Cyclobutenone Ethylenedithioacetals and Their Ready Electrocyclic Ring Opening

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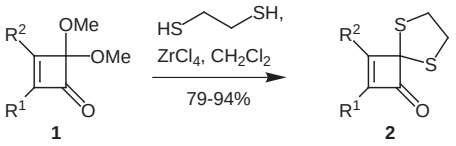
Abstract: Reported here is a general regiospecific synthesis of cyclobutenedione monoethylendithioacetals which readily undergo ring opening after addition of an organolithium reagent. The generated acyclic enols either tautomerize to the corresponding carbonyl compounds or can be trapped as silylenol ethers, which serve as electron rich dienes in Diels–Alder additions with tetracyanoethylene or maleic anhydride.

Key words: cyclobutenones, dithioacetals, transthioacetalization, electrocyclic ring opening, Diels–Alder reaction

Cyclobutenone derivatives have been efficiently used for the synthesis of highly substituted *p*-quinones and related annulated compounds over the last 15 years.[1–3] The thermal ring expansion is presumed to proceed via ring opening of the cyclobutenone to a vinyl ketene intermediate which then undergoes elecrocyclic ring closure to form the six-membered ring. Starting materials of particular note are cyclobutenedione monoketals. Such compounds having predictable regiochemistry are readily prepared and serve as useful precursors to asymmetrically substituted *p*-quinones.[4,5]

Our interest in organosulfur derivatives of cyclobutenones[6] led us to investigate the chemistry of cyclobutenone dithioacetals. In particular, we were interested in 1,3-dithiolane derivatives because of their potential utility for the generation of cyclobutenediones via a base induced [3 + 2] cycloreversion reaction.[7]

Reported herein is an efficient preparation of cyclobutenedione monodithioacetals involving the transthioacetalization of the corresponding dialkyl acetals. Firouzabadi and Iranpoor[8] have developed a method for a selective transthioacetalization of open chain acetals in the presence of cyclic acetals by the use of catalytic amounts of $ZrCl_4$. This methodology could be extended to the transthioacetalization of cyclobutenedione monoacetals. Thus, the readily available dimethyl acetals **1** were converted to the corresponding 1,3-dithiolanes **2** in the presence of 1,2-ethanedithiol (1.05 equivalents) and $ZrCl_4$ (15 mol%) in very good yields and with complete control of chemoselectivity (Scheme 1).



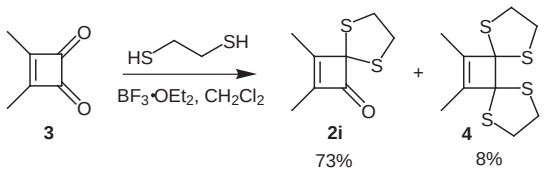
Scheme 1

Bisthioacetalization or other by-products were not observed for any of the examples listed above. It is noted that even a vinylic methoxy group was tolerated under these conditions (Table 1).

Table 1 Transthioacetalization with $ZrCl_4$

Product	R^1	R^2	Yield (%)	Mp (° C)
2a	Bu	Me	83	oil
2b	*t*-Bu	Me	85	89–90
2c	Ph	Me	88	104–105
2d	*t*-Bu	vinyl	79	oil
2e	Bu	OMe	86	oil
2f	*t*-Bu	OMe	84	100–101
2g	Ph	OMe	94	148–150
2h	C≡C-Bu	OMe	80	oil

The symmetrically substituted cyclobutenedione monoethylendithioacetal **2i** was prepared by a $BF_3{\cdot}OEt_2$ catalyzed thioacetalization of 3,4-dimethylcyclobutenedione (**3**) (Scheme 2). The degree of the accompanying bisthioacetalation was reduced by a very slow addition of a CH_2Cl_2 solution of ethanedithiol and $BF_3{\cdot}OEt_2$ to a solution of the dione in CH_2Cl_2 at 0 °C. However, under these conditions, we obtained 8% of the bisthioacetal **4** and 73% of the desired monoethylenedithioacetal **2i**.



Scheme 2

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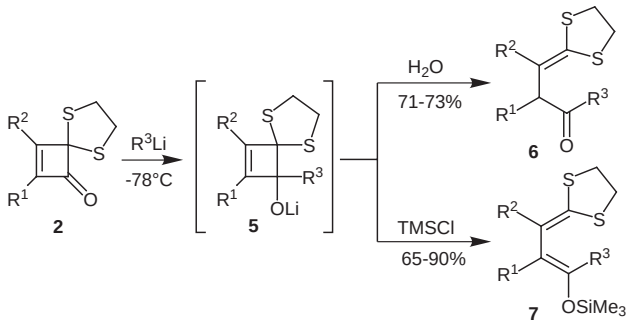
The cyclobutenedione monoethylendithioacetals **2** were treated with an organolithium reagent (R^3Li) in THF at −78 °C followed by an aqueous work up to furnish the ring opening products **6** (Scheme 3, Table 2). Thus, in contrast to the stable 4-hydroxy-cyclobutenone dialkyl acetals,[3,4] the dithiolane derivatives readily undergo ring opening and subsequent tautomerization of the primary enols to the ketones **6** under the reaction conditions.



Scheme 3

Quenching of the 1,2-adducts **5** with chlorotrimethylsilane led to the vinyl ketenethioacetals **7** (Scheme 3, Table 3). The 1-(hex-1-ynyl)-silylenol ether **7e** was obtained by reversing the addition and adding a THF solution of the dithiolane to a solution of the acetylide at 0 °C before quenching with chlorotrimethylsilane (method C).

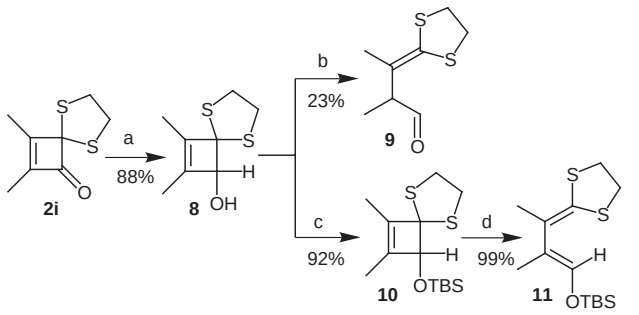
Table 2 1,2-Addition and Subsequent Electrocyclic Ring Opening to Ketones **6** and Silylenol Ethers **7**

Product	R^1	R^2	R^3	Method[a]	Yield (%)
6a	Me	Me	Ph	A	73
6b	Bu	OMe	Ph	A	71
6c	*t*-Bu	OMe	Ph	A	73
7a	*t*-Bu	OMe	Bu	B	81
7b	*t*-Bu	OMe	vinyl	B	65
7c	*t*-Bu	OMe	Ph	B	79
7d	Bu	OMe	Ph	B	77
7e	*t*-Bu	OMe	C≡C-Bu	C	90

[a] See experimental.

Dienes **7** warrant further study as multifunctional synthetic building blocks; it is noted that they are thermally stable and do not cyclize even in refluxing *p*-xylene solution. Even more flexibility can be expected for sterically less hindered derivatives with $R^3 = H$, e.g., diene **11** (Scheme 4).

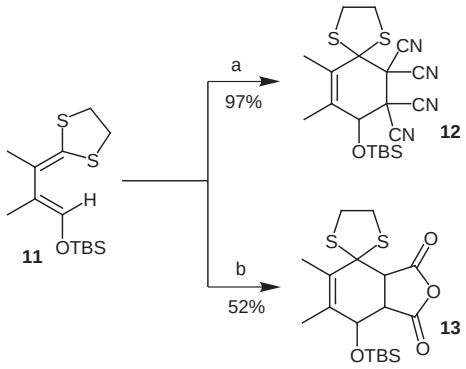
The synthesis of **11** started with the reduction of cyclobutenedione **2i** with DIBALH in THF at 0 °C to give alcohol **8** in 88% yield. Subsequent ring opening of the



Scheme 4 Reagents and conditions: a) DIBALH, THF, −5 °C, 10 min; b), d) $CHCl_3$, 50 °C, 4 h; c) TBSOTf, Et_3N, 4-DMAP, CH_2Cl_2, 0 °C, 1 h

secondary alcohol to the acyclic aldehyde **9** was completed in 4 hours at 50 °C. At room temperature, this ring opening is comparatively slow. Thus, isolation and subsequent silylation of the alcohol **8** by *tert*-butyldimethylsilyl triflate (TBSOTf), triethylamine and 4-DMAP in CH_2Cl_2 at 0 °C were possible and allowed clean conversion to the silylether **10** in 92% yield. The silylenol ether **11** was obtained in 99% yield by heating a solution of **10** in $CHCl_3$ at 50 °C for 4 hours.

To illustrate the utility of diene **11** in Diels–Alder cycloaddition reactions, it was treated with tetracyanoethylene (TCNE) in $CHCl_3$ at room temperature to give the desired adduct **12** within 30 minutes in 97% yield. The cycloaddition with maleic anhydride required the higher reaction temperature of refluxing toluene and led to the cycloadduct **13** in 52% yield.



Scheme 5 a) Reagents and conditions: TCNE, $CHCl_3$, r.t., 15 min; b) maleic anhydride, toluene, reflux, 24 h

The scope of these [4 + 2] cycloadditions is so far limited to reactive dienophiles.

NMR spectra were recorded on a Bruker ARX-400 or G.E. Omega 500 spectrometer using $CDCl_3$ or TMS as internal standard. IR spectra were recorded on a Perkin–Elmer 1600 FT-IR spectrometer. MS were recorded on a VG Analytic 7070E instrument. THF was dried by passing through two 4 × 36 in.[2] columns of anhyd neutral A-2 alumina. CH_2Cl_2 and toluene were distilled from CaH_2. All reactions were followed by TLC using Merck precoated plates of silica gel 60 F_{254}. Merck silica gel 60 (mesh 230–400) was used in

Table 3 Spectroscopic Data[a] for Cyclobutenedione Monoethylenedithioacetals **2** Prepared

Product	IR ν (cm^{-1})	^{1}H NMR ($CDCl_3$; 400 MHz) δ (ppm), *J* (Hz)	^{13}C NMR ($CDCl_3$; 100 MHz) δ (ppm)	MS *m/z*
2a	2958, 2929, 1765, 1631, 1425, 1377	3.36 (m, 4H), 2.17 (s, 3H), 2.09 (t, 2H, *J* = 7.5), 1.46 (m, 2H), 1.29 (m, 2H), 0.89 (t, 3H, *J* = 7.2)	189.5, 173.2, 150.3, 82.7, 40.6 (2C), 28.7, 23.5, 22.5, 13.7, 10.0	229 (MH^+), 228 (M^+), 200, 158, 143, 130
2b	2962, 1761, 1621, 1372, 1319	3.35 (m, 4H), 2.24 (s, 3H), 1.22 (s, 9H)	188.5, 169.3, 156.8, 82.7, 40.7 (2C), 32.7, 28.0 (3C), 10.9	229 (MH^+), 248 (M^+), 220, 191, 115
2c	1756, 1624, 1448, 1420, 1368, 1302	7.69 (m, 2H), 7.38 (m, 3H), 3.43 (m, 4H), 2.50 (s, 3H)	187.7, 170.5, 144.6, 129.4, 129.0, 128.8 (2C), 127.5 (2C), 83.9, 40.9 (2C), 11.7	249 (MH^+), 228 (M^+), 200, 136
2d	2964, 1758, 1621, 1476, 1363	6.82 (dd, 1H, *J* = 17.5, 11.1), 6.33 (d, 1H, *J* = 17.5), 5.82 (d, 1H, *J* = 11.1), 3.41 (m, 4H), 1.22 (s, 9H)	188.9, 160.8, 155.6, 128.3, 125.1, 79.9, 40.6 (2C), 33.5, 28.3 (3C)	241 (MH^+), 240 (M^+)
2e	2955, 2929, 1766, 1620, 1459, 1350	4.24 (s, 3H), 3.39 (m, 4H), 2.05 (t, 2H, *J* = 7.6), 1.47 (m, 2H), 1.28 (m, 2H), 0.87 (t, 3H, *J* = 7.3)	186.0, 176.6, 125.8, 78.6, 59.3, 40.6 (2C), 29.5, 22.5, 22.3, 13.7	245 (MH^+), 244 (M^+), 154, 136
2f	2965, 1760, 1614, 1479, 1353	4.29 (s, 3H), 3.49 (m, 2H), 3.35 (m, 2H), 1.14 (s, 9H)	185.0, 173.4, 125.8, 78.4, 58.8, 40.6 (2C), 31.5, 28.0 (3C)	245 (MH^+), 244 (M^+), 154, 136
2g	1768, 1633, 1601, 1456, 1361	7.72 (d, 2H, *J* = 7.7), 7.34 (t, 2H, *J* = 7.7), 7.27 (t, 1H, *J* = 7.7), 4.47 (s, 3H), 3.56 (m, 2H), 3.43 (m, 2H)	183.7, 173.7, 128.5 (2C), 128.3, 128.2, 127.0 (2C), 122.9, 79.5, 59.6, 40.8 (2C)	264 (M^+), 236, 221, 165, 121
2h	2956, 2222, 1771, 1614, 1456, 1360	4.37 (s, 3H), 3.38 (m, 4H), 2.31 (t, 2H, *J* = 7.1), 1.50 (m, 2H), 1.38 (m, 2H), 0.89 (t, 3H, *J* = 7.3)	183.4, 180.1, 106.1, 95.0, 79.6, 67.1, 61.1, 40.8 (2C), 30.2, 21.9, 19.1, 13.5	268 (M^+), 240, 225, 183, 170

[a] Exact masses with maximum deviation of ± 0.0008 were obtained.

flash chromatography. Solvents for chromatography were distilled prior to use.

Cyclobutenedione Monoethylendithioacetals 2; General Procedure

A solution of cyclobutenedione monodimethylacetal **1** (1 mmol) and 1,2-ethanedithiol (87 μL, 1.05 mmol) in dry CH_2Cl_2 (5 mL) was stirred at 0 °C when $ZrCl_4$ (35 mg, 0.15 mmol) was added. After 2 h at 0 °C, the reaction mixture was quenched with NaOH (10%, 5 mL). The aqueous layer was separated and extracted with CH_2Cl_2 (2 × 5 mL). The combined organic layers were washed with H_2O (10 mL), then with brine (10 mL), and dried. Removal of the solvent in vacuo followed by flash chromatography (hexanes–EtOAc) on silica gel provided the desired product.

Thioacetalization of 3,4-Dimethylcyclobutenedione 3

A solution of 1,2-ethanedithiol (0.42 mL, 5 mmol) and $BF_3{\cdot}OEt_2$ (0.65 mL, 5 mmol) was added dropwise over 3 h to a solution of 3,4-dimethylcyclobutenedione **3** (550 mg, 5 mmol) in dry CH_2Cl_2 (5 mL). After complete addition the resulting solution was stirred at r.t. for 1 h and then neutralized with sat. $NaHCO_3$ (30 mL). The aqueous layer was separated and extracted with CH_2Cl_2 (2 × 20 mL). The combined organic layers were washed with brine (30 mL) and dried. Removal of solvent in vacuo followed by flash chromatography (hexanes–EtOAc, 20:1) provided products **2i** and **4**.

2,3-Dimethyl-5,8-dithiaspiro[3.4]oct-2-en-1-one (**2i**)
Yield: 679 mg (73%) of a slightly yellow solid; mp 63 °C.

IR (film): ν = 2966, 2923, 2850, 1768, 1637, 1423, 1378, 1303, 1277, 1117, 957, 842, 785 cm^{-1}.

^{1}H NMR (500 MHz): δ = 3.35 (m, 4H), 2.16 (s, 3H), 1.66 (s, 3H).

^{13}C NMR (125 MHz): δ = 189.5, 174.0, 146.0, 82.6, 40.6, 9.7, 8.1

MS (CI): *m/z* (%) = 187 (M^+, 94), 186 (M^+, 77), 158 (100), 127 (65).

HRMS (CI): *m/z* calcd for $C_8H_{10}OS_2$: 186.0173. Found: 186.0167.

11,12-Dimethyl-1,4,7,10-tetrathiadispiro[4.0.4.2]dodec-11-ene (**4**)
Yield: 105 mg (8%) of a colorless solid; mp 110–111 °C.

IR (film): ν = 2964, 2924, 2908, 1684, 1440, 1425, 1371, 1276, 1242, 991, 852, 766, 724 cm^{-1}.

^{1}H NMR (500 MHz): δ = 3.24 (m, 8H), 1.68 (s, 6H).

^{13}C NMR (125 MHz): δ = 139.6 (2C), 84.5 (2C), 40.3 (4C), 8.8 (2C).

MS (CI): *m/z* (%) = 263 (MH^+, 42), 262 (M^+, 100), 234 (47), 206 (61), 142 (43), 130 (50).

HRMS (CI): *m/z* calcd for $C_{10}H_{14}S_4$: 261.9978. Found: 261.9981.

Ketenedithioacetals 6; General Procedure
Method A:

Phenyllithium (2.0 M, 0.75 mL, 1.5 mmol) was added dropwise to a solution of the 1,3-dithiolane **2** (1.0 mmol) in anhyd THF (5 mL) at –78 °C. The resulting solution was stirred at –78 °C for 30 min and then quenched with sat. $NaHCO_3$ (5 mL) and Et_2O (5 mL). The aqueous layer was separated and extracted with Et_2O (2 × 5 mL). The combined organic layers were washed with brine (10 mL) and dried. Removal of the solvent in vacuo followed by flash chromatography (hexanes–EtOAc) provided the product.

Silylenolethers 7; General Procedure
Method B:

An organolithium reagent (1.5 mmol) was added dropwise to a solution of the 1,3-dithiolane **2** (1.0 mmol) in anhyd THF (5 mL) at –78 °C. The resulting solution was stirred at –78 °C for 30 min, then chlorotrimethylsilane (0.25 mL, 2.0 mmol) was introduced. The re-

Table 4 Spectroscopic Data[a] for 3-[1,3]Ditholan-2-ylidene-1-phenyl-but-1-ones **6** and (3-[1,3]Ditholan-2-ylidene-but-1-enyloxy)-trimethylsilanes **7** Prepared

Product	IR ν (cm^{-1})	^{1}H NMR ($CDCl_3$; 500 MHz) δ (ppm), *J* (Hz)	^{13}C NMR ($CDCl_3$; 125 MHz) δ (ppm)	MS *m/z*
6a	2973, 2928, 1682, 1596, 1447, 1217	8.00 (m, 2H), 7.53 (m, 1H), 7.42 (m, 2H), 4.37 (q, 1H, *J* = 6.7), 3.45 (m, 2H), 3.40 (m, 2H), 1.60 (s, 3H), 1.28 (d, 3H, *J* = 6.7)	205.0, 136.6, 132.9, 131.8, 128.5 (2C), 128.3 (2C), 122.4, 50.3, 38.0, 37.9, 18.0, 13.8	265 (MH^+), 264 (M^+)
6b	2956, 2929, 1683, 1596, 1448, 1212	8.02 (m, 2H), 7.53 (m, 1H), 7.44 (m, 2H), 4.29 (t, 1H, *J* = 7.2), 3.55 (s, 3H), 3.37 (m, 4H), 2.06 (m, 1H), 1.86 (m, 1H), 1.36 (m, 4H), 0.91 (t, 3H, *J* = 7.0)	198.3, 142.9, 137.0, 132.9, 128.5 (2C), 128.2 (2C), 124.6, 59.4, 53.6, 38.1, 37.8, 29.8, 28.9, 22.8, 14.0	323 (MH^+), 322 (M^+), 217, 161
6c	2955, 2932, 1687, 1594, 1446, 1364	8.03 (m, 2H), 7.53 (m, 1H), 7.45 (m, 2H), 4.28 (s, 1H), 3.49 (s, 3H), 3.36 (m, 4H), 1.13 (s, 9H)	198.8, 143.4, 138.8, 132.7, 128.5 (2C), 128.0 (2C), 126.8, 61.0, 59.1, 38.1, 37.9, 37.0, 28.8 (3C)	323 (MH^+), 322 (M^+)
7a	2956, 2930, 1625, 1606, 1253, 1102	3.46 (s, 3H), 3.33 (m, 2H), 3.20 (m, 2H), 2.20 (m, 1H), 2.07 (m, 1H), 1.64 (m, 1H), 1.39 (m, 1H), 1.29 (m, 2H), 1.17 (s, 9H), 0.89 (t, 3H, *J* = 7.3), 0.27 (s, 9H)	154.9, 143.4, 119.8, 116.3, 55.4, 37.7, 37.4, 35.2, 34.5, 29.9, 29.8 (3C), 23.1, 14.0, 1.2 (3C)	375 (MH^+), 374 (M^+), 343, 289, 189
7b	2954, 2929, 1565, 1280, 1253, 1082	6.60 (dd, 1H, *J* = 17.3, 11.1), 5.43 (d, 1H, *J* = 17.3), 5.11 (d, 1H, *J* = 11.1), 3.44 (s, 3H), 3.33 (m, 2H), 3.23 (m, 2H), 1.22 (s, 9H), 0.30 (s, 9H)	151.1, 141.8, 134.8, 125.5, 118.3, 115.7, 55.3, 37.7, 37.6, 35.2, 29.7 (3C), 1.8 (3C)	345 (MH^+), 344 (M^+), 287, 240, 227
7c	2955, 2929, 1624, 1593, 1252, 1108	7.41 (m, 2H), 7.23 (m, 3H), 3.40 (s, 3H), 3.19 (m, 3H), 2.95 (m, 1H), 1.30 (s, 9H), −0.02 (s, 9H)	152.7, 142.7, 139.3, 128.5 (2C), 127.7, 127.1 (2C), 121.8, 116.2, 55.4, 37.5, 37.2, 35.0, 29.5 (3C), 0.9 (3C)	395 (MH^+), 394 (M^+)
7d	2956, 2928, 1598, 1252, 1140, 1108	7.42 (m, 2H), 7.23 (m, 3H), 3.60 (s, 3H), 3.12 (m, 2H), 2.90 (m, 2H), 2.29 (t, 2H, *J* = 7.8), 1.45 (m, 2H), 1.36 (m, 2H), 0.92 (t, 3H, *J* = 7.2), 0.05 (s, 9H)	151.3, 142.0, 138.8, 128.2 (2C), 127.6, 127.3 (2C), 117.8, 117.5, 56.1, 37.3, 37.1, 29.7, 29.2, 23.1, 14.0, 0.5 (3C)	394 (M^+), 323, 217, 191, 136
7e	2955, 2931, 2222, 1587, 1250, 1082	3.51 (s, 3H), 3.26 (m, 4H), 2.30 (t, 2H, *J* = 6.8), 1.47 (m, 4H), 1.18 (s, 9H), 0.90 (t, 3H, *J* = 7.2), 0.30 (s, 9H)	142.2, 135.8, 128.7, 120.6, 91.4, 78.5, 55.6, 37.7, 37.6, 35.3, 30.6, 29.1 (3C), 21.9, 18.9, 13.6, 0.7 (3C)	399 (MH^+), 398 (M^+), 383, 341, 202

[a] Exact masses with maximum deviation ± 0.0008 were obtained.

action mixture was stirred at r.t. for 1 h and then quenched with sat. $NaHCO_3$ (5 mL) and Et_2O (5 mL). The aqueous layer was separated and extracted with Et_2O (2 × 5 mL). The combined organic layers were washed with brine (10 mL) and dried.

Silylenolether 7e
Method C:
To a solution of 1-hexyne (0.18 mL, 1.6 mmol) in dry THF (5 mL) at −78 °C, *n*-BuLi (0.75 mL, 1.5 mmol, 2.0 M) was introduced dropwise via syringe. The resulting mixture was stirred at −78 °C for 30 min, then allowed to warm up to 0 °C before a solution of the dithiolane **2f** in THF (5 mL) was transferred under a positive pressure of N_2, via cannula, to the reaction mixture. After stirring at 0 °C for 30 min, chlorotrimethylsilane (0.25 mL, 2 mmol) was added. The solution was stirred at r.t. for 1 h, then worked up and purified as described in method B.

2,3-Dimethyl-5,8-dithiaspiro[3.4]oct-2-ene-1-ol (8)
A solution of 2,3-dimethyl-5,8-dithia-spiro[3.4]oct-2-en-1-one **2i** (186 mg, 1 mmol) in anhyd THF (2 mL) at −5 °C was treated with diisobutylaluminum hydride (1 M in hexanes, 1.1 mL, 1.1 mmol). The reaction was completed after 10 min, and sat. sodium potassium tartrate (10 mL) and Et_2O (10 mL) were added. The resulting mixture was vigorously stirred for 30 min. The aqueous phase was separated and extracted with Et_2O (3 × 5 mL). The combined organic layers were washed with brine (10 mL) and dried. Removal of the solvent in vacuo followed by flash chromatography (hexanes–EtOAc, 8:1) provided the product as a colorless oil (165 mg, 88% yield).

IR (film): ν = 3419, 2952, 2916, 2844, 1429, 1375, 1274, 1207, 1148, 1124, 1058, 980, 825, 735 cm^{-1}.

^{1}H NMR (500 MHz): δ = 4.32 (d, 1H, *J* = 9.7 Hz), 3.21 (m, 4H), 2.66 (d, 1H, *J* = 9.7 Hz), 1.63 (s, 3H), 1.60 (s, 3H).

^{13}C NMR (125 MHz): δ = 143.2, 137.1, 82.0, 76.9, 39.6, 38.5, 10.5, 8.5.

MS (EI): *m/z* (%) = 188 (M^+, 35), 159 (100), 99 (18), 85 (72), 55 (19).

HRMS (EI): *m/z* calcd. for $C_8H_{12}OS_2$: 188.0329. Found: 188.0322.

3-(1,3-Dithiolane-2-ylidene)-2-methylbutanal (9)
A solution of alcohol **8** (188 mg, 1mmol) in dry $CHCl_3$ (5 mL) was stirred at 50 °C for 4 h. After cooling the solution to r.t., the solvent was removed in vacuo. The crude product was purified by flash

chromatography (hexanes−EtOAc, 15:1) to give a colorless oil (43 mg, 23% yield). The product has to be stored in a refrigerator.

IR (film): ν = 2973, 2931, 2807, 2714, 1720, 1597, 1421, 1384, 1279, 1149, 1063 cm^{-1}.

^1H NMR (500 MHz): δ = 9.53 (s, 1H), 3.52 (q, 1H, *J* = 6.8 Hz), 3.40 (m, 4H), 1.71 (s, 3H), 1.18 (q, 3H, *J* = 6.8 Hz).

^{13}C NMR (125 MHz): δ = 200.1, 135.0, 117.3, 55.4, 37.9 (2C), 18.6, 10.8.

MS (CI): *m/z* (%) = 189 [$(M+H)^+$, 91], 188 (M^+, 39), 159 (100), 132 (34), 113 (39).

HRMS (CI): *m/z* calcd. for $C_8H_{12}OS_2$: 188.0329. Found: 188.0330.

tert-Butyl-(2,3-dimethyl-5,8-dithia-spiro[3.4]oct-2-en-1-yloxy)-dimethylsilane (10)

A solution of alcohol **8** (188 mg, 1 mmol) in dry CH_2Cl_2 (4 mL) was stirred at 0 °C. Et_3N (0.28 mL, 2mmol), 4-DMAP (12 mg, 0.1 mmol) and TBSOTf (0.25 mL, 1.1 mmol) were added and the solution was stirred for 1 h at 0 °C. The resulting reaction mixture was quenched with sat. $NaHCO_3$ (10 mL) and CH_2Cl_2 (10 mL). The aqueous phase was separated and extracted with CH_2Cl_2 (2 × 5 mL). The combined organic layers were washed with brine (10 mL) and dried. Removal of solvent in vacuo followed by flash chromatography (hexanes−EtOAc, 50:1) provided the product as a colorless oil (278 mg, 92% yield).

IR (film): ν = 2953, 2926, 2855, 1648, 1471, 1433, 1371, 1291, 1251, 1219, 1166, 1130, 1086, 1005, 937, 893, 836, 778 cm^{-1}.

^1H NMR (500 MHz): δ = 4.63 (s, 1H), 3.27 (m, 1H), 3.17 (m, 3H), 1.64 (s, 3H), 1.59 (s, 3H), 0.94 (s, 9H), 0.16 (s, 3H), 0.14 (s, 3H).

^{13}C NMR (125 MHz): δ = 141.5, 140.4, 82.4, 76.5, 40.0, 38.9, 25.9 (3C), 18.6, 10.5, 8.4, −4.3, −4.8.

tert-Butyl-(3-[1,3]dithiolane-2-ylidene-2-methyl-but-1-enyloxy)-dimethylsilane (11)

A solution of **10** (278 mg, 0.92 mmol) in dry $CHCl_3$ (5 mL) was stirred at 50 °C for 4 h. After cooling the solution to r.t., the solvent was removed in vacuo. The crude product was purified by flash chromatography (hexanes−EtOAc, 15:1) to give a colorless oil (275 mg, 99% yield).

IR (film): ν = 2955, 2928, 2857, 1649, 1472, 1279, 1255, 1172, 1093, 839, 810, 781 cm^{-1}.

^1H NMR (500 MHz): δ = 6.26 (q, 1H, *J* = 1.4 Hz), 3.37 (m, 2H), 3.24 (m, 2H), 1.87 (s, 3H), 1.70 (d, 3H, *J* = 1.4 Hz), 0.94 (s, 9H), 0.16 (s, 6H).

^{13}C NMR (125 MHz): δ = 138.6, 129.5, 123.5, 121.5, 37.6, 37.4, 25.7 (3C), 21.5, 18.2, 11.6, −5.1 (p, 2C).

MS (CI): *m/z* (%) = 303 (MH^+, 34), 302 (M^+, 12), 275 (92), 261 (16), 243 (28), 203 (36), 187 (100), 175 (87), 147 (80), 133 (62), 115 (26).

HRMS (CI): *m/z* calcd. for $C_{14}H_{26}OS_2Si$: 302.1194. Found: 302.1185.

8-(_tert_-Butyl-dimethyl-silyloxy)-1,4-dithiaspiro[4.5]dec-9-ene-6,6,7,7-tetracarbonitrile (12)

A solution of silylenol ether **11** (121 mg, 0.4 mmol) in dry $CHCl_3$ (2 mL) was treated with tetracyanoethylene (56 mg, 0.44 mmol) at r.t. The reaction was completed after 15 min. The solvent was removed in vacuo and the crude product was purified by flash chromatography (hexanes−EtOAc, 4:1) to give a colorless oil (167 mg, 97% yield).

IR (film): ν = 2958, 2932, 2860, 2255, 1472, 1263, 1164, 1105, 909, 832, 783, 734 cm^{-1}.

^1H NMR (500 MHz): δ = 4.84 (s, 1H), 3.70 (m, 2H), 3.61 (m, 1H), 3.48 (m, 1H), 2.00 (s, 3H), 1.81 (s, 3H), 1.00 (s, 9H), 0.37 (s, 3H), 0.26 (s, 3H).

^{13}C NMR (125 MHz): δ = 130.6, 129.5, 111.9, 110.6, 110.4, 108.3, 72.5, 72.5, 52.8, 46.5, 43.4, 42.2, 25.8 (3C), 18.4, 17.7, 17.6, −3.6, −4.2.

MS (CI): *m/z* (%) = 431 (MH^+, 7), 373 (77), 302 (97%), 274 (55), 245 (43), 234 (45), 217 (100), 184 (41), 171 (29), 143 (63), 127 (34).

HRMS (CI): *m/z* calcd. for $C_{20}H_{27}N_4OS_2Si$ ((MH^+)): 431.1317. Found: 431.1315.

Preparation of the Cycloadduct 13 with Maleic Anhydride

A solution of silylenol ether **11** (121 mg, 0.4 mmol) and maleic anhydride (43 mg, 0.44 mmol) in dry toluene (2 mL) was refluxed for 24 h. The solvent was removed in vacuo and the crude product was purified by flash chromatography (hexanes−EtOAc, 10:1) to give a colorless oil (83 mg, 52% yield).

IR (film): ν = 2952, 2928, 2857, 1864, 1779, 1472, 1282, 1251, 1231, 1090, 1054, 999, 956, 921, 894, 839, 776, 733 cm^{-1}.

^1H NMR (500 MHz, C_6D_6): δ = 4.20 (d, 1H, *J* = 4.8 Hz), 3.30 (m, 2H), 3.05 (d, 1H, *J* = 11.0 Hz), 2.87 (m, 1H), 2.59 (m, 1H), 2.45 (dd, 1H, *J* = 11.0, 4.8 Hz), 1.79 (s, 3H), 1.48 (s, 3H), 0.99 (s, 9H), 0.16 (s, 3H), 0.03 (s, 3H).

^{13}C NMR (125 MHz, C_6D_6): δ = 169.4 (2C), 136.5, 130.4, 68.6, 65.8, 53.2, 48.5, 42.5, 42.4, 26.2 (3C), 19.8, 18.4, 15.4, −4.1, −5.1.

MS (CI): *m/z* (%) = 401 (MH^+, 77), 357 (24), 343 (67), 299 (100), 269 (35), 239 (60), 234 (48), 225 (37), 208 (28), 165 (53), 135 (23).

HRMS (CI): *m/z* calcd. for $C_{18}H_{28}O_4S_2Si$: 400.1198. Found: 400.1196.

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