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Direct Synthesis of 2-Norbornanone Dithioacetals from 2-Cyclopentenone Dithioacetals and Dienophiles. Synthetic Application of Thermal Interconversion between Cyclic Dithioacetals and the Ring-Opened Vinyl Sulfide Forms

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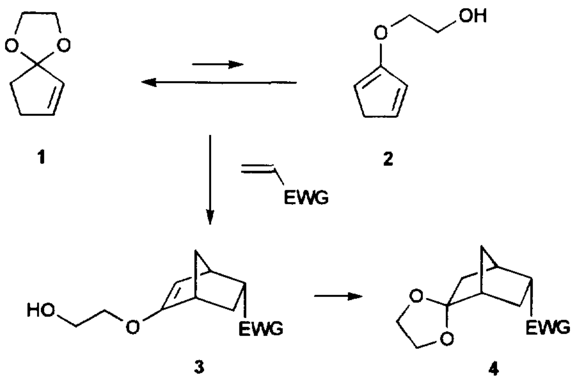
Abstract: Readily accessible 1,3-dithiane and 1,3-dithiolane derivatives of 3-substituted 2-cyclopentenones react with a variety of dienophiles via the in situ generated 1,3-cyclopentadien-2-yl sulfide tautomers, in acetonitrile at 120 °C to give 2-norbornanone dithioacetals in 79-93% yields. This transformation represents, to our knowledge, the first synthetic application of thermal interconversion between cyclic dithioacetals and the ring-opened vinyl sulfide forms.

INTRODUCTION

We have recently demonstrated that 2-(2-hydroxyethoxy)-1,3-cyclopentadiene (**2**) which is generated reversibly from 2-cyclopentenone acetal (**1**) under mild heating conditions (50-100 °C) can be intercepted with a variety of dienophiles to give 2-norbornanone acetals **4** in good yields (Scheme 1).[1,2] This reaction is of considerable synthetic value since the transformation can be conducted under essentially neutral conditions and the 2-norbornanones are directly produced in a protected form. There is a small drawback in this method, however, in that 2-cyclopentenone acetals are often difficult to prepare from the corresponding carbonyl compounds.[3] In this context, we were interested in extending the reaction to dithioacetals since they are readily accessible at least when the β-position of enone is substituted, that is, when the conjugated addition of thiol to the enone moiety is hindered.[4] Moreover, the dithioacetal group is amenable to further synthetic manipulation. We therefore studied the extention of the reaction to dithioacetals and found that the transfomation similar to those of the oxygen analogues took place successfully albeit at a somewhat higher temperature (120 °C).[5] We

Scheme 1

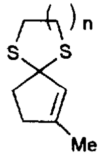


found, moreover, that the reaction was significantly facilitated under the influence of a catalytic amount (5-20 mol%) of acidic additive such as lanthanum (III) triflate or trifluoroacetic acid, and proceeded even at 60 °C though the product yield was less satisfactory compared to that of the thermal reaction at 120 °C. In this paper we wish to report the details of these reactions using dithioacetals, which provide a simple and efficient access to functionalized 2-norbornanone dithioacetals, together with the results of mechanistic investigation. The chemistry of dithioacetal functionality has been well studied,[6] but there has been no report, to our knowledge, on the reversible thermal interconversion between cyclic dithioacetals and the ring-opened vinyl sulfide forms. The present study, however, clearly demonstrates that cyclic dithioacetals also undergo reversible isomerization to the ring-opened vinyl sulfide forms, as in the case of oxygen analogues, and that this thermal process can be synthetically exploited.

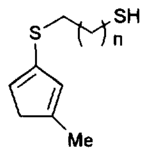
RESULTS AND DISCUSSION

Reaction of 3-Methyl-2-cyclopentenone Dithioacetal (5) with Dienophiles.

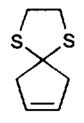
Dithioacetal **5** is readily obtained by the direct dithioacetalization of 3-methyl-2-cyclopentenone with ethanedithiol while the corresponding oxygen analogue is rather laborious to prepare.[7] Thus we chose it as a model substrate and investigated its reaction with typical dienophiles **10-14**. The reaction of **5** with the dienophiles smoothly proceeded in acetonitrile at 120 °C to afford the corresponding adducts in good yields. Acetonitrile was the solvent of choice and the use of other less polar solvents such as benzene, toluene, or chloroform resulted in slower reaction rates. The structural elucidation of the adducts was primarily based on their spectroscopic properties. The stereochemistry of the adducts was assigned by examining the characteristic coupling pattern in the bicyclo[2.2.1]heptane system in their ^{1}H NMR spectra. It is well documented that vicinal coupling to a bridgehead proton in this system is significantly smaller for the endo methylene protons (0-2 Hz) than for the exo protons (3-4 Hz) and that the long-range coupling of the endo proton to the anti methylene-bridge proton is generally in the range of 3-4 Hz whereas that of the exo proton to the methylene-bridge protons is negligibly small.[8] It should be noted that the reaction was regioselective with respect to **5** and not complicated by the formation of isomeric adducts resulting either from 1,4-elimination in **5** or from 1,5-hydrogen migration in the probable intermediate **7**.[9] The addition of dienophiles to **5** in the [2 + 4] manner was also *endo*-selective in consistent with the intermediacy of **7**.[10] The results are summarized in Table 1.



5: n = 1
6: n = 2



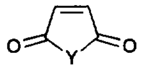
7: n = 1
8: n = 2



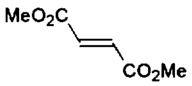
9

$MeO_2CC\equiv CCO_2Me$

10



11: Y = O
12: Y = NPh



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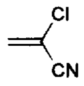

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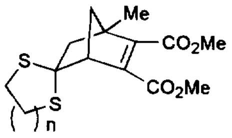
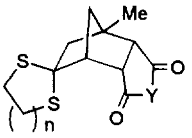
Table 1. Reactions of 2-cyclopentenone Dithioacetals with dienophiles[a]

Dithioacetal	Dienophile	Time(h)	Product	Yield(%)[b]	**a**:**b**[c]
5	**10**	9	**15**	75	
5	**11**	5	**17**	93	62:38
5	**12**	20	**18**	81	87:13
5	**13**	12	**21**	92	81:19
5	**14**	24	**23**	82	d
6	**10**	4	**16**	79	
6	**11**	3	**19**	87	67:33
6	**12**	16	**20**	75	85:15
6	**13**	6	**22**	87	84:16
6	**14**	20	**24**	83	e
26	**10**	96	**30**	75	
27	**10**	18	**31**	68	
27	**14**	22	**36**	72	f
32	**10**	18	**34**	63	

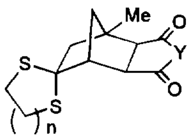
[a] Reactions were carried out in acetonitrile (3 ml) using dithiacetal (1 mmol) and 1.7 equiv of dienophile at 120 °C (in a sealed tube). [b] Isolated yield based on amount of the dithioacetal used. Conversion of the dithiacetal was almost complete. [c] Determined by ^{1}H NMR and/or GC. [d] A mixture of two stereoisomers in a ratio of 79:21. [e] A mixture of two stereoisomers in a ratio of 66:34. [f] A ratio of stereoisomers was not determined.



15: n = 1
16: n = 2

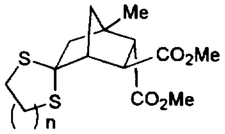


a

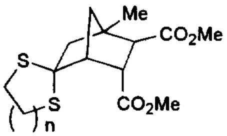


b

17: n = 1, Y = O
18: n = 1, Y = NPh
19: n = 2, Y = O
20: n = 2, Y = NPh

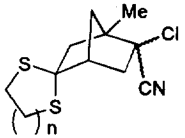


a



b

21: n = 1
22: n = 2



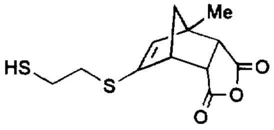
23: n = 1
24: n = 2

Mechanistic Studies.

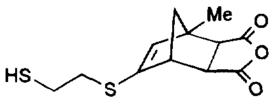
The formation of the adducts is best accounted for in terms of the [2 + 4] cycloaddition of dienophiles to **7** generated in situ from **5**, followed by recyclization in the initial adduct to the dithioacetal products as in the reaction of **1** (Scheme 1). The observed regio- and stereoselectivities of the cycloaddition are also consistent with the intermediacy of **7**. The possible participation of radical species in the reaction may be eliminated, since the efficiency of the reaction was not affected by the addition of radical inhibitor, hydroquinone.

Although attempts to observe **7** directly by ^1H NMR spectroscopy were unsuccessful presumably owing to its low equilibrium concentration, the initial adduct before the recyclization was readily detectable. Thus, when the reaction of **5** with **11** in CD_3CN was carried out inside the probe of an NMR spectrometer preheated at 120 °C and monitored intermittently, resonance lines consistent with the structure **25a** initially grew[11] but were subsequently overwhelmed by those due to **17a**. The resonances assigned to **25a** remained observable even after the sample was stood overnight at room temperature though their intensities had decreased considerably. Interestingly, exo intermediate **25b** was not detected in the NMR monitoring in spite of the formation of **17b** in a significant product ratio. This observation may suggest that the ring closure in **25a** giving **17a** is much slower than in **25b** owing to the repulsive interaction between the pendant thiol and acid anhydride moieties in the cyclization of **25a**.

To our surprise, β,γ-unsaturated **9** lacked reactivity toward the addition of dienophile via its ring-opened form, though the hydrogen to be abstracted was allylic, and was recovered intact after 2 days at 120 °C in the presence of **10** in CD_3CN. Although a possibility that **9** was in equilibrium with 1-(2-mercaptoethylthio)-1,3-cyclopentadiene under the above conditions but the latter was not intercepted efficiently by **10** owing to its insufficient reactivity may not be rigorously ruled out, the above observation strongly suggests that the activation of the spiro carbon-sulfur bond by the adjacent unsaturated bond is crucial for the smooth ring-opening in **5** to give **7**. Consistently, neither the regeneration of **25a** from **17a** nor the cycloreversion of **17a** to give **5** and **11** was detected even at 180 °C in CD_3CN.



25a

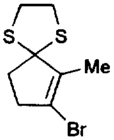


25b

Reactions of Other Dithioacetals.

To explore the generality and scope of the present method, the reactions of other dithioacetals were also examined. The reaction of 1,3-dithiane derivative **6** with dienophiles **10-14** also proceeded smoothly and, rather unexpectedly, more rapidly than that of **5** in acetonitrile at 120 °C to afford the corresponding adducts in good yields (Table 1). The competitive reaction of **6** with **5** using 10 equiv of dienophile, either **10** or **11**, indeed revealed that **6** was twice more reactive than **5** in acetonitrile at 120 °C.

The present method is applicable for the stereoselective construction of rather complex ring systems as exemplified by the following reactions. Thus, the reactions of **26** and **27**, readily obtainable from the corresponding enones, with **10** in acetonitrile at 120 °C led to the formation of products to which the structures **30** and **31** were assigned, respectively. Similarly, the reaction of **32** with **10** afforded **34** in 63% yield. It should be noted that those adducts were formed in regio- and stereoselective manner. Their stereochemistry could be assigned on the basis of the absence (H^1-H^2 in **30** and **31**) and the presence (H^4-H^5 in **34**, J = 3 Hz) of appreciable long-range coupling in the norbornene system. The exclusive formation of the 6-endo products **30** and **31** is rationalized in terms of the preferential protonation from the *exo*-faces of the vinyl sulfide double bonds in **28** and **29**, respectively, upon recyclization. The selective formation of **34**, on the other hand, is consistent with the π-facial selectivity expected for **33** to which the dienophile **10** would approach from the sterically less hindered face syn to the angular hydrogen H^3.



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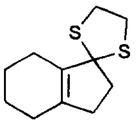

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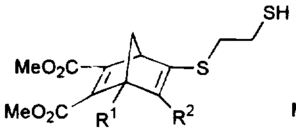
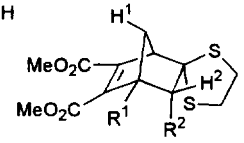
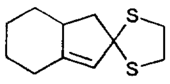


28: R^1 = Br, R^2 = Me
29: R^1 R^2 = $(CH_2)_4$



30: R^1 = Br, R^2 = Me
31: R^1, R^2 = $(CH_2)_4$



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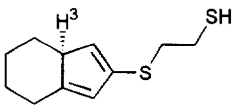

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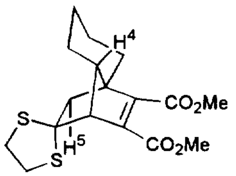

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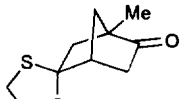
Preparation of Singly Protected 2,5-Norbornanedione Derivatives.

A salient feature of the present reaction is direct production of the adducts in the dithioacetalized form, which provides a unique and simple method for the preparation of selectively protected 2-norbornanone derivatives. For example, by employing a ketene equivalent as dienophile,[12] singly protected 2,5-norbornanedione derivatives were readily prepared with complete selectivity. Thus, treatment of a mixture of the chloroacrylonitrile adducts **23** with KOH-Na_2S in refluxing 95% ethanol[13] afforded singly and selectively protected 2,5-norbornanedione derivative **35** in 75% yield. Similarly, the addition of 2-chloroacrylonitrile **14** to **27** followed by alkaline hydrolysis of the resultant adducts **36** provided **37** in two-steps in a yield of 52%.



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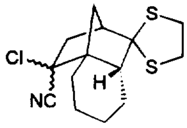

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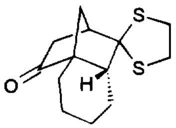


37

Acid Promoted Reaction.

Since equilibration between enone dithioacetal and the corresponding vinyl sulfide is anticipated to be subject to catalysis by Lewis and/or Brønsted acids,[14] acidic additives are expected to exert a facilitating effect on the reaction of **5** with dienophiles. Activation of dienophile by Lewis acids is also expected. Therefore, the reaction of **5** with **10** was examined in the presence of a catalytic amount (10 mol%) of an acidic additive in acetonitrile. Among several acids screened, lanthanum (III) triflate was found to be most effective (Table 2). Under the influence of 10 mol% of lanthanum (III) triflate, the reaction was complete after 24 h at 60 °C and the adduct **15** was produced in 41% yield. No reaction occurred at this temperature without the catalyst. The

Table 2. Reaction of **5** with **10** in the Presence of 10 mol% of Additives[a]

Additive	Time (h)	Conversion of **5** (%)[b]	Yield of **15** (%)[c]
none	48	<1	<1
$La(OTf)_3$	24	100	41
$Yb(OTf)_3$	24	100	18
$Sc(OTf)_3$	24	100	3
$Zn(OTf)_2$	12	89	31(35)
$ZnCl_2{\cdot}OEt_2$	24	85	33(39)
$Cu(OTf)_2$	12	93	8(9)
$Cu(OTf)_2$[d]	12	75	22(29)
CF_3CO_2H	24	63	26(41)

[a] Reactions were carried out in acetonitrile (3 ml) using **5** (1 mmol) and 1.7 equiv of **10** at 60 °C. [b] Determined by GC. [c] GC yield. GC yield based on the conversion of **5** in parenthesis. [d] Lithium carbonate (50 mol%) was added.

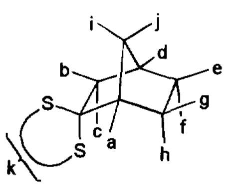
reaction was also promoted by a Brønsted acid and 63% of **5** was consumed within 24 h at 60 °C in the presence of 10 mol% of trifluoroacetic acid to afford **15** in 26% yield (41% on the basis of an amount of **5** consumed). The adduct **15** was also produced at 60 °C by using other catalysts such as zinc (II) triflate and chloride, and copper (II) triflate, though in a poorer yield and/or in lower efficiency.

CONCLUSIONS

Cyclic dithioacetals of 2-cyclopentenones undergo [4 + 2] cycloadditions with a variety of dienophiles via the ring-opened dienyl sulfide forms directly to give 2-norbornanone dithioacetals in good yields. The reaction is promoted in the presence of acidic additives including lanthanum (III) triflate and trifluoroacetic acid. The dithioacetals are readily accessible via dithioacetalization of the corresponding enones. Moreover, dithioacetal functionality will allow further elaboration of the products through a variety of functional group transformations. Given the simplicity of the procedure coupled with the high regio- and stereoselectivity of the reaction, we believe that the present one-pot reaction would provide one of the most straightforward and practical methods for regio- and stereoselective synthesis of functionalized 2-norbornanone derivatives.

EXPERIMENTAL SECTION

General. ^1H and ^{13}C NMR spectra were measured on a JEOL FX-500 spectrometer in $CDCl_3$ unless otherwise indicated. Mass spectra were recorded at an ionizing voltage of 70 eV. Elementary analysis was performed by the Center for Instrumental Analysis of Hokkaido University. In the ^1H NMR spectral data of products, protons are designated with alphabetical suffix in the order shown in the formula **38**. The dithioacetals **5**, **6**,[7] and **26**[15] were prepared following known procedures. The dienophiles used in this study



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were purchased from commercial sources and purified by recrystallization or distillation prior to use.

Preparation of 9. To a solution of 3-cyclopentenone[16] (1.0 g, 12 mmol) and 1,2-ethanedithiol (1.9 g, 20 mmol) in 50 mL of CH_2Cl_2 was added $BF_3 \cdot OEt_2$ (425 mg, 3 mmol) at 0 °C over 5 min. The mixture was stirred at room temperature for 2 h, washed successively with 1 N aqueous NaOH and brine, and dried with Na_2SO_4. After removal of the solvent, the residue was distilled to give 1.6 g of **9** (84%): bp 65-72 °C (bath temperature) / 1 mmHg; ^{1}H NMR (90 MHz) δ 3.04 (s, 4H), 3.36 (s, 4H), 5.79 (s, 2H); IR (neat) 3065, 2925, 2835, 1610, 1426, 1340, 1260, 940, 705 cm^{-1}; UV λ_{max} 236 nm (ε 380); MS *m/z* 158 (M^+, 90), 130 (67), 97 (80), 66 (33), 54 (100), 45 (32), 40 (30); HRMS calcd for $C_7H_{10}S_2$ 158.0224, found 158.0222.

Preparation of 27. A mixture of bicyclo[4.3.0]non-1(6)-en-7-one[17] (2.7 g, 20 mmol), 1,2-ethanedithiol (2.4 g, 25 mmol), and $TsOH \cdot H_2O$ (0.19 g, 1 mmol) in 50 mL of benzene was heated to boiling, and the condensate was returned to the mixture through a column packed with 4-Å molecular sieves (pellets) to remove the water formed. After 4 h, GLC (APL 3%, 1 m, 100-220 °C) showed the complete consumption of the ketone, and the mixture was cooled, washed successively with 1 N aqueous NaOH and brine, and dried with Na_2SO_4. After removal of the solvent, the residue was distilled to give 3.05 g of **27** as colorless oil (72%): bp 130-135 °C / 0.5 mmHg; ^{1}H NMR (90 MHz) δ 1.55-1.80 (m, 4 H), 1.85-2.22 (m, 6 H), 2.25-2.65 (m, 2 H), 3.32 (s, 4 H); ^{13}C NMR (22.5 MHz) δ 21.66, 22.64, 22.90, 26.48, 34.02, 40.73 (2 C), 45.55, 77.48, 136.34, 138.09; IR (neat) 2925, 2840, 1670, 1445, 1275 cm^{-1}; MS *m/z* 212 (M^+, 23), 184 (39), 152 (100), 119 (54), 117 (36), 91 (56); HRMS calcd for $C_{11}H_{16}S_2$ 212.0694, found 212.0683.

Preparation of 32. A mixture of bicyclo[4.3.0]non-1(9)-en-8-one[18] (2.03 g, 15 mmol), 1,2-ethanedithiol (1.41 g, 15 mmol), and $TsOH \cdot H_2O$ (0.15 g, 0.8 mmol) in 50 mL of benzene was heated to boiling, and the condensate was returned to the mixture through a column packed with 4-Å molecular sieves (pellets) to remove the water formed. After 4 h, GLC (APL 3%, 1 m, 100-220 °C) showed the complete consumption of the ketone, and the mixture was cooled, washed successively with 1 N aqueous NaOH and brine, and dried with Na_2SO_4. After removal of the solvent, the residue was distilled to give 2.31 g of **32** as colorless solid (73%): bp 90-95 °C / 0.05 mmHg; mp 57.5-58.5 °C; ^{1}H NMR (400 MHz) δ 1.03 (m, 1 H), 1.16-1.38 (m, 2 H), 1.71-1.83 (m, 2 H), 1.89-2.01 (m, 2 H), 2.13 (dd, *J* = 13.6 an 6.3 Hz, 1 H), 2.44 (br. d, 14 Hz, 1H), 2.56 (m, 1 H), 2.81 (dd, *J* = 13.6 and 7.3 Hz, 1 H), 3.23-3.39 (m, 4 H), 5.37 (br. s, 1 H); ^{13}C NMR (100 MHz) δ 25.53, 26.65, 28.42, 34.66, 40.22, 40.84, 44.79, 52.49, 73.01, 126.02, 147.40; IR (KBr) 2930, 2850, 1645, 1445, 1430, 1275, 975, 850, 845 cm^{-1}; MS *m/z* 212 (M^+, 70), 152 (100), 151 (56), 124 (42), 119 (54), 91 (83); HRMS calcd for $C_{11}H_{16}S_2$ 212.0694, found 212.0674.

Reaction of 5 with Dimethyl Acetylenedicarboxylate (10). A solution of **5** (172 mg, 1 mmol) and **10** (242 mg, 1.7 mmol) in 1.5 mL of CH_3CN was heated at 120 °C for 9 h in a glass ampoule. After removal of the solvent in vacuo, the residue was chromatographed on silica gel (1:1 ether-hexane) to afford 236 mg (75%) of **15**: ^{1}H NMR δ 1.32 (s, CH_3), 1.73 (dd, *J* = 9.8, 1.5 Hz, H_i), 1.86 (ddd, *J* = 9.8, 2.9, 2.0 Hz, H_j), 2.25 (dd, *J* = 13.2, 2.9 Hz, H_c), 2.33 (d, *J* = 13.2 Hz, H_b), 3.26-3.50 (m, 4 H_k). 3.30 (br. s, H_a), 3.75 (s, 3 H), 3.84 (s, 3 H); IR (neat) 1720, 1630, 1435, 1270, 1055 cm^{-1}; MS *m/z* 314 (M^+, 9), 118 (100); HRMS calcd for $C_{14}H_{18}O_4S_2$ 314.0647, found 314.0648. Anal. Calcd for $C_{14}H_{18}O_4S_2$: C, 53.47; H, 5.78; S, 20.40. Found: C, 53.03; H, 5.44; S, 20.48.

Reaction of 5 with Maleic Anhydride (11). A solution of **5** (172 mg, 1 mmol) and **11** (167 mg, 1.7 mmol) in 1.5 mL of CH_3CN was heated at 120 °C for 6 h in a glass ampoule. After removal of the solvent in vacuo, the residue was chromatographed on silica gel (1:1 ether-hexane) to afford 97 mg of **17b** (36%) and

155 mg of **17a** (57%). **17a**: mp 120.5-121.5 °C; ^{1}H NMR δ 1.42 (s, CH_3), 1.74 (ddd, *J* = 10.7, 2.9, 1.5 Hz, H_j), 2.06 (dd, *J* = 10.7, 1.5 Hz, Hi), 2.30 (dd, *J* = 15.6, 2.9 Hz, H_c), 2.39 (dd, *J* = 15.6, 2.5 Hz, H_b), 3.03 (dt, *J* = 5.4, 1.5 Hz, H_a), 3.18 (dd, *J* = 10.7, 2.5 Hz, H_e), 3.43 (dd, *J* = 10.7, 5.4 H_g), 3.21-3.46 (m, 4 H_k); IR (KBr) 1775, 1225, 1090, 905 cm^{-1}; MS *m/z* 270 (M^+, 64), 242 (100), 214 (33), 144 (46), 118 (49), 80 (40). Anal. $C_{12}H_{14}O_3S_2$: C, 53.30; H, 5.23; S, 23.72. Found: C, 53.23; H,5.21; S, 23.64. **17b**: mp 151-152.5 °C; ^{1}H NMR δ 1.34 (s, CH_3), 1.43 (ddd, *J* = 12.2, 2.9, 1.5 Hz, H_j), 1.82 (dq, *J* = 12.2, 1.5 Hz, Hi), 2.02 (dd, *J* = 14.7, 2.9 Hz, H_c), 2.25 (d, *J* = 14.7 Hz, H_b), 2.71 (dd, *J* = 7.8, 1.5 Hz, H_f), 2.77 (dd, *J* = 1.5, 1 Hz, H_a), 3.20-3.45 (m, 4 H_k), 3.85 (ddd, *J* = 7.8, 1.5, 1 H_h); IR (KBr) 1775, 1245, 1100, 920 cm^{-1}; MS *m/z* 270 (M^+, 37), 242 (100), 144 (20). Anal. Calcd for $C_{12}H_{14}O_3S_2$: C, 53.30; H, 5.23; S, 23.72. Found: C, 53.38; H, 5.42; S, 23.64.

Reaction of 5 with *N*-Phenylmaleimide (12). A solution of **5** (172 mg, 1 mmol) and **12** (300 mg, 1.7 mmol) in 1.5 mL of CH_3CN was heated at 120 °C for 24 h in a glass ampoule. After removal of the solvent in vacuo, the residue was chromatographed on silica gel (1:1 ether-hexane) to afford 35 mg of **18b** (10%). Further elution (ether) afforded 244 mg of **18a** (71%). **18a**: mp 213-214.5 °C; ^{1}H NMR δ 1.46 (s, CH_3), 1.79 (br. d, *J* = 10.8 Hz, H_j), 2.08 (dd, *J* = 10.8, 1.5 Hz, H_i), 2.37 (br. s, H_b and H_c), 3.01 (br. d, *J* = 9.8 Hz, H_e), 3.05 (dt, *J* = 5.4, 1.5 Hz, H_a), 3.21-3.30 (m, 2 H_k), 3.32-3.40 (m, H_g and 2 H_k), 7.35-7.50 (m, 5 H); IR (KBr) 1710, 1495, 1370, 1170 cm^{-1}; MS *m/z* 345 (M^+, 33), 317 (100), 241 (43), 143 (61). Anal. $C_{18}H_{19}NO_2S_2$: C, 62.57; H, 5.55; N, 4.05; S, 18.56. Found: C, 62.51; H, 5.62; N, 4.00; S, 18.37. **18b**: mp 138.5-139 °C; ^{1}H NMR δ 1.35 (s, CH_3), 1.48 (br. d, *J* = 11.7 Hz, H_j), 1.78 (br. d, *J* = 11.7 Hz, H_i), 2.09 (dd, *J* = 14.7, 2.9 Hz, H_c), 2.27 (d, *J* = 14.7 Hz, H_b), 2.60 (br. d, *J* = 6.8 Hz, H_f), 2.78 (br. s, H_a), 3.21-3.45 (m, 4 H_k). 3.72 (br.d, *J* = 6.8 Hz, H_h), 7.35-7.50 (m, 5 H); IR (KBr) 1710, 1500, 1380, 1185 cm^{-1}; MS *m/z* 345 (M^+, 25), 317 (100), 144 (23), 143 (23); HRMS calcd for $C_{18}H_{19}NO_2S_2$ 345.0857, found 345.0865.

Reaction of 5 with Dimethyl Fumarate (13). A solution of **5** (172 mg, 1 mmol) and **13** (245 mg, 1.7 mmol) in 1.5 mL of CH_3CN was heated at 120 °C for 24 h in a glass ampoule. After removal of the solvent in vacuo, the residue was chromatographed on silica gel (1:4 ether-hexane) to afford 277 mg (92%) of **21a** and **21b** as a 81:19 mixture: ^{1}H NMR (400 MHz, **21a**) δ 1.28 (s, CH_3), 1.67 (ddd, *J* = 10.8, 2.9, 1.5 Hz, H_j), 1.77 (ddd, *J* = 10.8, 2.5, 2.0 Hz, H_i), 1.97 (dd, *J* = 14.7, 2.0 Hz, H_b), 2.16 (dd, *J* = 14.7, 2.9 Hz, H_c), 2.55 (br.s, H_a), 2.96 (dd, *J* = 5.9, 2.5 Hz, H_h), 3.12-3.41 (m, 4 H_k), 3.71 (s, OCH_3), 3.72 (dd, *J* = 5.9, 2.0 Hz, H_e), 3.73 (s, OCH_3); IR (neat) 1735, 1435, 1270, 1200, 1020 cm^{-1}; MS *m/z* 316 (M^+, 54), 288 (100), 143 (82), 112 (38), 79 (34), 59(37); HRMS calcd for $C_{15}H_{22}O_4S_2$ 316.0803, found 316.0832.

Reaction of 5 with 2-Chloroacrylonitrile (14). A solution of **5** (172 mg, 1 mmol) and **14** (175 mg, 2.0 mmol) in 1.5 mL of CH_3CN was heated at 120 °C for 24 h in a glass ampoule. After removal of the solvent in vacuo, the residue was chromatographed on silica gel (1:4 ether-hexane) to afford 213 mg (82%) of **23** as a 79:21 mixture of the stereoisomers: ^{1}H NMR (the major component) δ 1.34 (s, CH_3), 1.97 (ddd, *J* = 11.7, 2.9, 1.5 Hz, H_j), 2.01 (ddd, *J* = 11.7, 3.4, 1.5 Hz, H_i), 2.14 (d, *J* = 15.6 Hz, H_b), 2.34 (dt, *J* = 4.9, 1.5 Hz, H_a), 2.66 (dd, *J* =15.1, 3.4 Hz, H_h), 2.75 (dd, *J* = 15.1, 4.9 Hz, H_g), 2.76 (dd, *J* = 15.6, 2.9 Hz, H_c), 3.12-3.41 (m, 4 H_k); IR (neat) 2230, 1445, 835 cm^{-1}; MS *m/z* 261 (M^++2, 26), 259 (M^+, 58), 231 (100), 172 (35), 144 (63), 112 (37). Anal. Calcd for $C_{11}H_{14}NS_2Cl$: C, 50.84; H, 5.44; N, 5.39; S, 24.68; Cl, 13.64. Found: C, 50.22; H, 5.46; N, 5.20; S, 24.93; Cl, 14.19.

1-Methylnorbornane-2,5-dione Monodithioacetal (35). A mixture of **23** (0.43 g, 1.7 mmol), $Na_2S\cdot 9H_2O$ (2.0 g, 8.3 mmol), KOH (0.5 g, 8.9 mmol) in 10 mL of 95% EtOH was refluxed for 8 h. The mixture was cooled to room temperature, diluted with 30 mL of water, and extracted with ether (3 x 30 mL). The extracts were combined, washed with brine, and dried with Na_2SO_4. After removal of the solvent, the residue was chromatographed on silica gel (1:1 ether-hexane) to afford 364 mg (75%) of **35**: ^1H NMR δ 1.14 (s, CH_3), 1.78 (ddd, *J* = 10.7, 2.9, 1.5 Hz, H_j), 2.12 (ddd, *J* = 10.7, 4.5, 1.5 Hz, H_i), 2.18 (dd, *J* = 14.7, 2.9 Hz, H_c), 2.21 (dd, *J* = 18.6, 4.9 Hz, H_g), 2.35 (d, *J* = 14.7 Hz, H_b), 2.64 (dd, *J* = 18.6, 4.5 Hz, H_h), 2.65 (br. d, *J* =4.9 Hz, H_a), 3.19-3.31 (m, 2 H_k), 3.35-3.43 (m, 2 H_k); IR (neat) 1738, 1448, 1424, 1408, 1276, 1246, 1082, 1054, 972 cm^{-1}; MS *m/z* 214 (M^+, 21), 186 (100), 131 (46); HRMS calcd for $C_{10}H_{14}OS_2$ 214.0486, found 214.0496.

Reaction of 6 with Dimethyl Acetylenedicarboxylate (10). A solution of **6** (186 mg, 1 mmol) and **10** (242 mg, 1.7 mmol) in 1.5 mL of CH_3CN was heated at 120 °C for 4 h in a glass ampoule. After removal of the solvent in vacuo, the residue was chromatographed on silica gel (1:1 ether-hexane) to afford 259 mg (79%) of **16**: ^1H NMR δ 1.29 (s, CH_3), 1.76 (dd, *J* = 13.6, 2.9 Hz, H_c), 1.77 (d, *J* =13.6 Hz, H_b), 1.82 (ddd, *J* = 9.3, 2.9, 1.5 Hz, H_j), 1.86 (m, H_k), 1.99 (dd, *J* = 9.3, 1 Hz, H_i), 2.09 (m, H_k), 2.52 (dd, *J* =14.7, 2.0 Hz, H_k), 2.71 (dd, *J* = 14.7, 2.0 Hz, H_k), 3.21 (ddd, *J* = 14.7, 12.7, 2.5 Hz, H_k), 3.27 (ddd, *J* = 14.7, 12.7, 2.5 Hz, H_k), 3.75 (s, OCH_3), 3.83 (s, OCH_3), 3.94 (m, H_a); IR (neat) 1725, 1630, 1435, 1225, 1055 cm^{-1}; MS *m/z* 328 (M^+, 8), 132 (100); HRMS calcd for $C_{15}H_{20}O_4S_2$ 328.0803, found 328.0794.

Reaction of 6 with Maleic Anhydride (11). A solution of **6** (186 mg, 1 mmol) and **11** (167 mg, 1.7 mmol) in 1.5 mL of CH_3CN was heated at 120 °C for 3 h in a glass ampoule. After removal of the solvent in vacuo, the residue was chromatographed on silica gel (1:1 ether-hexane) to afford 82 mg of **19b** (29%) and 165 mg of **19a** (58%). **19a**: mp 189-189.5 °C; ^1H NMR δ 1.40 (s, CH_3), 1.66 (ddd, *J* = 10.7, 2.9, 1.5 Hz, H_j), 1.78 (dd, *J* = 15.1, 2.4 Hz, H_b), 1.86 (ddd, *J* = 15.1, 2.9 Hz, H_c), 1.86 (m, H_k), 2.09 (m, H_k), 2.34 (dd, *J* = 10.7, 1.5 Hz, H_i), 2.59 (m, H_k), 2.71 (m, H_k), 2.93 (ddd, *J* = 15.1, 12.7, 2.4 Hz, H_k), 3.13 (ddd, *J* = 15.1, 12.7, 2.4 Hz, H_k), 3.20 (m, H_e), 3.45-3.48 (m, H_a and H_g); IR (KBr) 1775, 1230, 1090, 900 cm^{-1}; MS *m/z* 284 (M^+, 73), 210 (30), 186 (61), 132 (43), 112 (68), 74 (100). Anal. Calcd for $C_{13}H_{16}O_3S_2$: C, 54.89; H, 5.68; S, 22.55. Found: C, 54.81; H,5.91; S, 22.49. **19b**: mp 147.5-149 °C; ^1H NMR δ 1.33 (s, CH_3), 1.35 (ddd, J = 12.2, 2.9, 1.5 Hz, H_j), 1.48 (dd, J =14.2, 2.9 Hz, H_c), 1.71 (d, J = 14.2 Hz, H_b), 1.90 (m, H_k), 2.09 (ddd, J = 12.2, 2.9, 1.5 Hz, H_i), 2.12 (m, H_k), 2.66 (m, H_k), 2.72 (m, H_k), 2.69 (br. d, J = 7.3 Hz, H_f), 2.99 (ddd, J = 15.1, 12.2, 2.9 Hz, H_k), 3.13 (ddd, J = 15.1, 12.2, 2.9 Hz, H_k), 3.24 (m, H_a), 3.95 (ddd, J = 7.3, 2.9, 1 Hz, H_h); IR (KBr) 1775, 1245, 1085, 915 cm^{-1}; MS *m/z* 284 (M^+, 45), 186 (23), 112 (30), 74 (100); HRMS calcd for $C_{13}H_{16}O_3S_2$ 284.0541, found 284.0524.

Reaction of 6 with *N*-Phenylmaleimide (12). A solution of **6** (186 mg, 1 mmol) and **12** (300 mg, 1.7 mmol) in 1.5 mL of CH_3CN was heated at 120 °C for 16 h in a glass ampoule. After removal of the solvent in vacuo, the residue was chromatographed on silica gel (ether) to afford 222 mg (62%) of **20a**. ^1H NMR spectrum of the crude reaction mixture showed the formation of isomeric minor product to which we tentatively assighned structure **20b**. **20a**: mp 210-211 °C; ^1H NMR δ 1.46 (s, CH_3), 1.70 (ddd, *J* = 10.8, 2.9, 1.5 Hz, H_j), 1.77 (dd, *J* = 15.1, 2.4 Hz, H_b), 1.84 (m, H_k), 1.88 (dd, *J* = 15.1, 2.9 Hz, H_c), 2.06 (m, H_k), 2.38 (dd, *J* = 10.8, 1.5 Hz, H_i), 2.55 (m, H_k), 2.70 (m, H_k), 3.01 (ddd, *J* = 14.6, 12.7, 2.4 Hz, H_k), 3.05 (dd, *J* = 10.3,.2.4 Hz, H_e), 3.17 (ddd, *J* = 14.6, 12.7, 2.4 Hz, H_k), 3.38 (dd, *J* = 10.3, 4.9 Hz, H_g), 3.49 (br.d, *J* = 4.9 Hz, H_a), 7.32-7.48 (m, 5 H); IR (KBr) 1705, 1500, 1370, 1170, 735 cm^{-1}; MS *m/z* 359

(M^+, 100), 285 (58), 186 (67), 112 (67). Anal. Calcd for $C_{19}H_{21}NO_2S_2$: C, 63.47; H, 5.90; N, 3.90; S, 17.84. Found: C, 63.41; H, 5.93; N, 3.84; S, 17.88.

Reaction of 6 with Dimethyl Fumarate (13). A solution of **6** (186 mg, 1 mmol) and **13** (245 mg, 1.7 mmol) in 1.5 mL of CH_3CN was heated at 120 °C for 6 h in a glass ampoule. After removal of the solvent in vacuo, the residue was chromatographed on silica gel (1:4 ether-hexane) to afford 286 mg (87%) of **22a** and **22b** as a 84:16 mixture: ^1H NMR (the major isomer) δ 1.20 (s, CH_3), 1.46 (dd, J = 14.2, 2.5 Hz, H_b), 1.52 (ddd, J = 10.8, 2.5, 1.5 Hz, H_j), 1.71 (dd, J = 14.2, 2.5 Hz, H_c), 1.90 (m, H_k), 2.04 (ddd, J = 10.8, 2.0, 1.5 Hz, H_i), 2.05 (m, H_k), 2.64 (m, 2 H_k), 2.94 (ddd, J = 14.6, 12.2, 2.9 Hz, H_k), 2.99 (br. s, H_a), 3.02 (dd, J = 5.9, 2.5 Hz, H_e), 3.11 (ddd, J = 14.6, 12.2, 2.9 Hz, H_k), 3.68 (s, OCH_3), 3.73 (s, OCH_3), 3.95 (dd, J = 5.9, 2.0 Hz, H_h); IR (neat) 1735, 1435, 1260, 1020 cm^{-1}; MS *m/z* 330 (M^+, 76), 255 (49), 186 (75), 112 (100). Anal. Calcd for $C_{15}H_{22}O_4S_2$: C, 54.51; H, 6.72; S, 19.41. Found: C, 54.11; H, 6.66; S, 19.10.

Reaction of 6 with 2-Chloroacrylonitrile (14). A solution of **6** (186 mg, 1 mmol) and **14** (175 mg, 2.0 mmol) in 1.5 mL of CH_3CN was heated at 120 °C for 20 h in a glass ampoule. After removal of the solvent in vacuo, the residue was chromatographed on silica gel (1:4 ether-hexane) to afford 227 mg (83%) of **24** as a 66:34 mixture of the stereoisomers: ^1H NMR (the major component) δ 1.35 (s, CH_3), 1.69 (d, J = 15.1 Hz, H_b), 1.92 (m, H_j), 1.94 (m, H_k), 2.05 (m, H_k), 2.28 (dd, J = 15.1, 2.9 Hz, H_c), 2.36 (ddd, J = 11.7, 3.9, 1.5 Hz, H_i), 2.69 (dd, J = 14.7, 5.4 Hz, H_g), 2.69 (m, H_k), 2.78 (br. d, J = 5.4 Hz, H_a), 2.86 (m, 2 H_k), 3.01 (dd, J = 14.7, 3.9 Hz, H_h), 3.03 (m, H_k); IR (neat) 2225, 1440, 1275, 1110, 905 cm^{-1}; MS *m/z* 275 (M^++2, 30), 273 (M^+, 63), 237 (49), 186 (72), 112 (75), 74 (100). Anal. Calcd for $C_{12}H_{16}NS_2Cl$: C, 52.62; H, 5.90; N, 5.12; S, 23.42; Cl, 12.94. Found: C, 52.09; H, 5.93, N, 5.25; S, 23.77; Cl, 12.96.

Reaction of 26 with Dimethyl Acetylenedicarboxylate (10). A solution of **26** (251 mg, 1 mmol) and **10** (242 mg, 1.7 mmol) in 3 mL of CH_3CN was heated at 120 °C for 4 d in a glass ampoule. After removal of the solvent in vacuo, the residue was chromatographed on silica gel (1:1 ether-hexane) to afford 294 mg (75%) of **30**: mp 93.5-94 °C; ^1H NMR δ 1.29 (d, J = 7.3 Hz, CH_3), 2.31 (dd, J = 9.3, 1.5 Hz, H_i or H_j), 2.49 (dd, J = 9.3, 2.0 Hz, H_j or H_i), 2.79 (q, J = 7.3 Hz, H_b), 3.19-3.33 (m, 4 H_k), 3.48 (br. s, H_a), 3.76 (s, OCH_3), 3.83 (s, OCH_3); IR (KBr) 1740, 1620, 1440, 1280, 1105, 830 cm^{-1}; MS *m/z* 394 ($M+2^+$, 0.3), 392 (M^+, 0.3), 313 (29), 281 (100), 253 (34), 132 (61).

Reaction of 27 with Dimethyl Acetylenedicarboxylate (10). A solution of **27** (212 mg, 1 mmol) and **10** (242 mg, 1.7 mmol) in 3 mL of CH_3CN was heated at 120 °C for 18 h in a glass ampoule. After removal of the solvent in vacuo, the residue was chromatographed on silica gel (1:4 ether-hexane) to afford 240 mg (68%) of **31**: mp 142.5-143 °C; ^1H NMR δ 1.14 (qt, J= 13.7, 4.4 Hz, 1 H), 1.29 (m, 2 H), 1.46 (td, J = 13.7, 4.7 Hz, 1 H), 1.64 (br. d, J = 13.5 Hz, 1 H), 1.66 (dd, J = 8.3, 1.5 Hz, H_i or H_j), 1.88 (m, 2 H), 2.05 (dd, J = 8.3, 1.5 Hz, H_j or H_i), 2.20 (dd, J = 12.2, 3.4 Hz, H_b), 2.27 (br. d, J = 13.7 Hz, 1 H), 3.18-3.37 (m, 4 H_k), 3.41 (br. s, H_a), 3.74 (s, OCH_3), 3.84 (s, OCH_3); ^{13}C NMR δ 22.17 26.45, 27.69, 29.21, 37.67, 39.36, 51.99, 52.31, 56.64, 56.69, 56.88, 58.63, 74.47, 140.27, 151.21, 163.15, 168.18; IR (KBr) 1725, 1630, 1440, 1280, 1110, 1065, 785 cm^{-1}; MS *m/z* 354 (M^+, 25), 326 (32), 294 (23), 157 (41), 131 (100), 105 (32), 71 (36); HRMS calcd for $C_{17}H_{22}O_4S_2$ 354.0960, found 354.0978.

Reaction of 32 with Dimethyl Acetylenedicarboxylate (10). A solution of **32** (212 mg, 1 mmol) and **10** (242 mg, 1.7 mmol) in 3 mL of CH_3CN was heated at 120 °C for 18 h in a glass ampoule. After removal of the solvent in vacuo, the residue was chromatographed on silica gel (1:1 ether-hexane) to afford 224 mg (63%) of **34**: mp 83-84.5 °C; ^1H NMR δ 1.02-1.12 (m, 1 H), 1.40-1.46 (m, 1 H), 1.56-1.69

(m, 4 H), 1.72-1.76 (m, 1 H), 1,85-1.94 (m, 1 H), 1.87 (dddd, *J* = 12.2, 4.9, 1.5, 1.0 Hz, H_j), 2.02 (dd, *J* = 14.2, 1.5 Hz, H_c), 2.85 (d, *J* = 14.2 Hz, H_b), 3.12-3.22 (m, 2 H_k), 3.26-3.42 (m, 2 H_k), 3.38 (br.s, H_a), 3.76 (s, OCH_3), 3.82 (s, OCH_3); ^{13}C NMR δ 21.00, 24.95, 24.98, 26.12, 38.13, 40.22, 44.09, 51.99 (2 C), 56.53, 60.72, 61.87, 70.28, 141.61, 153.15, 163.68, 166.59; IR (KBr) 1712, 1612, 1436, 1284, 1094 cm^{-1}; MS *m/z* 354 (M^+, 20), 324 (42), 300 (30), 157 (47), 131 (100), 101 (30); HRMS calcd for $C_{17}H_{22}O_4S_2$ 354.0960, found 354.o956.

6-*endo*-1,6-Tetramethylenenorbornane-2,5-dione Monodithioacetal (37). A solution of **27** (636 mg, 3.0 mmol) and **14** (893 mg, 10.2 mmol) in 9 mL of CH_3CN was heated at 120 °C for 22 h in a glass ampoule. After removal of the solvent in vacuo, the residue was chromatographed on silica gel (1:9 ether-hexane) to afford 646 mg (72%) of **36**: IR (neat) 2224, 1450, 1424, 1278, 840 cm^{-1}; MS *m/z* 301 (M^+, 39), 271 (80), 263 (60), 212 (46), 184 (100), 105 (41); HRMS calcd for $C_{14}H_{18}NS_2Cl$ 299.0569, found 299.0562.

A mixture of **36** (0.2 g, 0.67 mmol), $Na_2S \cdot 9H_2O$ (2.0 g, 8.3 mmol), KOH (0.5 g, 8.9 mmol) in 30 mL of 95% EtOH was refluxed for 37 h. The mixture was cooled to room temperature, diluted with 30 mL of water, and extracted with ether (3 x 30 mL). The extracts were combined, washed with brine, and dried with Na_2SO_4. After removal of the solvent, the residue was chromatographed on silica gel (1:4 ether-hexane) to afford 123 mg (72%) of **37** as a colorless solid. Recrystalization from hexane gave analytically pure sample. **37**: mp 84.5-85.5 °C; ^1H NMR δ 1.04-1.26 (m, 2 H), 1.42-1.54 (m, 3 H), 1.66-1.76 (m, 2 H), 1.85 (ddd, *J* = 12.2, 5.8, 2.0 Hz, 1 H), 1.92-2.04 (m, 2 H), 2.18 (dd, *J* = 18.5, 4.9 Hz, H_g), 2.61 (br. d, *J* = 4.9 Hz, H_a), 2.80 (dd, *J* = 18.5, 4.4 Hz, H_h), 3.11-3.34 (m, 4 H_k); ^{13}C NMR δ 22.29, 24.12, 24.95, 29.21, 38.24, 38.46, 39.74, 43.62, 48.81, 49.67, 57.63, 76.94, 216.90; IR (KBr) 1732, 1446, 1180, 1096; MS *m/z* 254 (M^+, 13), 226 (81), 131 (100); HRMS calcd for $C_{13}H_{18}OS_2$ 254.0799, found 254.0783.

Acid Promoted Reactions. To a solution of **5** (172 mg, 1.0 mmol) and **10** (426 mg, 3.0 mmol) in 5 mL of CH_3CN was added an acidic additive (0.1 mmol) and the resultant mixture was stirred at 60 °C. After an appropriate reaction time (12 or 24 h), dibutyl phthalate was added as an internal standard to the cooled reaction mixture, which was subsequently analyzed by GLC (10% Silicon SE-30, 0.5 m, 80-230 °C).

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