Synthesis of Nucleosides and Related Compounds. XVII.[1] Dialkyl 1,3-Dithiethan- and 1,3-Dithiolan-2-ylidenemalonate *S*-Oxides: Equivalents to Dialkoxycarbonylketenes[2]

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Dialkyl 1,3-dithiethan- and 1,3-dithiolan-2-ylidenemalonate *S*-oxides have been found to serve as new dienophiles for Diels–Alder reaction with cyclopentadiene. Furthermore, since the adducts thus obtained were transformed to dialkyl 3-oxobicyclo[2.2.1]heptane-2,2-dicarboxylates, these dienophiles behaved as dialkoxycarbonylketene equivalents. Synthesis of di-*l*-methyl [1*R* and 1*S*]-1,3-dithiethan-2-ylidenemalonate 1-oxides and their successful use in asymmetric Diels–Alder reactions with cyclopentadiene are also described.

Keywords 1,3-dithiethan-2-ylidenemalonate; 1,3-dithiolan-2-ylidenemalonate; dienophile; Diels–Alder reaction; cyclopentadiene; 3-oxobicyclo[2.2.1]heptane; ketene equivalent; carbocyclic *C*-nucleoside; chiral dienophile; asymmetric Diels–Alder reaction

Ketenes are versatile reagents and useful intermediates for organic synthesis.[3] For example, ketenes react not only with olefins in a 2+2 manner to give cyclobutanones but also with α,β-unsaturated ketones in a 4+2 manner to give γ,δ-unsaturated δ-lactones. However the carbon–carbon double bond of ketenes cannot react with an alkadiene (*e.g.* cyclopentadiene) as the dienophile, though the adducts, if obtained, would be useful intermediates for the synthesis of pharmacologically active substances including natural products.[4] In this connection, several dienophiles have been elaborated which act as ketene equivalents.[4] For example, 2-chloroacryloyl chloride,[5] 2-acetoxyacrylonitrile,[6] and 1,1-bis(*p*-tolylsulfinyl)ethene[7] were found to behave as alternatives to ketene itself whereas dimethyl allene-1,3-dicarboxylate[8] acts as an equivalent to methoxycarbonylketene.

Previously, we have demonstrated that 3-acetoxyacrylates (A) having an electron-withdrawing group at the 2-position behave as suitable dienophiles for the Diels–Alder reaction with furan or cyclopentadiene and the adducts (B) thus formed can be used as versatile precursors for the synthesis (including the enantiomeric synthesis) of *C*-nucleosides and their carbocyclic analogues.[9] Thus, dienophiles A reacted with cyclopentadiene either under heating[10] or in the presence of a Lewis acid catalyst at $-78\,^{\circ}C$,[11] and with furan under high pressure (11 kbar)[12] to give the adducts B. The acetonides C derived from B were then subjected to reductive retrograde aldol (RRA) reaction (C→E→F→D: K_2CO_3–$NaBH_4$/MeOH) to give the nucleoside precursors D.

In connection with our continuing interest in the synthesis of *C*-nucleosides, we have found that dialkyl 1,3-dithiethan- and 1,3-dithiolan-2-ylidenemalonate *S*-oxides are not only suitable as dienophiles for cyclopentadiene but also act as equivalents to dialkoxycarbonylketenes.[13] Here, we report these results in detail, as well as the conversion of the adducts to carbocyclic *C*-nucleoside precursors.

1,3-Dithiethan- (**1a**, **c**) and 1,3-dithiolan-2-ylidenemalonates (**2a**, **b**) were prepared by the following modification of the previously reported method.[14] Thus, dialkyl malonates were treated with carbon disulfide and appropriate dibromoalkanes in the presence of potassium carbonate in acetone under reflux to give the desired compounds **1a**, **c** and **2a**, **b**, all in good yields. In particular, di-*l*-menthyl 1,3-dithiethan-2-ylidenemalonate (**1c**) was synthesized with the intention of elaborating a chiral dialkoxycarbonylketene equivalent (*vide infra*).

Though dimethyl 1,3-dithiethan-2-ylidenemalonate (**1a**) was inert in the Diels–Alder reaction with cyclopentadiene, its 1-oxide (**3**) derived from **1a** by treatment with *m*-chloroperbenzoic acid (*m*-CPBA) reacted with cyclopentadiene at room temperature to form the adduct in a quantitative yield as a mixture of *endo* (**4**) and *exo* isomers (**5**), which were chromatographically separable. Though four isomers were expected to be formed in this reaction, only two isomers were isolated; signals of the other isomers

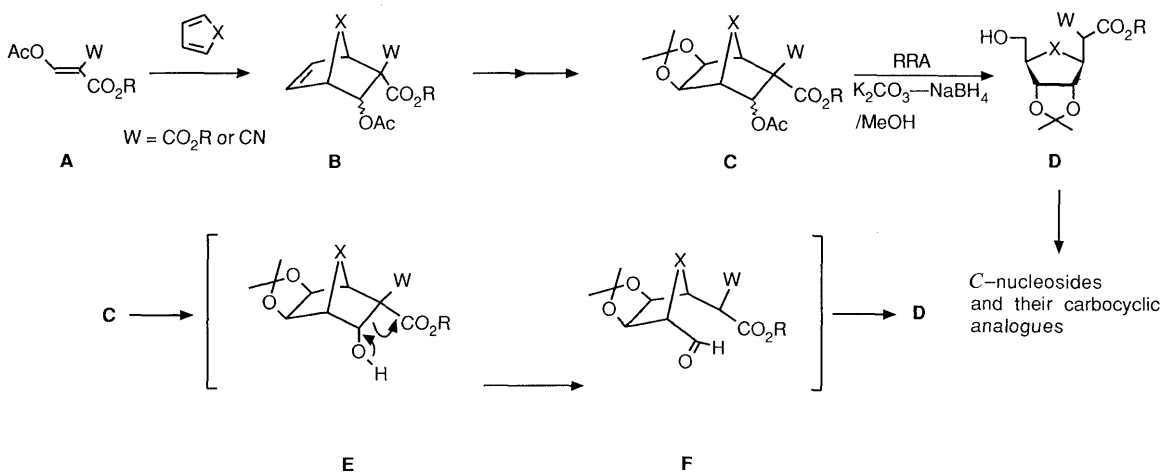


Chart 1

were not detected in the proton nuclear magnetic resonance (^{1}H-NMR) spectrum of the reaction mixture. The ratio of **4** and **5** was 11 : 1, and assignment of their structures, especially *endo* and *exo* configurations, was based on the ^{1}H-NMR spectra, with the use of Tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium ($Eu(fod)_3$) as a shift reagent.Thus, since $Eu(fod)_3$ chelated predominantly with sulfoxide oxygen, in the *endo* isomer **4** the signals of the 4- and 5-protons were shifted to low field whereas only the 7-proton of the *exo* isomer (**5**) was affected by addition of this shift reagent.

As expected, dialkyl 1,3-dithiolan-2-ylidenemalonates (**2a, b**) did not react with cyclopentadiene under any conditions. Furthermore, dialkyl 1,3-dithiolan-2-ylidenemalonate 1-oxides (**6a, b**) were less active than the corresponding 1,3-dithiethane 1-oxide (**3**) and they did not react with the diene under atmospheric conditions. However, the dimethyl ester (**6a**) reacted with cyclopentadiene at high pressure (10 kbar) to give the adduct **8a** as a single isomer in 16% yield, with recovery of **6a** (79%). Though the configuration of **8a** has not been determined yet, such high stereoselectivity should be due to the envelope conformation of **6a** and secondary orbital interaction between sulfoxide and cyclopentadiene (upper side attack and *endo* preference: *cf.* **6a** in Chart 4). The 1,3-dioxides (**7a, b**) obtained from **6a, b** by further oxidation with *m*-CPBA, however, reacted with cyclopentadiene under atmospheric pressure even at room temperature to give the adducts as a mixture of two isomers (**9a, b** and **9'a, b**). The configuration of dioxides (**7a, b**) was speculated to be *anti* for the following reasons (*cf.* Chart 4). Due to the envelope conformation of **6a, b**, the oxygen of sulfoxide would assume quasi-equatorial configuration. Therefore, the lobe at the quasi-axial configuration of the other sulfur atom would be more accessible for oxidation to give the *anti* dioxides (**7a, b**). In compounds **7a, b**, if cyclopentadiene approaches from the upper side, **9a, b** would be obtained as the major products and **9'a, b** as the minor products because of the bulkiness of 4- (or 5-) methylene group in **7a, b**.

Next, we investigated the transformation of the Diels–Alder adducts to 3-oxobicyclo[2.2.1]heptane-2,2-dicar-

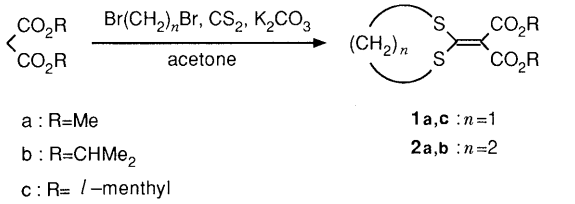


Chart 2

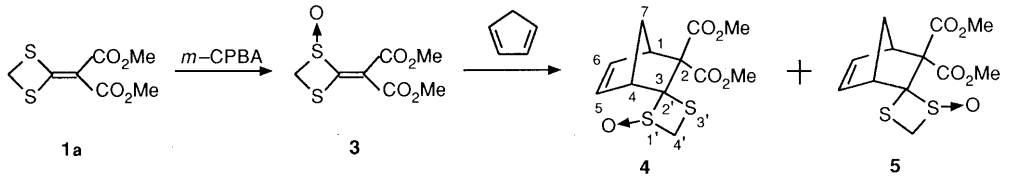
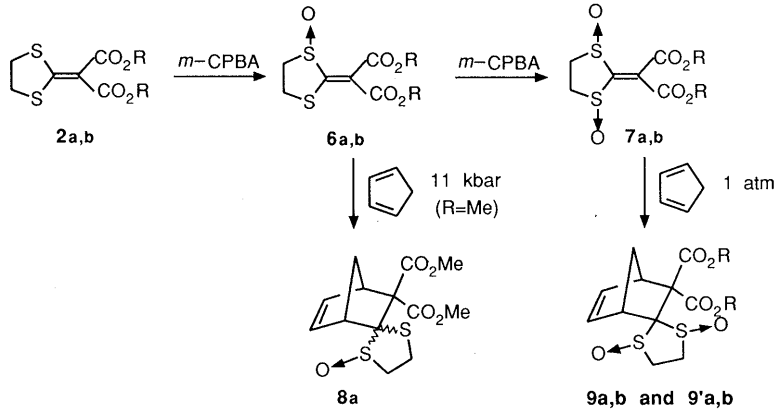


Chart 3



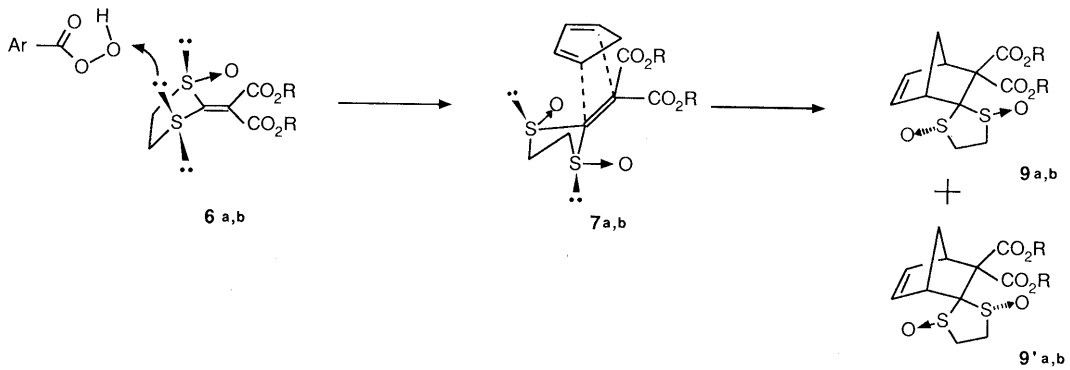


Chart 4

boxylates. Catalytic reduction of **4** with Pd–C gave the dihydro derivative **11** whereas in the case of using Raney Ni as the catalyst, dimethyl bicyclo[2.2.1]heptane-2,2-dicarboxylate (**10**) was obtained in good yield. Treatment of **11** with perchloric acid[15] in tetrahydrofuran (THF) gave the desired 3-oxobicyclic compound **12** together with a small amount of the hydrolyzed product **13**. Finally, **12** was subjected to RRA reaction to give the 1,3-*cis*-cyclopentane derivative (**14**).

Compound **9b** was also converted to 3-oxobicyclo[2.2.1]-heptane-2,2-dicarboxylate (**17**). In this case, the dihydro derivative **15** obtained from **9b** by catalytic reduction was initially transformed to the mono-oxide **16** by treatment with titanium trichloride.[7] Since in this reaction compound **16** was obtained as a sole product, the less hindered oxygen (*exo*-oxygen) of **15** would be removed selectively by titanium trichloride. Compound **16** was then treated with mercury chloride[15] to give the oxo derivative **17**. In order to confirm the structure of **17**, **17** was reduced with sodium borohydride to give the *endo* hydroxy compound **18** as a sole product. Again, compound **18** was subjected to RRA reaction to afford 1,3-*cis*-cyclopentane derivative (**19**).

The successful transformation of Diels–Alder adducts (**4** and **9b**) to bicyclic ketones (**12** and **17**) has shown clearly that the dienophiles (**3** and **9a, b**) can serve as equivalents of dialkoxycarbonylketene.

Finally, we extended this approach to the creation of a chiral dialkoxycarbonylketene equivalent. Asymmetric Diels–Alder reactions of vinylsulfoxides with cyclopentadiene have been extensively investigated by Koizumi and his coworkers.[16] Among them, they found that (+)-(*S,S*)-1,1-bis(*p*-tolylsulfinyl)ethene reacted with cyclopentadiene to give the 4+2 cycloadduct as a mixture of two isomers, whose major product was transformed to dehydronorcamphor by further appropriate manipulations.[7] This means that (+)-(*S,S*)-1,1-bis(*p*-tolylsulfinyl)ethene behaves as a chiral ketene equivalent as mentioned above. In our case, we chose di-*l*-menthyl 1,3-dithiethan-2-ylidenemalonate (**1c**) as the chiral dienophile. Since **1c**, just like **1a**, was inactive in the Diels–Alder reaction with cyclopentadiene, transformation of **1c** to the monoxide was carried out in order to activate **1c** as the dienophile. Treatment of **1c** with *m*-CPBA in dichloromethane gave the monoxide as a mixture of two diastereomers (ratio, 1 : 1). Careful separation of these isomers by silica gel column chromatography gave the less polar [1*S*]-isomer (**20**) and the more polar [1*R*]-isomer (**21**). The absolute configuration of these isomers was determined by chemical reactions (*vide*

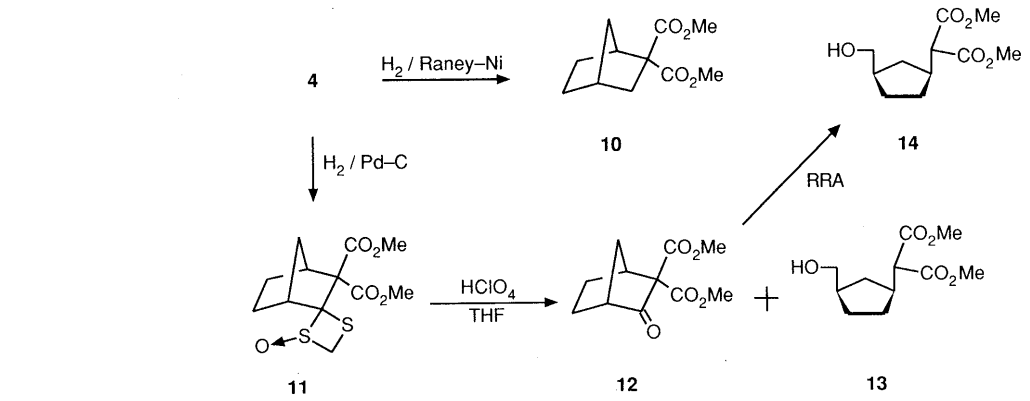


Chart 5

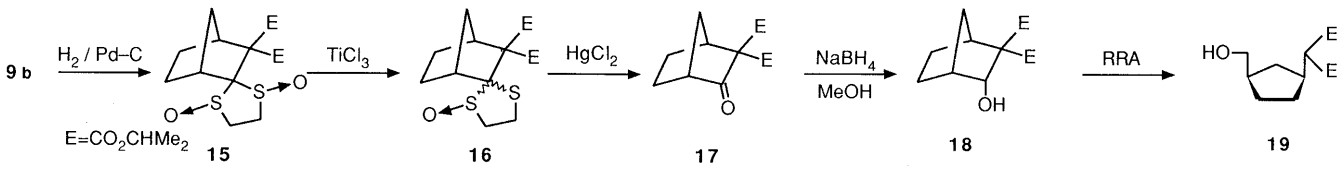


Chart 6

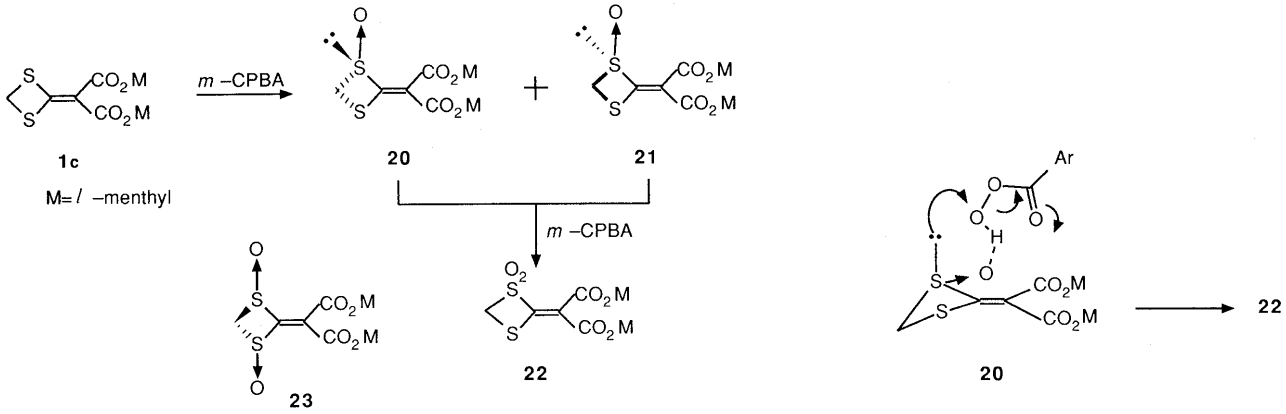


Chart 7

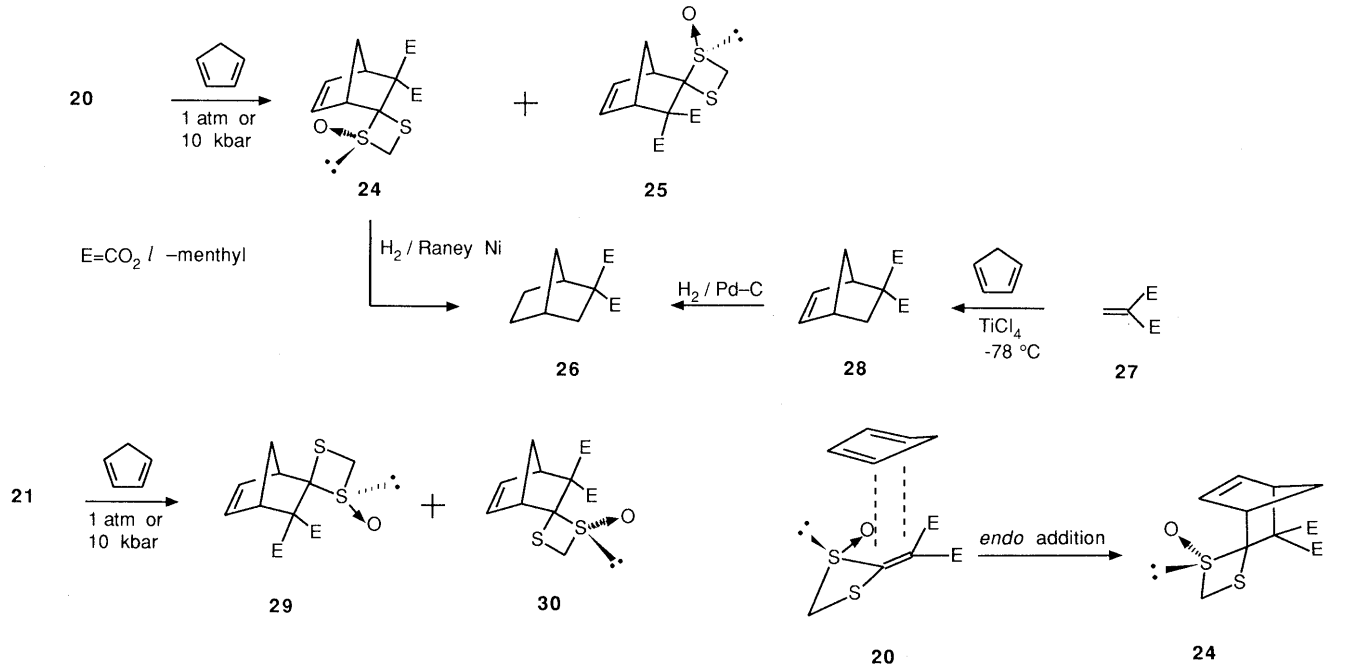


Chart 8

infra). In contrast to **6a, b**, further oxidation of **20** (or **21**) with *m*-CPBA did not give the 1,3-dioxide **23**, but gave the sulfone **22**. Even if the less hindered lone pair at the 3-position of **20** (or **21**) reacts with *m*-CPBA as in the case of **6a, b**, the 1,3-dioxide **23** formed would be unstable because of its ring strain. Therefore, *m*-CPBA reacts with the lone pair at the 1-position to give the sulfone **22**.[17]

Asymmetric Diels–Alder reaction of **20** with cyclopentadiene was completed in 2 d to give two isomers (**24** and **25**) when carried out at atmospheric pressure. However, the reaction was accelerated remarkably by high pressure (10 kbar) and was completed within 5 h. The ratio of *endo* and *exo* isomers was 9 : 1, and careful examination of the ^{1}H-NMR spectrum (500 MHz) revealed that the diastereomeric excess (de) was more than 98% (see Experimental). The same results were obtained when **21** was used instead of **20**. The *endo* isomer **24** obtained from the Diels–Alder reaction of **20** and cyclopentadiene was subjected to catalytic reduction with Raney Ni to give di-*l*-menthyl bicyclo[2.2.1]heptane-2,2-dicarboxylate (**26**), which was identical with an authentic sample prepared by Diels–Alder reaction of di-*l*-menthyl methylenemalonate (**27**) with cyclopentadiene followed by catalytic reduction with Pd–C according to the previous method.[11] Hence, the absolute structure of **24** was determined as [1*R*,4*S*], and that of **20** might be [1*S*] (*cf.* Chart 8). In compound **20**, cyclopentadiene approaches from the less hindered side (*Si-face*) to give the *endo* adduct **24** as the major product. From these results, the absolute structures of **25**, **29**, and **30** were determined to be as shown in Chart 8.

In conclusion, we have created new dienophiles equivalent to dialkoxycarbonylketene. These dienophiles are useful not only for the synthesis of *C*-nucleosides but also for the synthesis of other naturally occurring substances.

Experimental

All melting points were determined on a Yanagimoto micro-hot stage and are uncorrected. Optical rotations were measured with a JASCO DIP-340 digital polarimeter. Infrared (IR) spectra were measured on a JASCO A-102 spectrophotometer. ^{1}H-NMR spectra were recorded with a JEOL JNM-PMX 60 si or JEOL JNM-GX 500 spectrometer with tetramethylsilane (TMS) as an internal standard, and the abbreviations of signal patterns are follows: s, singlet; d, doublet; t, triplet; q, quartet; h, heptet; m, multiplet; dd, doublet of doublets; br, broad; brs, broad singlet. All de values of the compounds obtained in the present work were determined from the 500 MHz ^{1}H-NMR spectra in $CDCl_3$. Low- and high-resolution mass spectra (MS) were obtained on JEOL JMS-OISG-2 and JEOL JMS-DX-303 mass spectrometers, respectively. Wakogel (C-200) and Merck Kiesel-gel 60 F 254 were employed for silica gel column and thin layer chromatography (TLC), respectively. The ratios of mixtures of solvents for chromatography are shown as volume/volume. High-pressure reactions were carried out by using a piston-cylinder apparatus equipped with a pK. 15. B pump (Hikari Koatsu Kiki Co., Ltd.).

Dimethyl 1,3-Dithiethan-2-ylidenemalonate (1a) A mixture of dimethyl malonate (1.32 g, 10 mmol), dibromomethane (5.22 g, 30 mmol), carbon disulfide (3.04 g, 40 mmol), and K_2CO_3 (4.15 g, 30 mmol) in acetone (20 ml) was heated under reflux for 5 h. After evaporation of the solvent, the resulting residue was extracted with $CHCl_3$ (30 ml). The $CHCl_3$ extract was washed with 5% $NaHCO_3$ (15 ml × 2) and water (15 ml × 2) successively, and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the crystalline residue was purified by recrystallization from AcOEt to give **1a** as colorless prisms, mp 158—160 °C. Yield, 1.17 g (53%). *Anal.* Calcd for $C_7H_8O_4S_2$: C, 38.18; H, 3.64; S, 29.09. Found: C, 38.01; H, 3.58; S, 29.20. IR ($CHCl_3$): 1735 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.78 (6H, s, CO_2Me × 2), 4.02 (2H, s, $-CH_2-$).

Di-*l*-menthyl 1,3-Dithiethan-2-ylidenemalonate (1c) A mixture of di-*l*-menthyl malonate (2.61 g, 6.9 mmol), dibromomethane (2.39 g, 13.7 mmol), carbon disulfide (1.57 g, 20.6 mmol), and K_2CO_3 (1.90 g, 13.7 mmol) in acetone (50 ml) was heated under reflux. After 4 h, dibromomethane (1.20 g, 6.9 mmol), carbon disulfide (0.78 g, 10.3 mmol), and K_2CO_3 (0.95 g, 6.9 mmol) were added to the mixture successively. The resulting mixture was heated again under reflux for 3 h. This process was repeated once again. After evaporation of the solvent, the residue was extracted with $CHCl_3$ (40 ml). The $CHCl_3$ extract was washed with 5% K_2CO_3 (30 ml × 3) and water (30 ml × 2) successively, and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was subjected to silica gel column chromatography (silica gel 70 g). Elution with hexane–AcOEt (8 : 1) gave **1c** as a colorless oil. Yield, 2.60 g (81%). $[\alpha]_D^{22}$ −108.0° (c = 1.0, $CHCl_3$). High-resolution MS m/z: M^+ Calcd for $C_{25}H_{40}O_4S_2$: 468.2368. Found: 468.2403. IR ($CHCl_3$): 1715, 1660, 1635 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 4.00 (2H, s, $-CH_2-$), 4.75 (2H, m, menthyl 1-H).

Dimethyl 1,3-Dithiolan-2-ylidenemalonate (2a) A mixture of dimethyl

malonate (13.2 g, 0.1 mol), dibromoethane (56.4 g, 0.3 mol), carbon disulfide (45.6 g, 0.6 mol), and K_2CO_3 (41.5 g, 0.3 mol) in acetone (250 ml) was heated under reflux for 12 h. After evaporation of the solvent *in vacuo*, the residue was extracted with $CHCl_3$ (200 ml). The $CHCl_3$ extract was washed with 5% $NaHCO_3$ (150 ml × 3) and water (150 ml × 2) successively, and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the crystalline residue was purified by recrystallization from Et_2O to give **2a** as colorless prisms, mp 65 °C. Yield, 18.9 g (81%). *Anal.* Calcd for $C_8H_{10}O_4S_2$: C, 41.02; H, 4.27; S, 27.35. Found: C, 40.92; H, 4.21; S, 27.39. IR ($CHCl_3$): 1710 (sh), 1685 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.27 (4H, s, $-CH_2CH_2-$), 3.67 (6H, s, $CO_2Me \times 2$).

Dimethyl 1,3-Dithiethan-2-ylidenemalonate 1-Oxide (3) A solution of *m*-CPBA (443 mg, 2.57 mmol) in CH_2Cl_2 (3 ml) was added dropwise to a solution of **1a** (471 mg, 2.14 mmol) in CH_2Cl_2 (10 ml) with stirring and ice-cooling. The resultant solution was then stirred at room temperature for 5 h. The precipitate was filtered off, and the filtrate was washed with 5% $NaHCO_3$ (10 ml × 3) and water (10 ml × 2) successively. After evaporation of the solvent, the crystalline residue was purified by recrystallization from Et_2O to give **3** as colorless prisms, mp 135—136 °C. Yield, 237 mg (47%). *Anal.* Calcd for $C_7H_8O_5S_2$: C, 35.39; H, 3.39; S, 27.12. Found: C, 35.58; H, 3.39; S, 27.18. IR ($CHCl_3$): 1740, 1700 (sh) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.88 (6H, s, $CO_2Me \times 2$), 4.31 (2H, s, $-CH_2-$).

Diels–Alder Reaction of 3 with Cyclopentadiene A solution of **3** (605 mg, 2.56 mmol) and cyclopentadiene (846 mg, 12.8 mmol) in CH_2Cl_2 (3 ml) was allowed to stand at room temperature for 12 h. The reaction mixture was concentrated *in vacuo*, and then the residue was subjected to silica gel (20 g) column chromatography. Elution with hexane–AcOEt gave dimethyl *endo*-bicyclo[2.2.1]hept-5-ene-2,2-dicarboxylate-3-spiro-2′-(1′,3′-dithiethane 1′-oxide) (**4**) and its *exo*-isomer (**5**) successively.

4: Yield, 748 mg (84%), colorless prisms (AcOEt), mp 120—121 °C. *Anal.* Calcd for $C_{12}H_{14}O_5S_2$: C, 47.68; H, 4.64; S, 21.19. Found: C, 47.59; H, 4.64; S, 21.25. IR ($CHCl_3$): 1765 (sh), 1740 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.83 (1H, dt, J=10, 2 Hz, 7-H), 2.22 (1H, br d, J=10 Hz, 7-H), 3.43 (1H, br s, 4-H), 3.76 (1H, br s, 1-H), 3.74, 3.79 (3H each, s, CO_2Me), 4.02 (2H, s, 4′-CH_2), 6.02, 6.63 (1H each, dd, J=6, 3 Hz, 5-H and 6-H). ^{1}H-NMR [$CDCl_3$ (0.3 ml), sample (20 mg), addition of Eu(fod)$_3$ (10 mg)] δ: 3.72 (1H, br s, 1-H), 4.40 (1H, br s, 4-H), 6.36 (1H, dd, J=6, 3 Hz, 6-H), 7.43 (1H, dd, J=6, 3 Hz, 5-H).

5: Yield, 140 mg (14%), colorless oil. High-resolution MS *m/z*: M^+ Calcd for $C_{12}H_{14}O_5S_2$: 302.02829. Found: 302.02810. IR ($CHCl_3$): 1755 (sh), 1730 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.77 (1H, br d, J=10 Hz, 7-H_{syn}), 2.10 (1H, br d, J=10 Hz, 7-H_{anti}), 3.45 (1H, br s, 4-H), 3.70 (1H, br s, 1-H), 3.63, 3.90 (3H each, s, CO_2Me), 3.95 (2H, s, 4′-CH_2), 6.20 (1H, dd, J=6, 3 Hz, 5- or 6-H), 6.50 (1H, dd, J=6, 3 Hz, 5- or 6-H). ^{1}H-NMR [$CDCl_3$ (0.3 ml), sample (30 mg), addition of Eu(fod)$_3$ (10 mg)] δ: 2.05 (1H, br d, J=10 Hz, 7-H_{syn}), 3.20 (1H, br d, J=10 Hz, 7-H_{anti}), 3.75 (1H, br s, 1-H), 4.70 (1H, br s, 4-H), 6.48 (1H, dd, J=6, 3 Hz), 6.75 (1H, dd, J=6, 3 Hz).

Dimethyl 1,3-Dithiolan-2-ylidenemalonate 1-Oxide (6a) A solution of *m*-CPBA (380 mg, 2.2 mmol) in CH_2Cl_2 (3 ml) was added dropwise to a solution of **2a** (468 mg, 2.0 mmol) in CH_2Cl_2 (5 ml) with stirring and ice-cooling. The solution was stirred at room temperature for 2 h. The precipitate was filtered off, and the filtrate was washed with 5% $NaHCO_3$ (5 ml × 2) and water (5 ml × 2) successively, and dried over anhydrous Na_2SO_4. The solvent was evaporated off *in vacuo*, and the resulting residue was subjected to silica gel (15 g) column chromatography. Elution with hexane–AcOEt (1 : 2) gave **6a** as a colorless oil. Yield, 314 mg (63%). High-resolution MS *m/z*: M^+ Calcd for $C_8H_{10}O_5S_2$: 249.9970. Found: 249.9975. IR ($CHCl_3$): 1738, 1710 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.68—4.28 (4H, m, $-CH_2CH_2-$), 3.80, 3.85 (3H each, s, CO_2Me).

Diisopropyl 1,3-Dithiolan-2-ylidenemalonate 1-Oxide (6b) The same procedure as described above was applied to diisopropyl 1,3-dithiolan-2-ylidenemalonate (Isoprothiolane)[14] (**2b**) (2.90 g, 10 mmol) and *m*-CPBA (2.07 g, 12 mmol) to give **6b** (2.0 g, 65%) as colorless needles (hexane–CH_2Cl_2), mp 85—86 °C. *Anal.* Calcd for $C_{12}H_{18}O_5S_2$: C, 47.04; H, 5.92; S, 20.93. Found: C, 46.80; H, 5.82; S, 20.90. ^{1}H-NMR ($CDCl_3$) δ: 1.19—1.37 (12H, m, isopropyl-Me × 4), 2.55—4.32 (4H, m, $-CH_2CH_2-$), 4.97—5.47 (2H, m, isopropyl-CH × 2).

Dimethyl 1,3-Dithiolan-2-ylidenemalonate 1,3-Dioxide (7a) *m*-CPBA (2.16 g, 12.5 mmol) was added portionwise to a solution of **2a** (1.17 g, 5.0 mmol) in CH_2Cl_2 (30 ml) with stirring and ice-cooling. The mixture was allowed to stand at room temperature for 8 h. The precipitate was filtered off, and the filtrate was subjected to silica gel (40 g) column chromatography. Elution with AcOEt gave **7a** as pale yellow columns (AcOEt), mp 108—110 °C. Yield, 758 mg (57%). **7a** was partially decomposed on TLC, but was purified by recrystallization from AcOEt. *Anal.* Calcd for $C_8H_{10}O_6S_2$: C, 36.08; H, 3.78; S, 24.08. Found: C, 36.01; H, 3.80; S, 24.02. IR ($CHCl_3$): 1740 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.73 (4H, br s, $-CH_2CH_2-$), 3.98 (6H, s, $CO_2Me \times 2$).

Diisopropyl 1,3-Dithiolan-2-ylidenemalonate 1,3-Dioxide (7b) A solution of *m*-CPBA (8.63 g, 50 mmol) in CH_2Cl_2 (40 ml) was added dropwise to a solution of **2b** (5.80 g, 20 mmol) in CH_2Cl_2 (40 ml) with stirring and ice-cooling. The mixture was stirred at room temperature for 1 h. The precipitate was filtered off, and the filtrate was washed with 5% $NaHCO_3$ (50 ml × 3) and water (50 ml × 2) successively, and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the crystalline residue was purified by recrystallization from hexane–CH_2Cl_2 to give **7b** as yellow needles, mp 97—100 °C. Yield, 4.52 g (70%). *Anal.* Calcd for $C_{12}H_{18}O_6S_2$: C, 44.76; H, 5.63; S, 19.63. Found: C, 44.52; H, 5.57; S, 19.93. IR ($CDCl_3$): 1730 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.67 (12H, d, J=6 Hz, isopropyl-Me × 4), 3.77 (4H, br s, $-CH_2CH_2-$), 5.07—5.33 (2H, m, isopropyl-CH × 2). MS *m/z*: 322 (M^+).

Dimethyl Bicyclo[2.2.1]hept-5-ene-2,2-dicarboxylate-3-spiro-2′-(1′,3′-dithiolane 1′-oxide) (8a) A mixture of **6a** (314 mg, 1.26 mmol) and cyclopentadiene (249 mg, 3.77 mmol) was placed in a Teflon tube (1.2 ml) with a Teflon stopper, and the tube was filled with dry CH_2Cl_2. The tube was placed in a high-pressure reactor and pressurized to 10 kbar for 2 d. The pressure was released and the reaction mixture was concentrated *in vacuo*. The resulting residue was subjected to silica gel (15 g) column chromatography. Elution with hexane–AcOEt (1 : 2) gave **6a** (248 mg, 79%). Further elution with AcOEt–MeOH (5 : 1) gave **8a** as a colorless oil. Yield, 65 mg (16%). High-resolution MS *m/z*: M^+ Calcd for $C_{13}H_{16}O_5S_2$: 316.04394. Found: 316.04381. ^{1}H-NMR ($CDCl_3$) δ: 1.71—1.96 (2H, m, 7-2H), 3.23—4.02 (6H, m, 1-H, 4-H, $-CH_2CH_2-$), 3.72, 3.74 (3H each, s, CO_2Me), 6.24—6.67 (2H, m, 5-H and 6-H).

Dimethyl Bicyclo[2.2.1]hept-5-ene-2,2-dicarboxylate-3-spiro-2′-(1′,3′-dithiolane 1′,3′-dioxide) (9a) Cyclopentadiene (300 mg, 4.54 mmol) was added to a solution of **7a** (75 mg, 0.28 mmol) in CH_2Cl_2 (1 ml). The mixture was stirred at room temperature for 7 h. After evaporation of the solvent, the residue was subjected to silica gel (20 g) column chromatography. Elution with AcOEt–MeOH (10 : 1) gave **9′a** as colorless prisms (hexane–AcOEt), mp 158—160 °C. Yield, 20 mg (21%). *Anal.* Calcd for $C_{13}H_{16}O_6S_2$: C, 46.99; H, 4.82; S, 19.23. Found: C, 46.79; H, 4.80; S, 19.11. IR ($CHCl_3$): 1740 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.84 (1H, br d, J=10 Hz, 7-H), 2.75 (1H, br d, J=10 Hz, 7-H), 3.3—4.4 (6H, m, 1-H, 4-H, and $-CH_2CH_2-$), 3.67 (3H, s, CO_2Me), 3.77 (3H, s, CO_2Me), 6.35 (1H, dd, J=3, 6 Hz, 5-H or 6-H), 6.68 (1H, dd, J=3, 6 Hz, 5-H or 6-H).

Further elution with the same solvent gave **9a** as colorless prisms (MeOH), mp 178—180 °C. Yield, 72 mg (77%). *Anal.* Calcd for $C_{13}H_{16}O_6S_2$: C, 46.99; H, 4.82; S, 19.23. Found: C, 46.76; H, 4.67; S, 19.13. IR ($CHCl_3$): 1740 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.81—1.87 (2H, m, 7-2H), 3.22—4.42 (6H, m, 1-H, 4-H, and $-CH_2CH_2-$), 3.72, 3.77 (3H each, s, CO_2Me), 6.36—6.42 (2H, m, 5-H and 6-H). MS *m/z*: 332 (M^+).

Diisopropyl Bicyclo[2.2.1]hept-5-ene-2,2-dicarboxylate-3-spiro-(1′,3′-dithiolane 1′,3′-dioxide) (9b) A solution of **7b** (3.22 g, 10 mmol) and cyclopentadiene (3.3 g, 50 mmol) in CH_2Cl_2 (20 ml) was allowed to stand at room temperature for 12 h. After evaporation of the solvent *in vacuo*, the residue was subjected to silica gel (100 g) column chromatography. Elution with EtOAc gave **9b′** (less polar) and **9b** (more polar) successively.

9b′ (Less Polar): Colorless prisms (hexane–CH_2Cl_2), mp 116—117 °C. Yield, 382 mg (10%). *Anal.* Calcd for $C_{17}H_{24}O_6S_2$: C, 52.55; H, 6.23; S, 16.51. Found: C, 52.23; H, 6.51; S, 16.73. IR ($CHCl_3$): 1730 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.26 (3H, d, J=6 Hz, isopropyl-Me), 1.28 (9H, d, J=6 Hz, isopropyl-Me × 3), 1.80 (1H, br d, J=10 Hz, 7-H), 2.75 (1H, br d, J=10 Hz, 7-H), 3.4—4.5 (6H, m, 1-H, 4-H, and $-CH_2CH_2-$), 4.79—5.34 (2H, m, isopropyl-CH × 2), 6.42 (1H, dd, J=3, 6 Hz, 5-H or 6-H), 6.74 (1H, dd, J=3, 6 Hz, 5-H or 6-H). MS *m/z*: 388 (M^+).

9b (More Polar): Colorless prisms (hexane–CH_2Cl_2), mp 148—150 °C. Yield, 2.79 g (72%). *Anal.* Calcd for $C_{17}H_{24}O_5S_2$: C, 52.55; H, 6.23; S, 16.51. Found: C, 52.37; H, 6.36; S, 16.75. IR ($CHCl_3$): 1730 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.25, 1.29 (6H each, d, J=6 Hz, isopropyl-Me × 2), 1.81—1.85 (2H, m, 7-2H), 3.20—4.47 (6H, m, 1-H, 4-H, and $-CH_2CH_2-$), 4.86—5.33 (2H, m, isopropyl-CH × 2), 6.36—6.42 (2H, m, 5-H and 6-H).

Dimethyl Bicyclo[2.2.1]heptane-2,2-dicarboxylate (10) A mixture of **4** (50 mg, 0.17 mmol) and Raney Ni (500 mg) in MeOH (5 ml) was shaken in hydrogen gas under atmospheric pressure at room temperature for 3 h. The catalyst was filtered off, and the filtrate was concentrated *in vacuo*. The residue was subjected to silica gel column chromatography. Elution with hexane–AcOEt (10 : 1) gave **10** as a colorless oil. Yield, 36 mg (100%). *Anal.* Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.20; H, 7.75. IR ($CHCl_3$): 1735 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.0—2.0 (7H, m, 3-H_{exo},

5-2H, 6-2H, 7-2H), 2.1—2.5 (2H, m, 3-H_{endo}, 4-H), 3.67, 3.85 (3H each, s, CO_2Me). MS *m/z*: 212 (M^+).

Dimethyl *endo*-Bicyclo[2.2.1]heptane-2,2-dicarboxylate-3-spiro-2′-(1′,3′-dithiethane 1′-oxide) (11) A mixture of **4** (274 mg, 0.91 mmol) and 5% Pd–C (50 mg) in MeOH (10 ml) was shaken in hydrogen gas under a pressure of 4 atm at room temperature for 5 h. The catalyst was filtered off, and the filtrate was concentrated *in vacuo*. The crystalline residue was purified by recrystallization from MeOH to give **11** as colorless prisms, mp 153—154 °C. Yield, 194 mg (70%). *Anal.* Calcd for $C_{12}H_{16}O_5S_2$: C, 47.37; H, 5.26; S, 21.05. Found: C, 47.34; H, 5.47; S, 21.05. IR ($CHCl_3$): 1730 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.2—2.4 (6H, m, 5-2H, 6-2H, 7-2H), 2.92 (1H, br s, 4-H), 3.31 (1H, br s, 1-H), 3.75, 3.83 (3H each, s, CO_2Me), 4.04 (2H, s, 4′-2H).

Dimethyl 3-Oxobicyclo[2.2.1]heptane-2,2-dicarboxylate (12) and Dimethyl 2-(3β-Carboxycyclopent-1β-yl)malonate (13) A 70% $HClO_4$ solution (1 ml) was added to a solution of **11** (40 mg, 0.13 mmol) in THF (3 ml) with ice-cooling. The mixture was allowed to stand at room temperature for 12 h. After evaporation of the solvent, the residue was extracted with $CHCl_3$. The $CHCl_3$ extract was washed with water, and dried over anhydrous Na_2SO_4. The solvent was evaporated off *in vacuo*, and the residue was subjected to silica gel (8 g) column chromatography. Elution with hexane–AcOEt (3 : 2) gave **12** (20 mg, 68%) as a colorless oil. Further elution with AcOEt gave **13** (5 mg, 16%) as a colorless oil.

12: High-resolution MS *m/z*: M^+ Calcd for $C_{11}H_{14}O_5$: 226.0842. Found: 226.0843. IR ($CHCl_3$): 1780, 1745 (sh), 1730 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.6—2.0 (6H, m, 5-2H, 6-2H, and 7-2H), 2.77 (1H, br s, 4-H), 3.26 (1H, br s, 1-H), 3.78 (6H, s, $CO_2Me \times 2$).

13: IR ($CHCl_3$): 3550—2300 (br), 1730 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.2—3.1 (8H, m), 3.35 (1H, d, J=10 Hz, malonyl-H), 3.74 (6H, s, $CO_2Me \times 2$), 7.8—8.7 (1H, br, $-CO_2H$).

Dimethyl 2-(3β-Hydroxymethylcyclopent-1β-yl)malonate (14) $NaBH_4$ (12 mg, 0.33 mmol) and K_2CO_3 (8 mg, 0.06 mmol) were added successively to a solution of **12** (10 mg, 0.04 mmol) in absolute. MeOH (0.5 ml) with stirring and ice-cooling. The mixture was stirred at room temperature for 5 h, then neutralized with AcOH–MeOH (1 : 1). After evaporation of the solvent, the residue was extracted with $CHCl_3$. The $CHCl_3$ extract was washed with water, and dried over anhydrous Na_2SO_4. The solvent was evaporated off *in vacuo* to give **14**[10] (6 mg, 62%). IR ($CHCl_3$): 1750 (sh), 1730 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.24 (1H, d, J=10 Hz, malonyl-H), 3.51 (2H, d, J=6 Hz, $-CH_2OH$), 3.77 (6H, s, $CO_2Me \times 2$).

Diisopropyl Bicyclo[2.2.1]heptane-2,2-dicarboxylate-3-spiro-2′-(1′,3′-dithiolane 1′,3′-dioxide) (15) A mixture of **9b** (200 mg, 0.52 mmol) and 5% Pd–C (50 mg) in MeOH (15 ml) was shaken in hydrogen gas under atmospheric pressure at room temperature for 2 h. The catalyst was filtered off, and the filtrate was concentrated *in vacuo*. The crystalline residue was purified by recrystallization from hexane–CH_2Cl_2 to give **15** as colorless prisms, mp 154—157 °C. Yield, 179 mg (89%). *Anal.* Calcd for $C_{17}H_{26}O_6S_2$: C, 52.28; H, 6.71; S, 16.42. Found: C, 52.41; H, 6.75; S, 16.25. IR ($CHCl_3$): 1730 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.26 (12H, d, J=6 Hz, isopropyl-Me × 4), 1.5—2.2 (6H, m, 5-2H, 6-2H, and 7-2H), 2.59 (1H, br s, 4-H), 3.14 (1H, br s, 1-H), 3.2—4.3 (4H, m, $-CH_2CH_2-$), 4.8—5.4 (2H, m, isopropyl-CH × 2). MS *m/z*: 390 (M^+).

Diisopropyl Bicyclo[2.2.1]heptane-2,2-dicarboxylate-3-spiro-2′-(1′,3′-dithiolane 1′-oxide) (16) A 20% aqueous solution of $TiCl_3$ (1.16 g, 1.5 mmol) was added to a mixture of **15** (390 mg, 1 mmol) in AcOH (5 ml), and the mixture was stirred at room temperature for 1 h. The reaction mixture was then concentrated *in vacuo*, and the residue was extracted with $CHCl_3$ (5 ml). The $CHCl_3$ extract was washed with 10% NaOH (3 ml × 2) and water (3 ml × 2) successively, and dried over anhydrous Na_2SO_4. After evaporation of the solvent *in vacuo*, the residue was subjected to silica gel (20 g) column chromatography. Elution with AcOEt gave **16** as colorless prisms (hexane–CH_2Cl_2), mp 112—113 °C. Yield, 80 mg (21%). *Anal.* Calcd for $C_{17}H_{26}O_5S_2$: C, 54.52; H, 7.00; S, 17.12. Found: C, 54.48; H, 7.12; S, 17.00. IR ($CHCl_3$): 1725 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.1—2.0 (6H, m, 5-2H, 6-2H, and 7-2H), 1.25, 1.28 (6H each, d, J=7 Hz, isopropyl-Me × 2), 2.7—3.8 (6H, m, 1-H, 4-H, and $-CH_2CH_2-$), 5.01 (2H, h, J=7 Hz, isopropyl-CH × 2).

Diisopropyl 3-Oxobicyclo[2.2.1]heptane-2,2-dicarboxylate (17) $HgCl_2$ (160 mg, 0.59 mmol) was added to a solution of **16** (55 mg, 0.15 mmol) in THF–concentrated HCl (4 : 1, 2 ml) with ice-cooling. The mixture was stirred at room temperature for 4 h, and then at 45 °C for 3 h. After evaporation of the solvent, the residue was extracted with AcOEt (5 ml). The AcOEt extract was washed with water (3 ml × 2), and dried over anhydrous Na_2SO_4. The solvent was evaporated off *in vacuo*, and the resulting residue was subjected to silica gel (15 g) column chromatography. Elution with hexane–AcOEt (7 : 3) gave **17** as a colorless oil. Yield, 30 mg (72%). High-resolution MS *m/z*: M^+ Calcd for $C_{15}H_{22}O_5$: 282.1467. Found: 282.1465. IR ($CHCl_3$): 1775, 1730 (sh), 1720 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.23 (12H, d, J=6 Hz, isopropyl-Me × 4), 1.6—2.1 (6H, m, 5-2H, 6-2H, 7-2H), 2.68 (1H, br s, 4-H), 3.20 (1H, br s, 1-H), 5.05, 5.08 (1H each, h, J=6 Hz, isopropyl-CH).

Diisopropyl 3-*endo*-Hydroxybicyclo[2.2.1]heptane-2,2-dicarboxylate (18) $NaBH_4$ (13 mg, 0.35 mmol) was added to a solution of **17** (20 mg, 0.07 mmol) in absolute MeOH with stirring and ice-cooling. The mixture was stirred at room temperature for 1 h. The reaction mixture was neutralized with AcOH–MeOH (1 : 1), and concentrated *in vacuo*. The residue was extracted with Et_2O (3 ml). The Et_2O extract was washed with water (3 ml × 2), and dried over anhydrous Na_2SO_4. The solvent was evaporated off to give **18** as a colorless oil. Yield, 20 mg (99%). High-resolution MS *m/z*: M^+ Calcd for $C_{15}H_{24}O_5$: 284.1624. Found: 284.161. ^{1}H-NMR ($CDCl_3$) δ: 1.25 (12H, d, J=6 Hz, isopropyl-Me × 4), 1.0—1.8 (6H, m, 5-2H, 6-2H, 7-2H), 2.88 (1H, br s, 4-H), 2.83 (1H, br s, 1-H), 4.25 (1H, dd, J=7, 7.5 Hz, 3-H), 5.07, 5.13 (1H each, J=6 Hz, isopropyl-CH × 2), 5.47 (1H, d, J=7 Hz, OH).

Diisopropyl 2-(3β-Hydroxymethylcyclopent-1β-yl)malonate (19) $NaBH_4$ (20 mg, 0.53 mmol) and K_2CO_3 (20 mg, 0.14 mmol) were added successively to a solution of **18** (15 mg, 0.05 mmol) in absolute MeOH (1.0 ml) with stirring and ice-cooling. The mixture was stirred at room temperature for 3 h, and then neutralized with AcOH–MeOH (1 : 1). The resulting mixture was concentrated *in vacuo*, and the residue was extracted with Et_2O (3 ml). The Et_2O extract was washed with water (3 ml × 2), and dried over anhydrous Na_2SO_4. The solvent was evaporated off *in vacuo* to give **19** as a colorless oil. Yield, 15 mg (99%). High-resolution MS *m/z*: M^+ Calcd for $C_{15}H_{26}O_5$: 286.1781. Found: 286.1799. IR ($CHCl_3$): 1740 (sh), 1720 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.9—2.8 (8H, m), 1.24 (12H, d, J=6 Hz, isopropyl-Me × 4), 2.10 (1H, s, OH), 3.17 (1H, d, J=10 Hz, malonyl-H), 3.55 (2H, d, J=6 Hz, $-C\underline{H}_2OH$), 5.06 (2H, h, J=6 Hz, isopropyl-CH × 2).

Di-*l*-menthyl 1,3-Dithiethan-2-ylidenemalonate 1-Oxide (20 and 21) A solution of **1c** (700 mg, 1.5 mmol) and *m*-CPBA (518 mg, 3 mmol) in CH_2Cl_2 (10 ml) was allowed to stand at room temperature for 12 h. The mixture was washed with 5% $NaHCO_3$ and water successively. The organic layer was dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was subjected to silica gel (35 g) column chromatography. Elution with hexane–AcOEt (9 : 1) gave **1c** (160 mg, 22% recovery) and **22** (80 mg, 10%) successively. Further elution with hexane–AcOEt (5 : 1) gave a mixture of **20** and **21** (1 : 1, 500 mg, 68%). The mixture was rechromatographed on silica gel (30 g), and elution with hexane–AcOEt (10 : 1) gave **20** and **21** successively.

20 (1*S*, Less Polar): Colorless viscous oil. $[\alpha]_D^{22}$ −165.0° (c=0.5, $CHCl_3$). High-resolution MS *m/z*: $M^+ - O$ Calcd for $C_{25}H_{40}O_4S_2$: 468.2368. Found: 468.2362. IR ($CHCl_3$): 1725, 1690, 1665 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 4.25 (1H, d, J=10 Hz, –S–C$\underline{H}$H–), 4.33 (1H, d, J=10 Hz, –S–CH$\underline{H}$–), 4.81, 4.85 (1H each, dt, J=5, 10 Hz, menthyl 1-H).

21 (1*R*, More Polar): Colorless viscous oil. $[\alpha]_D^{23}$ −110.3° (c=1.3, $CHCl_3$). High-resolution MS *m/z*: $M^+ - O$ Calcd for $C_{25}H_{40}O_4S_2$: 468.2368. Found: 468.2365. IR ($CHCl_3$): 1725, 1685, 1660 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 4.21 (1H, d, J=10 Hz, –S–C$\underline{H}$H–), 4.32 (1H, d, J=10 Hz, –S–CH$\underline{H}$–), 4.83, 4.92 (1H each, dt, J=5, 10 Hz, menthyl-H).

22: Colorless needles (MeOH), mp 114—116 °C. $[\alpha]_D^{24}$ −89.2° (c=0.5, $CHCl_3$). *Anal.* Calcd for $C_{25}H_{40}O_6S_2$: C, 59.97; H, 8.05; S, 12.81. Found: C, 60.30; H, 7.96; S, 12.90. IR ($CDCl_3$): 1730, 1670 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 4.7—5.0 (2H, m, menthyl 1-H), 5.10 (2H, s, $-CH_2-$). MS *m/z*: 500 (M^+).

Di-*l*-menthyl 1,3-Dithiethan-2-ylidenemalonate 1,1-Dioxide (22) A mixture of mono-oxide (**20** and **21**, 1 : 1, 97 mg, 0.2 mmol) and *m*-CPBA (69 mg, 0.4 mmol) was placed in a Teflon tube (1.2 ml) equipped with a Teflon stopper. The tube was filled with CH_2Cl_2, and pressurized at 10 kbar for 10 h. The pressure was released, and the reaction mixture was subjected to silica gel column chromatography. Elution with hexane–AcOEt (9 : 1) gave **22** (28 mg, 28%).

Asymmetric Diels–Alder Reaction of 20 or 21 with Cyclopentadiene 1) At Atmospheric Pressure: A solution of **20** or **21** and excess cyclopentadiene was allowed to stand at room temperature for 2 d. After evaporation of the excess cyclopentadiene *in vacuo*, the residue was subjected to silica gel column chromatography. After initial elution with hexane, elution with hexane–AcOEt (8 : 1) gave **24** and **25** (or **29** and **30**) successively in quantitative total yield. The ratio of *endo* (**24** and **29**) to *exo* (**25** or **30**) product was 12 : 1.

24: Viscous oil. High-resolution MS *m/z*: M^+ Calcd for $C_{30}H_{46}O_5S_2$:

550.2787. Found: 550.2771. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 3.42 (1H, br s, 4-H), 3.70 (1H, br s, 1-H), 3.97 (1H, d, J=8 Hz, 4'-H_a), 4.01 (1H, d, J=8 Hz, 4'-H_b), 4.74 (1H, dt, J=5, 10 Hz, menthyl 1-H), 4.75 (1H, dt, J=5, 10 Hz, menthyl 1-H), 6.07 (1H, dd, J=6, 3 Hz, 5-H), 6.59 (1H, dd, J=6, 3 Hz, 6-H).

25: Viscous oil. High-resolution MS m/z: M^+ Calcd for $C_{30}H_{46}O_5S_2$: 550.2787. Found: 550.2769. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 3.41 (1H, br s, 4-H), 3.82 (1H, br s, 1-H), 3.91 (1H, d, J=8 Hz, 4'-H_a), 3.93 (1H, d, J=8 Hz, 4'-H_b), 4.54 (1H, dt, J=5, 10 Hz, menthyl 1-H), 4.81 (1H, dt, J=5, 10 Hz, menthyl 1-H), 6.21 (1H, dd, J=6, 3 Hz, 5-H), 6.53 (1H, dd, J=6, 3 Hz, 6-H).

29: Viscous oil. High-resolution MS m/z: M^+ Calcd for $C_{30}H_{46}O_5S_2$: 550.2787. Found: 550.2790. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 3.41 (1H, br s, 4-H), 3.68 (1H, br s, 1-H), 3.97 (2H, s, –S–CH_2–), 4.61 (1H, dt, J=5, 10 Hz, menthyl 1-H), 4.65 (1H, dt, J=5, 10 Hz, menthyl 1-H), 5.97 (1H, dd, J=6, 3 Hz, 5-H), 6.61 (1H, dd, J=6, 3 Hz, 6-H).

30: Viscous oil. High-resolution MS m/z: M^+ Calcd for $C_{30}H_{46}O_5S_2$: 550.2787. Found: 550.2797. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 3.43 (1H, br s, 4-H), 3.86 (1H, br s, 1-H), 3.90 (1H, d, J=8 Hz, 4'-H_b), 4.61 (1H, dt, J=5, 10 Hz, menthyl 1-H), 4.85 (1H, dt, J=5, 10 Hz, menthyl 1-H), 6.40 (1H, dd, J=6, 3 Hz, 5-H), 6.47 (1H, dd, J=6, 3 Hz, 6-H).

2) At High Pressure (10 kbar): A mixture of **20** (or **21**) and cyclopentadiene was placed in a Teflon tube (1.2 ml) equipped with a Teflon stopper. The tube was filled with toluene, and pressurized at 10 kbar for 5 h. The pressure was released, and the reaction mixture was concentrated *in vacuo*. Work up as above gave **24** and **25** (or **29** and **30**) in quantitative total yield. The ratio of *endo* (**24** or **29**) to *exo* (**25** or **30**) products was 9 : 1.

Di-*l*-menthyl [1*S*,4*R*]-Bicyclo[2.2.1]heptane-2,2-dicarboxylate (26) A mixture of **24** (80 mg, 0.15 mmol) and Raney Ni (500 mg) in MeOH (5 ml) was shaken in hydrogen gas under atmospheric pressure at room temperature for 5 h. The catalyst was filtered off, and the filtrate was concentrated *in vacuo*. The residue was subjected to silica gel column chromatography. Elution with hexane–AcOEt (15 : 1) gave **26** as colorless needles (MeOH), mp 125—127 °C (lit.[11] mp 123—126 °C).

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References and Notes

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