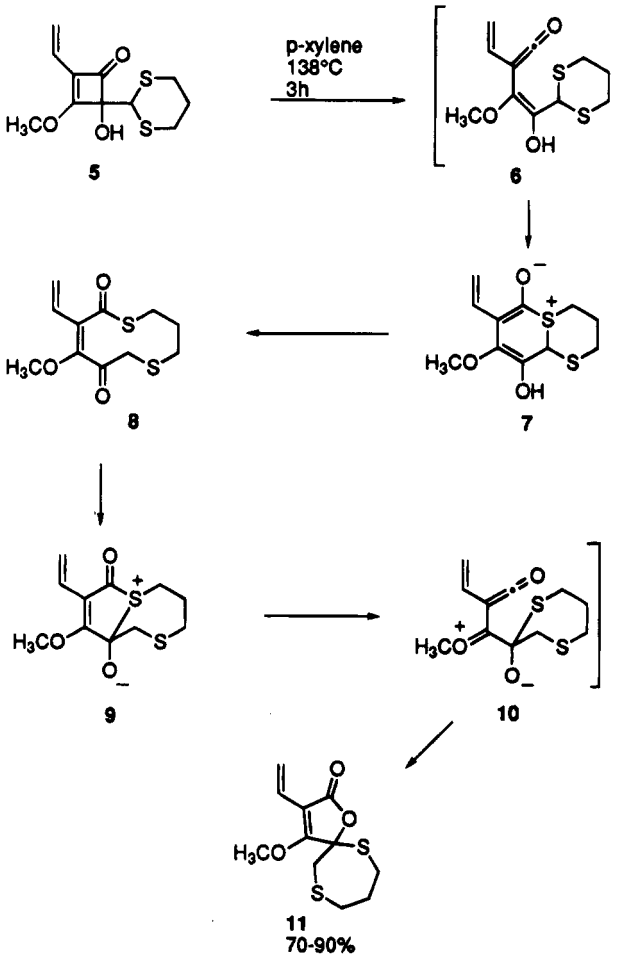
Another mode of rearrangement was observed when *p*-xylene solutions of the related cyclobutenones **14a** and **14b** were refluxed for a prolonged period of time. Here, rather than ring expansion to the spirobutenolides, the cyclopentenediones **17a** and **17b** were realized in good yields (Scheme 3). That **16** is an intermediate in these reactions was established by its isolation when the thermolysis time was decreased. For example, **17b** was isolated in 77% yield when **14b** was thermolyzed for 3 h and **16b** was obtained in 48% yield when the reaction time was reduced to 2 h. Similarly, **14c** gave a 79% isolated yield of **16c**.

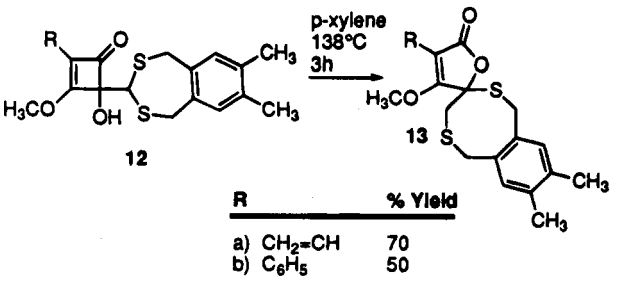
The formation of **16** and **17** is envisaged to be analogous to the formation of **11** in that the 10-membered thiolactone **15** is proposed as a key intermediate. However, rather than tautomerization to the corresponding enedione (e.g., formation of **8**) enol attack on the thiolac-

Scheme 1



Scheme 2

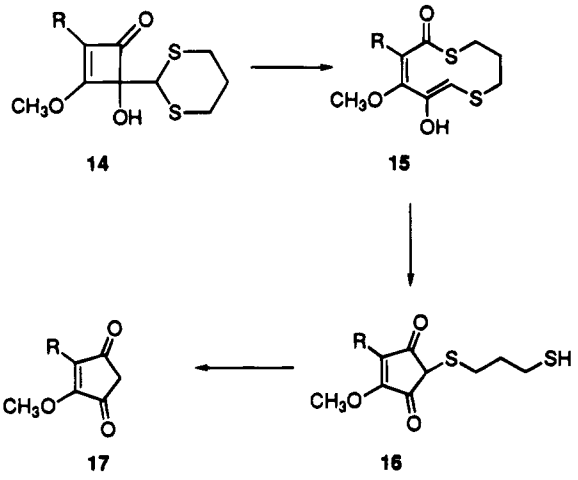




(1) For recent reviews of the ring expansions of cyclobutenones see: a) Moore, H. W.; Yerxa, B. R. *Chemtracts* **1992**, *5*, 273. (b) Moore, H. W.; Decker, O. H. W. *Chem. Rev.* **1986**, *86*, 821. (c) Liebeskind, L. S. *Tetrahedron* **1989**, *45*, 3053. (d) Moore, H. W.; Yerxa, B. R. *Advances in Strain in Organic Chemistry*, in press. For a review of the utility of cyclobutenones in natural product syntheses see: Bellus, D.; Ernst, B. *Angew. Chem.* **1988**, *100*, 820.

0022-3263/95/1960-0735$09.00/0

Scheme 3



R	% Yield of 17*	% Yield of 16
a) C_6H_5	42 (60)	---
b) CH_3O	37 (77)	48
c) n-C_4H_9	---	79

* Overall yield from the respective cyclobutenedione

( ) Yield from the cyclobutenones 14

tone carbonyl group leads to **16**. This then results in the cyclopentenediones *via* intramolecular attack of the thiol group on the sulfide sulfur with concomitant displacement of the enolates of **17**.

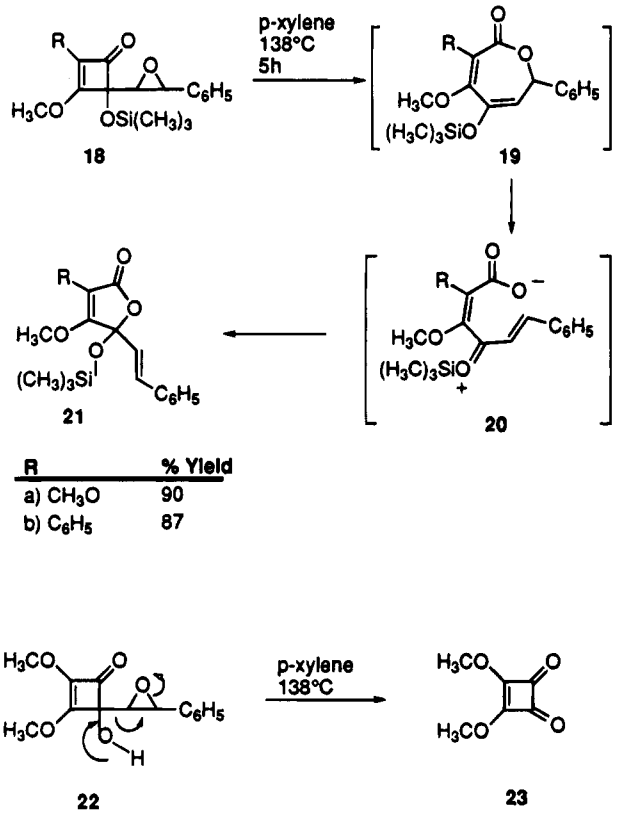
With regard to the above tautomer dependent product-forming step, it is of interest to note that thermolysis of the 4-(trimethylsiloxy) derivative of **5** gave 4-methoxy-5-ethenylcyclopentene-1,3-dione (30%) rather than the spirobutenolide **11**. This is consistent with the postulate that enediones such as **8** are required precursors for the spirobutenolides; i.e., the thiolactone is now held in the enol form, thus dictating cyclopentenedione formation.

The scope of this study was expanded to include selected examples of 4-oxiranylcyclobutenones **18a,b** (Scheme 4). These were prepared in approximately 30% yields upon addition of the lithium salt of 1-lithio-2-phenyloxirane to the respective cyclobutenedione in THF (−78 °C) in the presence of TMEDA followed by a TMSCl quench. In turn, the oxiranyllithium reagent was prepared from the corresponding oxiranyltin upon treatment with butyllithium.[2,3]

In analogy to the generalized mechanism outlined above, the seven-membered lactones **19a,b** are formed as intermediates in the thermolysis of **18** and these lead to the observed 2(5*H*)-furanone products **21a,b** (87−90%) via the zwitterions **20a,b**.

It is of interest to note that in order for rearrangement to occur it was necessary to use the 4-(trimethylsiloxy)-cyclobutenones **19a,b** as opposed to the 4-hydroxy ana-

Scheme 4



R	% Yield
a) CH_3O	90
b) C_6H_5	87

logs. When the hydroxy analogs were used a fragmentation occurred as illustrated by the nearly quantitative conversion of **22** to dimethyl squarate **23** under the thermolysis conditions.

The structures of **21a,b** are based upon their characteristic spectral properties (Experimental Section) as well as a complete X-ray crystal structure for **21a**.[4]

Experimental Section

4-Hydroxy-3-methoxy-4-(2,6-dithiacyclohexyl)-2-ethenyl-2-cyclobuten-1-one, 5. The title compound was prepared in 50% (128 mg) yield as white plates (mp, 111−112 °C) from 3-methoxy-4-ethenyl-3-cyclobutene-1,2-dione (138 mg, 1 mmol) by the general procedure used for the synthesis of 4-hydroxy-3-methoxy-2-phenyl-4-(2,6-dithiacyclohexyl)-2-cyclobuten-1-one, **14a**: IR ($CHCl_3$, cm^{-1}) 3424, 1757, 1646; ^1H NMR ($CDCl_3$, 500 MHz) δ 6.2 (ddd, J = 0.78, 10.16, 17.25 Hz, 1H), 5.97 (d, J = 17.25 Hz, 1H), 5.40 (d, J = 11.16 Hz, 1H), 4.34 (d, J = 1.02 Hz, 1H), 4.28 (s, 1H), 4.18 (d, J = 1.01 Hz, 3H), 3.08 (ddd, J = 3.04, 7.12, 7.78 Hz, 1H), 2.8 (ddd, J = 3.04, 7.78, 7.48 Hz, 1H), 2.6 (m, 2H), 1.9 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 188.2, 177.8, 126.6, 123.2, 122.4, 93.7, 61.2, 47.3, 28.7, 28.6, 25.7; MS (EI) m/z (rel intensity) 258 (7), 119 (100); MS (CI) m/z 259 (MH^+); HRMS m/z calcd for $C_{11}H_{14}O_3S_2$ 258.0384, found 258.0376.

1,5-Dithia-4′-methoxy-3′-ethenylspiro[4.6]-2′(5′*H*)-furanone, 11. A *p*-xylene solution (30 mL) of 4-hydroxy-3-methoxy-4-(2,6-dithiacyclohexyl)-2-ethenyl-2-cyclobuten-1-one, **5** (52 mg, 0.2 mmol), was refluxed for 3 h. After being cooled to rt, the solution was concentrated *in vacuo* at 45 °C. Flash column chromatography (3:1 hexanes/ethyl acetate) gave 47 mg (90%) of **11** as a pale yellow oil: IR (CCl_4, cm^{-1}) 1771, 1658; ^1H NMR ($CDCl_3$, 500 MHz) δ 6.60 (dd, J = 17.9, 11.4 Hz, 1H), 6.15 (dd, J = 17.4, 1.8 Hz, 1H), 5.45 (dd, J = 11.7, 1.8 Hz, 1H), 4.22 (s,

(2) Lohse, P.; Loner, H.; Acklin, P.; Stenfeld, F.; Pfaltz, A. *Tetrahedron Lett.* **1991**, *32*, 615.

(3) For other leading references on oxiranyl anions see: Eisch, J. J.; Galle, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 4646. Eisch, J. J.; Galle, J. E. *J. Organomet. Chem.* **1976**, *121*, C10. Eisch, J. J.; Galle, J. E. *J. Organomet. Chem.* **1988**, *341*, 293. Eisch, J. J.; Galle, J. E. *J. Org. Chem.* **1990**, *55*, 4835. Ashwell, M.; Jackson, R. F. W. *J. Chem. Soc., Chem. Commun.* **1988**, 645. Ashwell, M.; Jackson, R. F. W. *J. Chem. Soc., Perkin Trans. 1* **1989**, 835. Dubuffet, T.; Sauvetre, R.; Normant, J. F. *Tetrahedron Lett.* **1988**, *29*, 5923. Molander, G. A.; Mautner, K. *J. Org. Chem.* **1989**, *54*, 4042.

(4) The authors have deposited atomic coordinates for compounds **13b** and **21a** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

3H), 3.75 (m, 1H), 3.30 (d, J = 14.7 Hz, 1H), 3.0 (m, 3H), 2.85 (dt, J = 15.3, 3.9 Hz, 1H), 2.15 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 172.5, 168.8, 122.3, 120.5, 99.8, 87.4, 60.9, 46.1, 33.3, 32.1, 27.6, 20.8; MS (EI) m/z (rel intensity) 258 (1.6), 106 (100); HRMS m/z calcd for $C_{11}H_{14}O_3S_2$ 258.0384, found 258.0384.

At lower temperature (81 °C), 4 mg (14%) of 4-ethenyl-5-methoxycyclopentene-1,3-dione was also isolated as a yellow oil: IR ($CHCl_3$, cm^{-1}) 1737, 1698; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.45 (dd, J = 11.5, 18 Hz, 1H), 6.44 (dd, J = 18, 1.8 Hz, 1H), 5.70 (dd, J = 1.8, 11.5 Hz, 1H), 4.38 (s, 3H), 2.95 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 195.8, 195.5, 164.7, 133.9, 126.6, 123.7, 60.9, 43.3; MS (EI) m/z (rel intensity) 152 (45), 57 (100); HRMS m/z calcd for $C_8H_8O_3$ 152.0473, found 152.0475.

4-(3,8-Dihydro-5,6-dimethyl-2,9-benzodithiepinyl)-4-hydroxy-3-methoxy-2-ethenyl-2-cyclobuten-1-one, 12a. In a manner analogous to the synthesis of **12b** starting with 463 mg (2.2 mmol) of 1,5-dihydro-7,8-dimethyl-2,4-benzodithiepine (463 mg, 2.2 mmol) and 276 mg (2 mmol) of 3-methoxy-4-ethenyl-3-cyclobutene-1,2-dione the title compound was prepared in 80% yield (557 mg) as a white solid: mp 141−142 °C; IR ($CHCl_3$, cm^{-1}) 3690, 1758, 1645; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.93 (s, 1H), 6.91 (s, 1H), 6.23 (dd, J = 11.5, 17.6 Hz, 1H), 6.03 (d, J = 17.6 Hz, 1H), 5.43 (d, J = 11.5 Hz, 1H), 4.53 (s, 1H), 4.12 (brs, 4H), 4.16 (s, 3H), 2.20 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 177.2, 138.4, 137.0, 136.9, 131.4, 131.3, 131.2, 126.9, 123.6, 122.3, 116.1, 93.2, 61.1, 19.9; MS (CI) m/z (rel intensity) 349 (MH$^+$, 9), 153 (100); HRMS m/z calcd for $C_{18}H_{20}O_3S_2$ 348.0854, found 349.0928 (MH$^+$).

4-(3,8-Dihydro-5,6-dimethyl-2,9-benzodithiepinyl)-4-hydroxy-3-methoxy-2-phenyl-2-cyclobuten-1-one, 12b. To the solution of commercially available 1,5-dihydro-7,8-dimethyl-2,4-benzodithiepine (442 mg, 2.1 mmol) in dry THF (100 mL) was slowly added n-BuLi (1.6 M in hexanes, 1.3 mL, 2.1 mmol) at −78 °C *via* syringe. After being stirred for 20 min at −78 °C, the resulting solution was transferred to a solution of 3-methoxy-4-phenyl-3-cyclobutene-1,2-dione (376 mg, 2 mmol) in dry THF (30 mL) *via cannula*. The reaction mixture was stirred for an additional 20 min and then quenched with a 5% NH_4Cl solution (3 mL) and poured into 100 mL of ether and 10 mL of water. The organic phase was washed with water (20 mL) and brine (10 mL) and dried over $MgSO_4$ and concentrated *in vacuo*. Flash column chromatography of the residue (3:1 hexanes/ethyl acetate) gave 543 mg (70%) of the desired cyclobutenone **12b** as a white solid: mp 145−146 °C; IR ($CHCl_3$, cm^{-1}) 3540, 1757; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.72 (d, J = 7.33 Hz, 2H), 7.34 (m, 3H), 6.94 (s, 1H), 6.92 (s, 1H), 4.30 (s, 3H), 4.21 (s, 3H), 4.01 (d, J = 1.1 Hz, 2H), 4.05 (d, J = 1.1 Hz, 2H), 2.21 (s, 3H), 2.20 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 177.8, 140.2, 136.3, 136.3, 130.7, 130.5, 128.5, 127.9, 127.4, 60.4, 19.3, 19.2; MS (CI) m/z (rel intensity) 399 (MH$^+$,9), 203 (100); HRMS m/z calcd for $C_{22}H_{22}O_3S_2$ 399.1088 (MH$^+$), found 399.1059 (MH$^+$).

Spiro[7*H*-2,3-dimethyl-6,9-benzodithiepine-7,5′-4′-methoxy-3′-vinyl-2′(5′*H*)-furanone], 13a. A p-xylene solution of the cyclobutenone **12a** (175 mg, 0.5 mmol) was refluxed for 3 h. After being cooled to rt, the solution was concentrated *in vacuo* at 45 °C. Flash column chromatography (3:1 hexanes/ethyl acetate) gave 159 mg (91%) of the desired spirobutenolide **13a** as a colorless oil: IR ($CDCl_3$, cm^{-1}) 1760, 1657; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.97 (s, 2H), 6.56 (dd, J = 11.5, 17.5 Hz, 1H), 6.19 (dd, J = 17.5, 1.7 Hz, 1H), 5.43 (dd, J = 11.5, 1.7 Hz, 1H), 4.56 (d, J = 15.22 Hz, 1H), 4.17 (s, 3H), 4.15 (d, J = 14.1 Hz, 1H), 3.92 (d, J = 13.95 Hz, 1H), 3.78 (d, J = 15.56 Hz, 1H), 3.12 (d, J = 15.9 Hz, 1H), 3.02 (d, J = 15.9 Hz, 1H), 2.22 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 173.9, 169.8, 137.5, 137.1, 135.3, 133.5, 132.3, 131.8, 123.0, 121.5, 100.7, 89.1, 61.6, 40.7, 35.7, 32.3, 20.0; MS (EI) m/z (rel intensity) 348 (11), 132 (100); HRMS m/z calcd for $C_{18}H_{20}O_3S_2$ 348.0854, found 349.0912 (MH$^+$).

Spiro[7*H*-2,3-dimethyl-6,9-benzodithiepine-7,5′-4′-methoxy-3′-phenyl-2′(5′*H*)-furanone, 13b. A p-xylene solution of the cyclobutenone **12b** (200 mg, 0.5 mmol) was refluxed for 3 h. After being cooled to rt, the solution was concentrated *in vacuo* at 45 °C. Flash column chromatography (3:1 hexanes/ethyl acetate) gave 141 mg (71%) of the spirobutenolide **13b** as white plates: mp 169−170 °C; IR ($CHCl_3$, cm^{-1}) 1756, 1694; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.39 (s, 5H), 7.36 (s, 2H), 4.63 (d, J = 15.22 Hz, 1H), 4.18 (d, J = 13.77 Hz, 1H), 3.97 (d, J = 13.77 Hz, 1H), 3.84 (d, J = 15.22 Hz, 1H), 3.75 (s, 3H), 3.22 (d, J = 15.8 Hz, 1H), 3.14 (d, J = 15.8 Hz, 1H), 2.24 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 174.4, 170.2, 136.7, 136.3, 134.6, 132.7, 131.6, 131.1, 130.4, 128.7, 128.5, 128.1, 102.8, 89.1, 61.3, 39.7, 35.0, 31.6, 19.2; MS (EI) m/z (rel intensity) 398 (3), 133 (100); MS (CI) m/z 399 (MH$^+$); HRMS m/z calcd for $C_{22}H_{22}O_3S_2$ 398.1010, found 399.1058 (MH$^+$).

4-Hydroxy-3-methoxy-2-phenyl-4-(2,6-dithiacyclohexyl)-2-cyclobuten-1-one, 14a. To the solution of 1,3-dithiane (156 mg, 1.3 mmol) in dry THF (40 mL) was slowly added n-BuLi (1.6 M in hexanes, 0.75 mL, 1.2 mmol) at −78 °C *via* syringe. After being stirred for 20 min at −78 °C, the resulting solution was transferred to the solution of 3-methoxy-4-phenyl-3-cyclobutene-1,2-dione (188 mg, 1 mmol) in dry THF (30 mL) *via cannula*. The reaction mixture was stirred for an additional 20 min and then quenched with 5% NH_4Cl solution (3 mL) and poured into 100 mL of ether and 10 mL of water. The organic phase was washed with water (20 mL) and brine (10 mL), dried over $MgSO_4$, and concentrated *in vacuo*. Flash column chromatography (3:1 hexanes/ethyl acetate) gave 216 mg (70%) of the desired cyclobutenone **14a** as a white solid: mp 156−157 °C; IR ($CHCl_3$, cm^{-1}) 3374, 1757, 1634; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.75−7.28 (m, 5H), 4.47 (s, 1H), 4.27 (s, 3H), 3.20 (ddd, J = 3.04, 7.44, 7.78 Hz, 1H), 2.88 (ddd, J = 3.04, 7.44, 3.38 Hz, 1H), 2.69 (m, 2H), 2.02 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 187.2, 178.9, 159.5, 129.2, 128.7, 128.0, 127.7, 95.2, 74.0, 61.1, 46.3, 28.9, 25.8; MS (EI) m/z (rel intensity) 308 (5), 202 (82), 119 (84), 89 (100); MS (CI) m/z 309 (MH$^+$); HRMS m/z calcd for $C_{15}H_{16}O_3S_2$ 308.0541, found 309.0607 (MH$^+$).

2-*n*-Butyl-4-hydroxy-3-methoxy-4-(2,6-dithiacyclohexyl)-2-cyclobuten-1-one, 14c. The title compound was prepared in 55% yield (74 mg) as a thick oil from 3-n-butyl-4-methoxy-3-cyclobutene-1,2-dione (84 mg, 0.5 mmol) by the general procedure used for the synthesis of **14a**: IR ($CDCl_3$, cm^{-1}) 3402, 1758, 1621; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.43 (s, 1H), 4.30 (s, 1H), 4.12 (s, 3H), 3.04 (ddd, J = 3.04, 2.7, 7.5 Hz, 1H), 2.86 (ddd, J = 3.04, 3.38, 7.44 Hz, 1H), 2.67 (m, 2H), 2.17 (m, 2H), 1.95 (m, 2H), 1.50 (m, 2H), 1.32 (m, 2H), 0.85 (t, J = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 190.6, 180.6, 130.8, 93.2, 60.5, 47.7, 30.6, 29.0, 29.0, 25.9, 23.2, 22.8, 14.4; MS (EI) m/z (rel intensity) 288 (2), 182 (99), 106 (100); HRMS m/z calcd for $C_{13}H_{20}O_3S_2$ 288.0854, found 289.0950 (MH$^+$).

2,3-Dimethoxy-5-(4-mercapto-1-thiabutyl)-2-cyclopentene-1,4-dione, 16b. To the solution of 1,3-dithiane (312 mg, 2.6 mmol) in dry THF (60 mL) was added n-BuLi (1.6 M in hexanes, 1.5 mL, 2.4 mmol) slowly at −78 °C *via* syringe. After being stirred for 20 min at −78 °C, the resulting solution was transferred to the solution of 3,4-dimethoxy-3-cyclobutene-1,2-dione (284 mg, 2 mmol) in dry THF (100 mL) *via cannula*. The reaction mixture was stirred for an additional 20 min and then quenched with 5% NH_4Cl solution (5 mL) and poured into a separatory funnel containing 150 mL of ether and 10 mL of water. The organic phase was washed with water (20 mL) and brine (10 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The crude cyclobutenone **14b** was heated at reflux in p-xylene (50 mL) for 2 h. After being cooled to rt, the solution was concentrated *in vacuo* at 45 °C. Flash column chromatography (3:1 hexanes/ethyl acetate) gave 251 mg (48%) of **16b** as a yellow oil: IR (neat, cm^{-1}) 1746, 1693; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.22 (s, 6H), 3.64 (s, 1H), 2.84 (t, J = 7.1 Hz, 2H), 2.63 (q, J = 7.1 Hz, 2H), 1.88 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 190.8, 151.6, 60.6, 48.8, 33.7, 30.1, 23.8; MS (EI) m/z (rel intensity) 262 (0.05), 156 (100); MS (CI) m/z 263 (MH$^+$); HRMS m/z calcd for $C_{10}H_{14}O_4S_2$ 262.0333, found 263.0406 (MH$^+$).

2-*n*-Butyl-5-(4-mercapto-1-thiabutyl)-3-methoxy-2-cyclopentene-1,4-dione, 16c. Cyclobutenone **14c** (57 mg, 0,2 mmol) and 50 mL of p-xylene was refluxed for 2 h. After being cooled to rt, the solution was concentrated *in vacuo* at 45 °C. Flash column chromatography (3:1 hexanes/ethyl acetate) gave 45 mg (79%) of **16c** as a yellow oil: IR (neat, cm^{-1}) 1738, 1693; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.29 (s, 3H), 3.61 (s, 1H), 2.83 (t, J = 6.95 Hz, 2H), 2.63 (q, J = 7.1 Hz, 2H), 2.38 (t, J = 7.6 Hz, 2H), 1.88 (t, J = 7.1 Hz, 2H), 1.40 (m, 4H), 0.89 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 195.3, 194.8, 165.7, 141.3, 60.5, 49.1, 33.7, 30.3, 30.0, 23.8, 23.4, 22.6, 14.4; MS (EI) m/z (rel intensity) 183 (15), 182 (100); MS (CI) m/z 289 (MH$^+$); HRMS m/z calcd for $C_{13}H_{20}O_3S_2$ 288.0854, found 288.0842.

2-Methoxy-3-phenyl-2-cyclopentene-1,4-dione, 17a. Cyclobutenone **14a** (62 mg, 0.2 mmol) in 30 mL of p-xylene was refluxed for 3 h. After being cooled to rt, the solution was

concentrated *in vacuo* at 45 °C. Flash column chromatography (3:1 hexanes/ethyl acetate) gave 25 mg (60%) of 2-methoxy-3-phenyl-2-cyclopentene-1,4-dione, **17a**, as a colorless oil: IR ($CHCl_3$, cm^{-1}) 1739, 1693; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.81 (d, J = 7.1 Hz, 2H), 7.32 (m, 3H), 4.32 (s, 3H), 3.06 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 196.1, 195.7, 165.1, 135.6, 130.2, 130.2, 129.1, 128.9, 61.1, 43.2; MS (EI) m/z (rel intensity) 202 (90), 89 (100); HRMS m/z calcd for $C_{12}H_{10}O_3$ 202.0630, found 202.0613.

2,3-Dimethoxy-2-cyclopentene-1,4-dione, 17b. Cyclobutenone **14b** (79 mg, 0.3 mmol) in 30 mL of *p*-xylene was refluxed for 60 h. After being cooled to rt, the solution was concentrated *in vacuo* at 45 °C. Flash column chromatography of the residue (3:1 hexanes/ethyl acetate) gave 60 mg (77%) of 2,3-dimethoxy-2-cyclopentene-1,4-dione, **17c**, as a yellow solid: mp 43.5–44.5 °C; IR ($CHCl_3$, cm^{-1}) 1732, 1697; ^1H NMR ($CDCl_3$, 500 MHz) δ 4.20 (s, 6H), 2.87 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 192.2, 152.6, 60.4, 41.8; MS (EI) m/z (rel intensity) 156 (100), 71 (59), 69 (52); HRMS m/z calcd for $C_7H_8O_4$ 156.0423, found 156.0428.

2,3-Dimethoxy-4-hydroxy-4-(2-phenyloxiranyl)-2-cyclobuten-1-one, 22. Butyllithium (1.6 M in hexanes, 0.75 mL, 1.2 mmol) was slowly added (2 min) via syringe to a solution of oxiranyltin[2] (409 mg, 1 mmol) in dry THF (20 mL) and TMEDA (0.3 mL, 2 mmol) at −100 °C (isooctane and dry ice). The resulting pink solution was stirred for 15 min at −100 °C and then transferred (cannula) to a solution of dimethyl squarate (142 mg, 1 mmol) in dry THF (20 mL). After being stirred for 30 min at −100 °C, the reaction solution was quenched with 5% NH_4Cl solution (3 mL). Ether (100 mL) was added to the reaction mixture, and the resulting organic layer was washed with water (2 × 10 mL) and brine (10 mL), dried over $MgSO_4$, and concentrated *in vacuo*. Flash column chromatography (1:1 hexanes/ethyl acetate) gave 56 mg (21.4%) of the desired **22** as a pale yellow oil: R_f 0.54 (silica gel, 1:1 hexanes/ethyl acetate); IR ($CDCl_3$, cm^{-1}) 3386, 1776, 1639; ^1H NMR (300 MHz, $CDCl_3$) δ, 7.39 (m, 5H), 4.21 (s, 3H), 4.10 (d, J = 2 Hz, 1H), 4.01 (s, 3H), 3.65 (s, 1H), 3.33 (d, J = 2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ, 183.1, 163.8, 136.0, 135.2, 128.5, 126.6, 125.7, 84.5, 60.4, 60.1, 58.6, 55.9; MS (EI) m/z (rel intensity) 262 (0.5), 91 (100); MS (CI); m/z 263 (MH^+); HRMS (EI) m/z calcd for $C_{14}H_{14}O_5$ 262.0841, found 262.0824.

2,3-Dimethoxy-4-(2-phenyloxiranyl)-4-(trimethylsiloxy)-2-cyclobuten-1-one, 18a. A solution of oxiranyltin[2] (370 mg, 0.9 mmol) in dry THF (15 mL) and TMEDA (0.3 mL, 2 mmol) was cooled to −100 °C (isooctane and dry ice), and *n*-BuLi (1.6 M in hexanes, 0.57 mL, 0.9 mL) was added slowly *via* syringe (color changed to pink) over 3 min. After being stirred for 15 min at −100 °C, the solution was transferred to a solution of dimethyl squarate (142 mg, 1 mmol) in dry THF (20 mL) *via cannula*. After being stirred for 30 min at −100 °C, the reaction solution was quenched with TMSCl (0.15 mL). The resulting solution was warmed to rt, and 100 mL of diethyl ether was added to the reaction mixture. The resulting organic layer was washed with water (2 × 10 mL) and brine (10 mL), dried over $MgSO_4$, and concentrated *in vacuo*. Flash column chromatography of the residue (3:1 hexanes/ethyl acetate) gave 95 mg (32%) of the desired cyclobutenone **18a** as a mixture of diastereomers (pale yellow liquid): R_f 0.45 (silica gel, 3:1 hexanes/ethyl acetate); IR ($CDCl_3$, cm^{-1}) 1758, 1642; ^1H NMR (500 MHz, $CDCl_3$) δ 7.29–7.33 (m, 5H), 4.17 (s, 3H), 3.98 (s, 3H), 4.12 (d, J = 1.8 Hz, 1H), 3.23 (d, J = 1.8 Hz, 1H), 0.17 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 183.3, 166.1, 137.3, 136.1, 129.1, 129.0, 126.4, 87.6, 61.6, 60.9, 59.2, 58.5, 1.9; MS (CI) m/z (rel intensity) 263 (33, M − TMS + H^+), 223 (100); HRMS m/z calcd for $C_{17}H_{22}SiO_5$ 334.1236, found 263.0905 (MH^+ − TMS + H^+).

3-Methoxy-2-phenyl-4-(2-phenyloxiranyl)-4-(trimethylsiloxy)-2-cyclobuten-1-one, 18b. In a manner analogous to the above the title compound was prepared in 30% yield (115mg) as a pale yellow oil: R_f 0.5 (silica gel, 3:1 hexanes/ethyl acetate); IR ($CHCl_3$) 1759, 1635, 1599 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ, 7.28–7.75 (m, 10H), 4.35 (s, 3H), 4.12 (d, J = 1.8 Hz, 1H), 3.26 (d, J = 1.8 Hz, 1H), 0.23 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ, 187.5, 186.1, 179.5, 136.9, 129.2, 129.2, 129.1, 129.0, 127.7, 126.5, 126.3, 93.7, 63.3, 62.2, 56.6, 1.7; MS (EI) m/z (rel intensity) 380 (1), 73 (100); MS (CI) m/z 381 (MH^+); HRMS calcd for $C_{22}H_{24}SiO_4$ 380.1444, found 380.1455.

3,4-Dimethoxy-5-(2-phenylethenyl)-5-(trimethylsiloxy)-2(5*H*)-furanone, 21a. 2,3-Dimethoxy-4-(2-phenyloxiranyl)-4-(trimethylsiloxy)-2-cyclobuten-1-one, **18a** (30 mg, 0.09 mmol), in 15 mL of *p*-xylene was refluxed for 5 h. The resulting solution was concentrated *in vacuo* at 50 °C. Flash column chromatography (3:1 hexanes/ethyl acetate) gave 27 mg (90%) of the desired butenolide **21a** as a white solid: mp 95–96 °C; R_f 0.4 (silica gel, 3:1 hexanes:ethyl acetate); IR ($CDCl_3$, cm^{-1}) 1773, 1688; ^1H NMR (500 MHz, $CDCl_3$) δ 7.2–7.4 (m, 5H), 6.89 (d, J = 15.8 Hz, 1H), 6.13 (d, J = 15.8 Hz, 1H), 4.14 (s, 3H), 3.87 (s, 3H), 0.23 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ, 167.6, 158.9, 136.0, 133.7, 129.3, 129.3, 127.7, 125.8, 122.4, 99.7, 61.1, 60.1, 2.0; MS (EI) m/z (rel intensity) 334 (4), 73 (100); MS (CI) m/z, 335 (MH^+); HRMS (EI) m/z calcd for $C_{17}H_{22}SiO_5$ 334.1236, found 334.1252.

4-Methoxy-3-phenyl-5-(2-phenylethenyl)-5-(trimethylsiloxy)-2(5*H*)-furanone, 21b. In a manner analogous to that above, 38 mg (0.1 mmol) of **18b** gave 33 mg (87%) of the butenolide **21b** as a colorless oil: R_f 0.4 (silica gel, 3:1 hexanes/ethyl acetate); IR ($CDCl_3$, cm^{-1}) 1756, 1668; ^1H NMR (500 MHz, $CDCl_3$) δ, 7.32–7.70 (m, 10H), 7.00 (d, J = 15.9Hz, 1H), 6.30 (d, J = 15.9Hz, 1H), 3.99 (s, 3H), 0.30 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ, 172.8, 170.4, 135.9, 134.4, 129.8, 129.7, 129.6, 129.5, 129.4, 129.1, 129.1, 128.9, 128.8, 128.7, 127.8, 126.1, 103.6, 100.9, 60.3, 2.0; MS (EI) m/z (rel intensity) 380 (2), 73 (100); MS (CI) m/z 381 (MH^+); HRMS (EI) m/z calcd for $C_{22}H_{24}SiO_4$ 380.1444, found 380.1434.

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Supplementary Material Available: Copies of ^{13}C NMR spectra of all compounds (18 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS, see any current masthead page for ordering information.

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