Synthesis and Asymmetric Diels–Alder Reaction of Dimethyl ('*d*-Isoborneol-10-sulphinyl')maleate: Novel Route to Key Intermediates for Synthesis of Some Carbocyclic Nucleosides and Terpenoids

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The chiral sulphoxide **1** was synthesized from 10-mercaptoisoborneol *via* diastereoselective oxidation. The dienophile **1** reacted with cyclopentadiene in the presence of a Lewis acid to give the adducts **7** and **8** with high diastereoselectivity (~100%). Diels–Alder reaction of **1** in the absence of a Lewis acid afforded the adduct **9** as the major product with reversed diastereoselectivity. The adduct **7** was transformed into a useful precursor **11** for synthesis of carbocyclic nucleosides. The adducts **7** and **9** were converted into a bridged bicyclic lactone **21** in an enantiodivergent manner *via* selective reduction followed by reaction with samarium diiodide.

Chiral sulphoxides are important tools for asymmetric reactions.[1] For the preparation of chiral sulphoxides, the Andersen method, which involves reaction of (−)-menthyl toluene-*p*-sulphinate with an appropriate organometallic reagent,[2] has been widely employed. However, the method is not very convenient for the preparation of sulphoxides with labile functional groups. In most cases this method entailed tedious steps, in contrast to the synthesis of the corresponding racemates. Therefore, wide access to asymmetric reactions by the use of chiral sulphoxides has been impeded by lack of a convenient preparation of a variety of these sulphoxides. In order to solve this problem, we investigated the '*d*-isoborneol-10-sulphinyl' moiety† as a candidate chiral auxiliary, instead of toluene-*p*-sulphinyl group. The cyclic hemithioacetal derivatives of 10-mercaptoisoborneol[3] have been used as Eliel's templates[4] for asymmetric synthesis. Recently, utility of (−)-10-mercaptoisoborneol as a resolution tool for 1,4-addition to 4-substituted cyclopentenones has been reviewed[5] as well as its use as a catalyst in asymmetric oxidation[6] and as a chiral auxiliary for efficient dienophiles in asymmetric Diels–Alder reactions.[7,8]

In preliminary reports we have already introduced a convenient preparation and the asymmetric Diels–Alder reaction of dimethyl (R_S)-(*d*-isoborneol-10-sulphinyl)maleate **1**.[8,‡] Herein we describe, in detail, the Diels–Alder cycloaddition of the dienophile **1** with cyclopentadiene and its application to the synthesis of useful precursors for natural product synthesis.

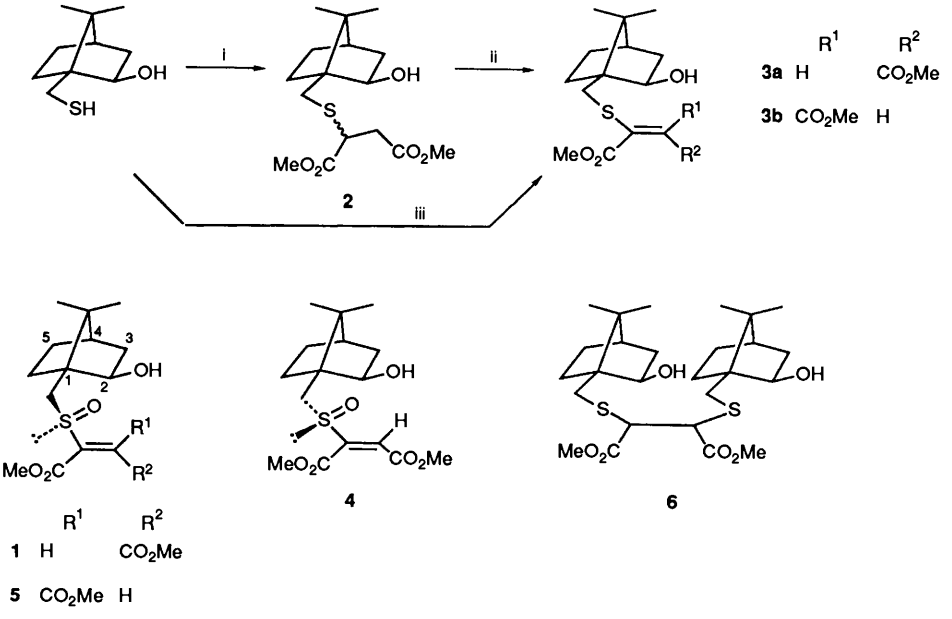
Results and Discussion

Following the method of preparation previously reported for sulphenylation of maleates,[9] we examined the nucleophilic addition of 10-mercaptoisoborneol to dimethyl maleate. The sulphenyl succinate **2** was obtained as a diastereoisomeric mixture in good yield (Scheme 1). Heating of compound **2** with *N*-chlorosuccinimide (NCS) in refluxing carbon tetrachloride afforded the diesters **3a** and **3b** in the ratio 1:2.7 in 31% yield from 10-mercaptoisoborneol. A more satisfactory route to the sulphoxide **1** was explored. Treatment of 10-mercaptoisoborneol with dimethyl acetylenedicarboxylate (DMAD) in the presence of methyl(diphenyl)phosphine[10] (room temp., 12 h) produced a mixture of isomers **3a** and **3b** in 74 and 19% yield, respectively. The use of triethylamine as base[9] in the reaction gave the fumarate **3b** as the major product. The major isomer **3a** was easily separated from the minor one **3b** by silica gel column chromatography. Structural assignments of compounds **3a** and **3b** were made by analogy to the results reported previously:[9] in the ^{1}H NMR spectrum, the olefinic proton in fumarate **3b** was more deshielded than that in maleate **3a**, due to the 3-methoxycarbonyl group. Oxidation of the sulphide **3a** with 3-chloroperbenzoic acid (MCPBA, 1.03 mol equiv.) afforded the sulphoxide **1** in 89% yield. As expected,[11] the diastereoselective oxidation reflects the directing influence of the secondary hydroxy group in the bornyl residue. The absolute configuration (R_S) of the sulphinyl centre in compound **1** can be deduced tentatively from the previous results on the oxidation of '*d*-isoborneol-10-sulphides'.[12] On the other hand we also examined the oxidation of the fumarate **3b** with MCPBA in a similar manner. Surprisingly, this reaction afforded the same sulphoxide **1** exclusively in high yield. The reason for the isomerisation of the double-bond geometry under these conditions is not at present obvious. In each case, the diastereoisomeric sulphoxide **4** was obtained as the minor product. However, no other sulphoxide, such as **5**, could be detected by ^{1}H NMR spectroscopy of the crude oxidation products. Therefore separation of maleate **3a** from fumarate **3b** was unnecessary. Accordingly, the sulphoxide **1** was obtained in 67% yield by treatment of a mixture of compounds **3a** and **3b** with MCPBA.

The results of the Diels–Alder reaction of compound **1** with cyclopentadiene are summarised in Table 1. In the presence of a zinc salt as a promoter, the reaction proceeded with high diastereoselectivity and produced the adduct **7** as the major product. The *exo* configuration of the sulphinyl group in adduct **7** was confirmed by ^{1}H NMR spectroscopy. The 3-H proton of adduct **7** resonanced at δ 2.68 as a doublet, coupled with the 4-H bridgehead proton (J 3 Hz). On the other hand the 3-H proton of the minor adduct **8** appeared at δ 3.17 as a singlet. The relative configuration of the sulphinyl group in adduct **8** was thus *endo*. The stereochemistry of adduct **7** could be assigned based upon the reaction mechanism we proposed previously.[13] Since the spectroscopic data were of less help in

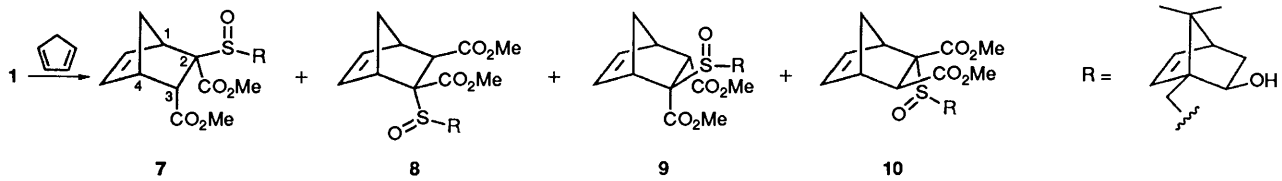
† '*d*-Isoborneol-10-sulphinyl' = {(1*S*,2*R*,4*R*)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methylsulphinyl.

‡ The symbol (R_S) given in this text indicates that the chirality at the sulphur is *R*.



Scheme 1 *Reagents:* i, Dimethyl maleate; ii, NCS; iii, DMAD, Ph_2PMe

Table 1 Diels–Alder reaction of **1** with cyclopentadiene



7 **8** **9** **10**

Entry	Lewis acid[a]	Solvent	Temp. (T/°C)	Time (t/h)	Product proportions[b] **7**:**8**:**9**:**10**	Yield (%)
1	$ZnCl_2$	CH_2Cl_2	0	2	7:1:0:0	69
2	$ZnCl_2$	Toluene	−20	24	8.8:1:0:0	*c*
3	$ZnCl_2$	CH_2Cl_2	−20	2.5	15.3:1:0:0	92
4	$ZnCl_2$	CH_2Cl_2	−50	22	8.2:1:0:0	*c*
5	$ZnBr_2$	CH_2Cl_2	−20	20	6.2:1:0:0	*c*
6	Et_2AlCl	CH_2Cl_2	−20	22	3:1:0:0	*c*
7	None	CH_2Cl_2	25	19	1:0:11.7:2.2	87

[a] 1.5 Mol equiv. of Lewis acid was used. [b] Proportions were determined by integration of the olefinic signals of the crude product in the ^1H NMR spectra. [c] Yields were not determined. No starting material **1** was detected in the ^1H NMR spectrum of the crude product.

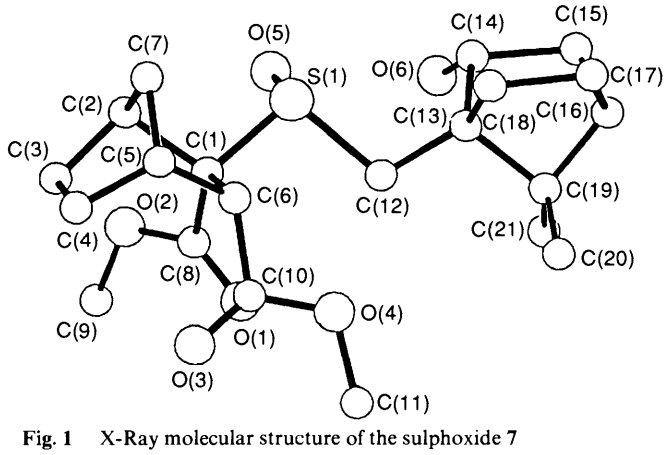
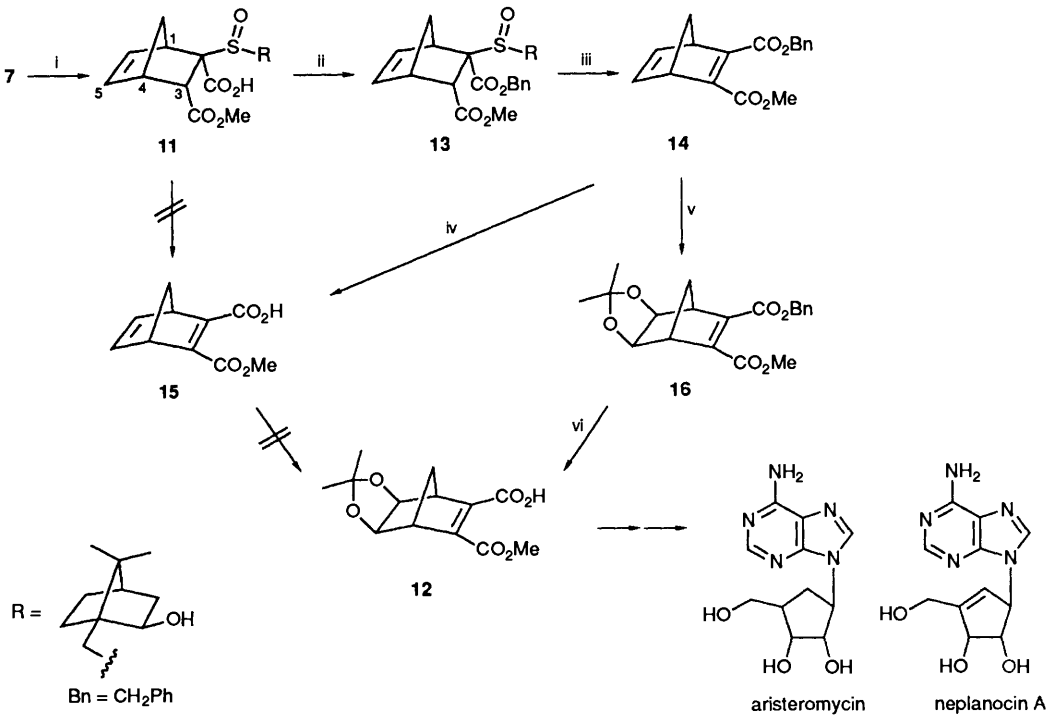


Fig. 1 X-Ray molecular structure of the sulphoxide **7**

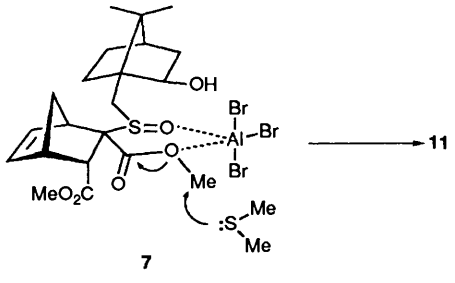
determining the absolute structure of the adducts, single-crystal X-ray analysis of adduct **7** was performed for unambiguous structural confirmation of this product. The X-ray structure is shown in Fig. 1. Full details of the crystal structure determination have been published elsewhere.[8a]

In contrast, in the absence of a Lewis acid the reaction produced the adduct **9** as the major diastereoisomer. The minor product **10** was easily separated from compound **9** by column chromatography. In the ^1H NMR spectrum the 3-H protons of isomers **9** and **10** appeared at δ 3.69 and 3.09, respectively. The latter signal coupled with the 7-H proton with a W-*letter* coupling (J 1.8 Hz). The configuration of the sulphinyl group in adduct **10** was therefore assigned as *endo*.

Having the adduct **7** in hand, we undertook the manipulation which differentiated the two ester groups in this adduct before removal of the chiral auxiliary (Scheme 2). For this purpose, selective hydrolysis seemed to be attractive. Some attempts at discrimination of the two esters by selective transesterification with titanium tetraisopropoxide and alcohol[14] proved to be unsuccessful. Demethylation of adduct **7** with $AlBr_3$–Me_2S[15] was accomplished to give the half-ester **11** in 71% yield. One possible explanation of the selectivity in this demethylation process may be that the aluminium atom can co-ordinate with the two oxygens, *i.e.* the sulphinyl oxygen and the methoxycarbonyl. Thus, dimethyl sulphide would attack the methyl group in the chelated methoxycarbonyl to give the half-ester **11**.



Scheme 2 *Reagents and yields:* i, $AlBr_3$, Me_2S, CH_2Cl_2, 71%; ii, BnBr, NaH, 18-crown-6, MeCN, 86%; iii, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), C_6H_6, 90%; iv, $AlCl_3$, Me_2S, $MeNO_2$, CH_2Cl_2, 89%; v, OsO_4 (cat.), Me_3NO, Me_2CO, Bu^{t}OH; 2,2-dimethoxypropane, PTSA (cat.), Me_2CO, 70%; vi, 5% Pd–C, cyclohexa-1,3-diene (1.2 mol equiv.), MeOH, 80%

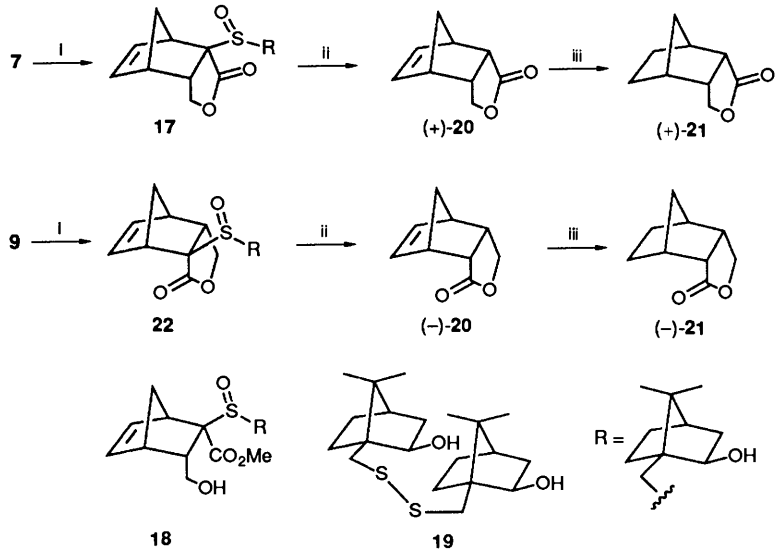


A combination of $AlBr_3$ and ethanethiol[16] produced a diacid exclusively. To determine the structure of half-ester **11**, we tried to transform this compound into Ohno's half-ester, a chiral precursor **12** for the synthesis of carbocyclic nucleosides.[17] Several attempts at elimination of the sulphinyl group in compound **11** to give the trinorbornadiene **15** by treatment with base or by heating were unfruitful. However, desulphinylation of the benzyl ester **13**, which was derived from half-ester **11** by benzylation (benzyl bromide–NaH–18-crown-6, MeCN; 50 °C; 12 h),[18] proceeded to give the trinorbornadiene **14** in 90% yield. Deprotection of the benzyl group in diester **14** with $AlCl_3$–dimethyl sulphide[19] gave the half-ester **15**, {$[\alpha]_D^{27}$ +28.0° (*c* 0.67, $CHCl_3$)}, in 89% yield. Although transformation of compound **15** into precursor **12** through selective *cis*-hydroxylation failed, catalytic osmylation of diester **14** and subsequent acetonidation afforded the dioxole **16** in 70% yield. The benzyl group was removed by a standard method (H_2/Pd–C) to give the desired half-ester **12** in poor yield. Under the conditions substantial amounts of the saturated ester were produced. Treatment of diester **16** with cyclohexa-1,3-diene (Pd–C)* afforded the half-ester **12**, m.p. 117–118 °C; $[\alpha]_D^{25}$ −29.5° (*c* 1.2, $CHCl_3$) {lit.,[17] $[\alpha]_D^{25}$ −23.8° (*c* 1.17, $CHCl_3$)}, which has been converted into (−)-neplanocin A and (−)-aristeromycin,[17] in 80% yield. The enantiomeric excess (e.e.) of compound **12** was shown to be 92%, judging from the diastereoisomeric excess (d.e.) of its L-α-phenylethylamine derivatives determined by 270 MHz ^{1}H NMR spectroscopy of the two singlets of the methoxycarbonyl groups (δ 3.76 and 3.82). The absolute configuration of compound **11** is thus shown as depicted in Scheme 2.

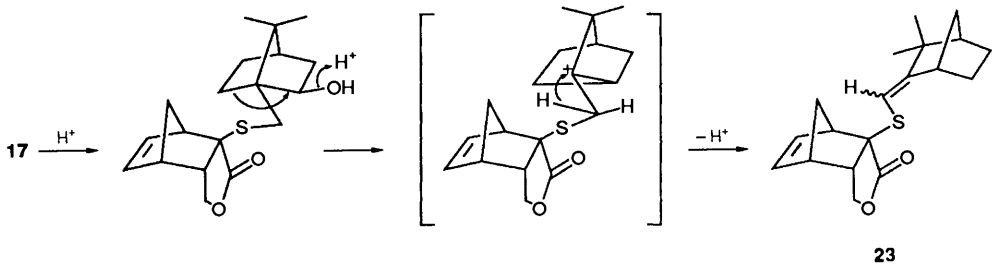
The utility of the asymmetric Diels–Alder reaction using the dienophile **1** was further exemplified by transformation of the adducts **7** and **9** into a useful precursor **21**[21,22] for natural product synthesis in an enantiodivergent manner (Scheme 3). Jones reported the transformation of a racemic diol into the (+)-lactone **21** by enzymatic oxidation.[21] Recently both enantiomers of lactone **21** were synthesized starting from D-mannitol, and were employed as chiral synthons for the synthesis of terpenoids.[22]

Reaction of compound **7** with 4 mol equiv. of diisobutylaluminium hydride (DIBAL) at −78 to 0 °C gave the lactone **17** in 61% yield. When the reaction was carried out with lower amounts (2.2–3.5 mol equiv.) of the reducing agent at −78 °C with shorter reaction times, the ester alcohol **18** was also obtained, in substantial yield. To remove the sulphinyl group in compound **17**, several reagents were examined. Deoxygenation of the sulphinyl group with titanium(III) chloride[23] in ethanol resulted only in recovery of the starting material **17**. Using either phosphorus tribromide[24] or zinc–acetic acid,[25] the deoxygenation proceeded smoothly, but was accompanied by concomitant skeletal rearrangement of the bornyl residue (Scheme 4). Although this product **23** could be transformed into the lactone **20** by the action of an appropriate reducing agent such as Raney Ni or an amalgamated metal, the recovery of the chiral auxiliary was difficult without concomitant alternation of the carbon framework also taking place. This impasse was finally solved by the use of samarium(II) iodide.[26] Treatment of compound **17** with SmI_2 and t-butyl alcohol

* The use of other olefins as hydrogen acceptors resulted in poor yields.[20]



Scheme 3 *Reagents:* i, DIBAL (4 mol equiv.), toluene; ii, SmI_2 (5 mol equiv.), THF, Bu^{t}OH (1 mol equiv.); iii, H_2, 5% Pd–C, EtOH



Scheme 4

(room temp.; 10 min) gave the lactone **20** in up to quantitative yield. At this stage the chiral auxiliary, 10-mercaptoisoborneol, could be recovered in high yield. Without t-butyl alcohol as a proton source, the disulphide **19**[27] was produced predominantly. In his pioneering studies Molander reported that Sm-induced reduction of the sulphinyl group attached to a quaternary carbon atom such as 2-methyl-2-(phenylsulphinyl)-cyclohexanone gave a complex mixture of products.[26] However, in our case, the reaction was very clean. Hydrogenation of lactone **20** furnished the (+)-lactone **21**, whose spectral and chiroptical characteristics were identical with those of compound **21** previously reported.[22] In a similar manner to the preparation of sulphoxide **17**, selective reduction of compound **9** followed by removal of the sulphinyl group and hydrogenation provided the (−)-lactone **21** in 88% yield.

In summary, the Diels–Alder reaction of dimethyl ('*d*-isoborneol-10-sulphinyl')maleate with cyclopentadiene provides adducts with a high degree of diastereoselectivity. The manipulation of the functionality of these adducts and the subsequent removal of the chiral auxiliary should prove to be a new reaction tool in natural product synthesis.

Experimental

M.p.s were taken with a YANACO micro melting-point apparatus and are uncorrected. IR spectra were measured as films, on KBr discs, or in chloroform solution on a JASCO A-102 spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL PMX 60SI or a JEOL GX-270 (270 MHz) spectrometer with deuteriochloroform as solvent; *J*-values are in Hz. Tetramethylsilane was used as internal standard. Mass spectra were recorded with a JEOL JMS-D 200 spectrometer. Optical rotations were measured on a JASCO DIP-140 digital polarimeter for samples in chloroform solution.

All organometallic and low-temperature reactions were carried out in oven-dried glassware under a slight positive pressure of argon. All solvents were distilled prior to use. Dry tetrahydrofuran (THF) was freshly distilled from sodium–benzophenone ketyl. Dry methylene dichloride was distilled from phosphorus pentaoxide and stored with molecular sieves 4 Å. Ether refers to diethyl ether. The combined organic extracts were dried over anhydrous magnesium sulphate which was later removed by filtration. Column chromatography was performed with Nakarai Chemicals 70–230 mesh silica gel. Merck pre-coated thin-layer silica $PF60_{254}$ plates were used for monitoring of the reactions. Visualisation of TLC plates was achieved by UV irradiation and/or by phosphomolybdic acid. Medium-pressure liquid chromatography (MPLC) was performed with an FMI pump on Nakarai 230–400 mesh silica gel. Analytical HPLC was carried out on a Waters Associates 6000A pump or a Shimadzu LC-6A pump by using a 5 μ-Develosil 60 column and by monitoring of the 254 nm. Peak ratios on HPLC were measured with a Shimadzu integrator (Chromatopac C-R3A).

Dimethyl 2-({(1S,2R,4R)-2-Hydroxy-7,7-dimethylbicyclo-[2.2.1]heptan-1-yl}methylthio)maleate **3a**.—To an ice-cold solution of 10-mercaptoisoborneol (903 mg, 4.9 mmol) in dry benzene (10 cm^3) was added one drop of triethylamine and then dimethyl maleate (0.74 cm^3, 5.1 mmol). The mixture was stirred at room temp. for 18 h. After dilution with $CHCl_3$ (20 cm^3) the organic layer was washed successively with saturated aq. NH_4Cl and brine, and dried. The extract was concentrated and the crude product **2** was used in the next step. The ^{1}H NMR

spectrum of the crude product showed a 4:1 mixture of compound **2** and dimethyl maleate.

To a suspension of NCS (786 mg, 5.9 mmol) in CCl_4 (30 cm^3) cooled to *ca.* 0 °C was added dropwise a solution of the crude product **2** in CCl_4 (30 cm^3). After an additional 10 min the mixture was heated to reflux for 12 h. The reaction mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was purified by chromatography [hexane–AcOEt (4:1)] on silica gel to give the *maleate* **3a** (560 mg, 35%) and the *fumarate* **3b** (176 mg, 11%).

Compound **3a**. M.p. 126–127 °C (from CCl_4) (Found: C, 58.5; H, 7.3. $C_{16}H_{24}O_5S$ requires C, 58.51; H, 7.37%); $[\alpha]_D^{26}$ −8.8° (*c* 1.0); ν_{max}(KBr)/cm^{-1} 3300, 2950, 1730, 1380 and 1260; δ_H 0.88 (3 H, s, Me), 1.08 (3 H, s, Me), 1.1–1.8 (7 H, m), 2.15 (1 H, br, OH), 2.76 (1 H, d, *J* 10.6, SCH), 3.10 (1 H, d, *J* 10.6, SCH), 3.72 (3 H, s, OMe), 3.86 (1 H, m, C*H*OH), 3.89 (3 H, s, OMe) and 5.78 (1 H, s, CH=); *m/z* 328 (M^+), 310, 295, 267, 176 and 144.

Compound **3b**. An oil (Found: M^+, 328.1350. $C_{16}H_{24}O_5S$ requires M, 328.1345); $[\alpha]_D^{25}$ +27.2° (*c* 1.3); ν_{max}(neat)/cm^{-1} 3500, 2950, 1730, 1380 and 1250; δ_H 0.83 (3 H, s, Me), 1.05 (3 H, s, Me), 1.1–1.8 (8 H, m), 2.90 (1 H, d, *J* 11.2, SCH), 3.05 (1 H, d, *J* 11.2, SCH), 3.78 (3 H, s, OMe), 3.88 (3 H, s, OMe), 4.0 (1 H, m, C*H*OH) and 6.53 (1 H, s, CH=); *m/z* 328 (M^+), 310, 295, 267, 176 and 144.

Improved Procedure for Preparation of Compound **3a**.—To a solution of DMAD (4.00 g, 28 mmol) and methyl(diphenyl)-phosphine (0.03 cm^3) in dry MeCN (30 cm^3) at ~0 °C was added dropwise 10-mercaptoisoborneol (5.00 g, 27 mmol) in dry MeCN (30 cm^3). After an additional 20 min, the mixture was kept at room temp. for 12 h. After removal of the solvent the reaction mixture was taken up with CH_2Cl_2 (50 cm^3). The organic layer was washed with 10% HCl, dried and concentrated. The residue was purified by MPLC on silica gel [hexane–AcOEt (4:1) as eluent] to give compounds **3a** and **3b** (8.23 g, 93%) in the ratio 4:1.

The inverse addition of DMAD to 10-mercaptoisoborneol resulted in the formation of a small amount of compound **6**.

Dimethyl (R_S)-2({(1S,2R,4R)-2-*Hydroxy*-7,7-*dimethylbicyclo*[2.2.1]*heptan*-1-*yl*}*methylsulphinyl*)*maleate* **1**.—To a solution of compounds **3a** and **3b** (442 mg, 1.3 mmol) in dry CH_2Cl_2 (10 cm^3) at ~0 °C was added dropwise a solution of MCPBA (80% purity; 305 mg, 1.4 mmol) in dry CH_2Cl_2 (10 cm^3). The mixture was stirred for 3 h at ~0 °C and was washed successively with dil. sodium thiosulphate, 20% aq. sodium hydroxide and brine. After being dried, the organic layer was concentrated under reduced pressure. The residual oil was chromatographed on silica gel [hexane–AcOEt (3:1)] to give compounds **1** and **4** in 89 and 3% yield, respectively.

Compound **1**. A pale yellow oil (Found: M^+, 344.1249. Calc. for $C_{16}H_{24}O_6S$: M, 344.1292); $[\alpha]_D^{25}$ +32.8° (*c* 3.1); ν_{max}($CHCl_3$)/cm^{-1} 3470, 2960, 1730, 1380 and 1260; δ_H 0.84 (3 H, s, Me), 1.07 (3 H, s, Me), 1.1–1.8 (7 H, m), 2.90 (1 H, d, *J* 13, SCH), 3.17 (1 H, d, *J* 13, SCH), 3.86 (3 H, s, OMe), 3.89 (3 H, s, OMe), 4.10 (1 H, m, C*H*OH) and 6.98 (1 H, s, CH=); *m/z* 344 (M^+), 328, 310, 144 and 108.

Compound **4**. A pale yellow oil (Found: M^+, 344.1264. $C_{16}H_{24}O_6S$ requires M, 344.1292); $[\alpha]_D^{27}$ −34.2° (*c* 0.4); ν_{max}($CHCl_3$)/cm^{-1} 3470, 2960 and 1730; δ_H 0.83 (3 H, s, Me), 1.06 (3 H, s, Me), 1.1–1.8 (7 H, m), 2.62 (1 H, d, *J* 13.8, SCH), 3.57 (1 H, d, *J* 13.8, SCH), 3.83 (3 H, s, OMe), 3.85 (4 H, br s, OMe and C*H*OH) and 7.00 (1 H, s, CH=); *m/z* 344 (M^+), 328, 310, 279 and 144.

Diels–Alder Reaction of Compound **1** *with Cyclopentadiene in the Presence of Zinc Chloride*.—To a suspension of compound **1** (2.300 g, 6.7 mmol) and zinc chloride (1.36 g, 10 mmol) in dry CH_2Cl_2 (50 cm^3) at −20 °C was added freshly distilled cyclopentadiene (5.5 cm^3, 67 mmol). After being stirred at that temperature for 2 h, the mixture was poured onto cold 1 mol dm^{-3} hydrochloric acid. The aq. layer was extracted with CH_2Cl_2 (3 × 20 cm^3). The combined organic phase was washed with brine, dried and evaporated under reduced pressure. The residual oil was chromatographed on silica gel. Elution with hexane gave cyclopentadiene dimer. Elution with hexane–AcOEt (2:1 ⟶ 1:2) gave the *adducts* **7** (2.359 g, 86%) and **8** (0.153 g, 5.6%).

Compound **7**. M.p. 126–127 °C (from hexane–AcOEt) (Found: C, 61.6; H, 7.4. $C_{21}H_{30}O_6S$ requires C, 61.44; H, 7.37%); $[\alpha]_D^{25}$ +36.8° (*c* 1.2); ν_{max}(KBr)/cm^{-1} 3450, 2950, 1755, 1720 and 1030; δ_H 0.87 (3 H, s, Me), 1.08 (3 H, s, Me), 1.2–1.9 (9 H, m), 2.68 (1 H, d, *J* 3, $CHCO_2$), 2.88 (1 H, d, *J* 13.7, SCH), 3.21 (1 H, br s, 1- or 4-H), 3.23 (1 H, d, *J* 13.7, SCH), 3.59 (1 H, d, *J* 3, OH), 3.7 (1 H, br, 4- or 1-H), 3.71 (3 H, s, OMe), 3.77 (3 H, s, OMe), 4.05 (1 H, m, C*H*OH), 6.19 (1 H, dd, *J* 5.5, 3.2, CH=) and 6.67 (1 H, dd, *J* 5.5, 3.0, CH=); *m/z* 379 (M^+ − 31) and 361.

Compound **8**. M.p. 159–160 °C (from hexane–AcOEt) (Found: 61.5; H, 7.3%); $[\alpha]_D^{25}$ −54.7° (*c* 0.13); ν_{max} (KBr)/cm^{-1} 3470, 2950, 1750, 1720 and 1240; δ_H 0.85 (3 H, s, Me), 1.10 (3 H, s, Me), 1.0–2.0 (9 H, m), 2.98 (2 H, s, SCH_2), 3.17 (1 H, br s, 4-H), 3.59 (1 H, d, *J* 3.2, OH), 3.77 (3 H, s, OMe), 3.77 (1 H, d, *J* 2.5, 3-H) 3.80 (1 H, br s, 1-H), 3.85 (3 H, s, OMe), 4.00 (1 H, m, C*H*OH), 6.37 (1 H, dd, *J* 5.5, 3.2, CH=) and 6.45 (1 H, dd, *J* 5.5, 3.2, CH=); *m/z* 410 (M^+), 379 and 361.

Diels–Alder Reaction of Compound **1** *in the Absence of Lewis Acid*.—To a solution of compound **1** (2.005 g, 5.8 mmol) in dry CH_2Cl_2 (8 cm^3) was added freshly distilled cyclopentadiene (14.4 cm^3, 0.18 mol). The reaction mixture was kept for 19 h. After evaporation of the solvent and cyclopentadiene, the residual oil was purified by MPLC on silica gel (90 g). Elution with hexane gave cyclopentadiene dimer. Early fractions eluted with hexane–AcOEt (4:1) contained the *adduct* **9** (1.618 g, 68%). Late fractions eluted with hexane–AcOEt (1:2) afforded the *adducts* **7** and **10** (443 mg, 19%) in the ratio 1:2.2.

Compound **9**. M.p. 125–126 °C (from hexane) (Found: C, 61.5; H, 7.3. $C_{21}H_{30}O_6S$ requires C, 61.44; H, 7.37%); $[\alpha]_D^{25}$ +106.2° (*c* 1.0); ν_{max}(KBr)/cm^{-1} 3500, 2950, 1740, 1430 and 1075; δ_H 0.78 (3 H, s, Me), 1.1–1.9 (7 H, m), 1.10 (3 H, s, Me), 1.33 (1 H, d, *J* 9, 7-H), 2.00 (1 H, d, *J* 9, 7-H), 2.15 (1 H, d, *J* 13.4, SCH), 3.10 (1 H, br s, 1- or 4-H), 3.43 (1 H, br s, 4- or 1-H), 3.63 (1 H, d, *J* 13.4, SCH), 3.68 (3 H, s, OMe), 3.69 (2 H, br, 3-H and OH), 3.72 (3 H, s, OMe), 4.07 (1 H, m, C*H*OH), 6.08 (1 H, dd, *J* 5.4, 2.9, CH=) and 6.80 (1 H, dd, *J* 5.4, 2.9, CH=).

Compound **10** (305 mg, 13%) as prisms, m.p. 163–164 °C (from hexane) (Found: C, 61.4; H, 7.4%); $[\alpha]_D^{26}$ +139.4° (*c* 0.65); ν_{max}(KBr)/cm^{-1} 3400, 2950, 1730, 1430 and 1030; δ_H 0.83 (3 H, s, Me), 1.08 (3 H, s, Me), 1.1–1.9 (7 H, m), 1.70 (1 H, dd, *J* 8.2, 1.8, 7-H), 2.19 (1 H, d, *J* 8.2, 7-H), 2.37 (1 H, d, *J* 13.2, SCH), 3.09 (1 H, d, *J* 1.8, 3-H), 3.16 (1 H, d, *J* 13.2, SCH), 3.20 (1 H, br s, 1- or 4-H), 3.38 (1 H, br s, 4- or 1-H), 3.56 (1 H, d, *J* 3.2, OH), 3.75 (3 H, s, OMe), 3.79 (3 H, s, OMe), 3.98 (1 H, m, C*H*OH), 6.10 (1 H, dd, *J* 5.6, 2.9, CH=) and 6.36 (1 H, dd, *J* 5.6, 2.9, CH=).

(+)-(1R,R_S)-3-*Methyl Hydrogen* 2-exo-({(1S,2R,4R)-2-*Hydroxy*-7,7-*dimethylbicyclo*[2.2.1]*heptan*-1-*yl*}*methylsulphinyl*)-*bicyclo*[2.2.1]*hept*-5-*ene*-2-endo, 3-endo-*dicarboxylate* **11**.—To a suspension of $AlBr_3$ (977 mg, 3.7 mmol) in dry CH_2Cl_2 (10 cm^3) was added dimethyl sulphide (2.7 cm^3, 37 mmol). To the solution cooled to −20 °C was added a solution of the sulphoxide **7** (500 mg, 1.2 mmol) in dry CH_2Cl_2 (10 cm^{-3}). After an additional 4 h, the reaction mixture was taken up with 1 mol dm^{-3} hydrochloric acid (20 cm^3). The aq. phase was extracted

with CH_2Cl_2. The organic phase was washed with brine, dried and concentrated. The solid was recrystallised from hexane–AcOEt to give *compound* **11** (344 mg, 71%) as needles. M.p. 167–169 °C (Found: C, 60.7; H, 7.2. $C_{20}H_{28}O_6S$ requires C, 60.59; H, 7.12%); $[\alpha]_D^{26}$ +13.8° (*c* 1.0); $\nu_{max}(CHCl_3)/cm^{-1}$ 3450, 2950, 2800–2500, 1745, 1710 and 1030; δ_H 0.87 (3 H, s, Me), 1.10 (3 H, s, Me), 1.1–1.9 (9 H, m), 2.58 (1 H, d, *J* 3.6, 3-H), 3.20 (1 H, d, *J* 13.8, SCH), 3.29 (1 H, br s, 1-H), 3.50 (1 H, d, *J* 13.8, SCH), 3.64 (1 H, d, *J* 3.6, 4-H), 3.70 (3 H, s, OMe), 4.05 (1 H, dd, *J* 8.0, 3.7, C*H*OH), 6.16 (1 H, dd, *J* 5.6, 3.2, CH=) and 6.75 (1 H, dd, *J* 5.6, 2.8, CH=).

(−)-(1R,R$_S$)-2-*Benzyl* 3-*Methyl* 2-exo-({(1S,2R,4R)-2-*Hydroxy*-7,7-*dimethylbicyclo*[2.2.1]*heptan*-1-*yl*}*methylsulphinyl*)-*bicyclo*[2.2.1]*hept*-5-*ene*-2-endo, 3-endo-*dicarboxylate* **13**.—To a suspension of sodium hydride (60% dispersion; 85 mg, 2.1 mmol, prewashed with dry ether) in dry acetonitrile (5 cm^3) was added a solution of compound **11** (704 mg, 1.78 mmol) in dry acetonitrile (5 cm^3). To the mixture was added a solution of 18-crown-6 (185 mg, 0.7 mmol) in dry acetonitrile (5 cm^3) and then benzyl bromide (0.4 cm^3). The mixture was heated at 50 °C for 12 h. After removal of the solvent, the crude mixture was partitioned between CH_2Cl_2 (20 cm^3) and water (10 cm^3). The organic phase was washed with brine, dried and concentrated. The residue was chromatographed on silica gel [hexane–AcOEt (3:1)] to give *compound* **13** (745 mg, 86%) as needles (from hexane–AcOEt), m.p. 119–120 °C (Found: C, 66.9; H, 7.0. $C_{27}H_{34}O_6S$ requires C, 66.64; H, 7.04%); $[\alpha]_D^{25}$ −2.7° (*c* 1.1); ν_{max}(KBr)/cm^{-1} 3450, 2980, 1735 and 750; δ_H 0.81 (3 H, s, Me), 1.00 (3 H, s, Me), 1.1–1.9 (10 H, m), 2.71 (1 H, d, *J* 2.9, 3-H), 2.88 (1 H, d, *J* 13.4, SCH), 3.17 (1 H, d, *J* 13.4, SCH), 3.20 (1 H, br s, 1-H), 3.61 (3 H, s, OMe), 3.73 (1 H, br s, 4-H), 4.03 (1 H, dd, *J* 7.8, 3.9, C*H*OH), 5.18 (2 H, AB q, *J* 13, CH_2Ph), 6.12 (1 H, dd, *J* 5.6, 3.2, CH=), 6.64 (1 H, dd, *J* 5.6, 3.2, CH=) and 7.4 (5 H, m, Ph).

(−)-(1R)-2-*Benzyl* 3-*Methyl Bicyclo*[2.2.1]*hepta*-2,5-*diene*-2,3-*dicarboxylate* **14**.—A mixture of compound **13** (450 mg, 0.9 mmol) and diazobicyclo[5.4.0]undecene (DBU) (0.29 cm^3, 1.8 mmol) in dry benzene (7 cm^3) was heated at 50 °C for 12 h. After removal of the solvent, the residue was diluted with CH_2Cl_2 (5 cm^3). The organic phase was washed with 1 mol dm^{-3} hydrochloric acid (5 cm^3) and the aq. layer was back-extracted with CH_2Cl_2 (3 × 10 cm^3). The organic layer was washed with brine, dried and concentrated. The residue was chromatographed with hexane–AcOEt (1:1) on silica gel to give *compound* **14** (253 mg, 90%) as an oil, $[\alpha]_D^{27}$ −10.6° (*c* 2.19) (Found: M$^+$, 284.1055. $C_{17}H_{16}O_4$ requires M, 284.1048); ν_{max}(neat)/cm^{-1} 2950, 1740 and 1710; δ_H 2.02 (1 H, ddd, *J* 8.3, 1.5, 1.5, 7-H), 2.21 (1 H, ddd, *J* 8.3, 1.5, 1.5, 7-H), 3.51 (3 H, s, OMe), 3.85 (1 H, m, 1- or 4-H), 3.89 (1 H, m, 4- or 1-H), 5.11 (1 H, d, *J* 12.2, C*H*Ph), 5.16 (1 H, d, *J* 12.2, C*H*Ph), 6.84 (1 H, m, CH=), 6.85 (1 H, m, CH=) and 7.3 (5 H, m, Ph).

(+)-(1R)-3-*Methyl Hydrogen Bicyclo*[2.2.1]*hepta*-2,5-*diene*-2,3-*dicarboxylate** **15**.—To a suspension of $AlCl_3$ (22 mg, 0.17 mmol) in dry CH_2Cl_2–$MeNO_2$ [0.4 cm^3 (1:1)] at ~0 °C was added a solution of compound **14** (15.6 mg, 0.05 mmol) in dry CH_2Cl_2 (0.2 cm^3). The mixture was kept for 48 h in a refrigerator. After dilution with CH_2Cl_2 (5 cm^3) the organic layer was washed with water (5 cm^3). The aq. layer was back-extracted with CH_2Cl_2 (3 × 10 cm^3). The organic phase was dried and concentrated to give a solid, recrystallisation of which from CCl_4 afforded compound **15** (9.5 mg, 89%) as plates, m.p. 129–131 °C; $[\alpha]_D^{27}$ +28.0° (*c* 0.67); the spectroscopic data were in good agreement with those previously reported for the racemic form.[28]

(−)-2-*Benzyl* 3-*Methyl*-5-exo,6-exo-(*Isopropylidenedioxy*)-*bicyclo*[2.2.1]*hept*-2-*ene*-2,3-*dicarboxylate* **16**.—To a solution of compound **14** (248 mg, 0.87 mmol) and Et_3NO dihydrate (388 mg, 3.5 mmol) in acetone (5 cm^3) at ~0 °C was added OsO_4 (0.4 cm^3, 0.04 mmol; 0.1 mmol dm^{-3} in Bu^{t}OH). The mixture was stirred at ~0 °C for 3 h and the precipitate was filtered off. The filtrate was concentrated and the crude product was used in the next step.

The crude oil was dissolved in a mixture of acetone (10 cm^3) and 2,2-dimethoxypropane (2 cm^3) with a pinch of toluene-*p*-sulphonic acid (PTSA) monohydrate and the mixture was heated under reflux for 7 h. The solution was concentrated and the residue was diluted with CH_2Cl_2 (30 cm^3). The organic phase was washed with brine, dried and concentrated. The residue was chromatographed with hexane–AcOEt (2:1) on silica gel to give *compound* **16** (216 mg, 70%) as an oil, $[\alpha]_D^{27}$ −3.9° (*c* 3.96) (Found: M$^+$, 358.1418. $C_{20}H_{22}O_6$ requires M, 358.1417); ν_{max}(neat)/cm^{-1} 3000, 1730, 1710, 1260 and 1180; δ_H 1.35 (3 H, s, Me), 1.49 (3 H, s, Me), 1.94 (1 H, d quin, *J* 9.8, 2.0, 7-H), 2.08 (1 H, dt, *J* 9.8, 1.5, 7-H), 3.18 (1 H, br d, *J* 1.5, 1- or 4-H), 3.23 (1 H, br d, *J* 1.5, 4- or 1-H), 3.60 (3 H, s, OMe), 4.44 (1 H, br s, OCH), 4.45 (1 H, br s, OCH), 5.17 (1 H, d, *J* 12.2, OC*H*Ph), 5.23 (1 H, d, *J* 12.2, OC*H*Ph) and 7.4 (5 H, m, Ph).

(1R)-3-*Methyl Hydrogen* 5-exo,6-exo-(*Isopropylidenedioxy*)-*bicyclo*[2.2.1]*hept*-2-*ene*-2,3-*dicarboxylate*† **12**.—A mixture of compound **16** (103 mg, 0.29 mmol), 5% Pd–C (184 mg) and cyclohexa-1,3-diene (0.03 cm^3, 0.34 mmol) was heated in a sealed tube at 40 °C for 12 h. The reaction mixture was filtered and the precipitate was washed with CH_2Cl_2. The filtrate and washings were concentrated to give compound **12** (61 mg, 80%) as a solid. Recrystallisation from hexane–AcOEt afforded an analytical sample, m.p. 117–117.5 °C; $[\alpha]_D^{25}$ −29.5° (*c* 1.21) {lit.,[17] $[\alpha]_D^{25}$ −23.8° (*c* 1.17, $CHCl_3$) for 80% e.e.}; the IR spectrum was superposable with that of an authentic sample.

(+)-(1R,R$_S$)-2-exo-{((1S,2R,4R)-2-*Hydroxy*-7,7-*dimethyl*-*bicyclo*[2.2.1]*heptan*-1-*yl*)*methylsulphinyl*}-3-endo-*hydroxy*-*methylbicyclo*[2.2.1]*hept*-5-*ene*-2-*carboxylic Acid Lactone* **17**.—To a solution of compound **7** (100 mg, 0.24 mmol) in dry toluene (2 cm^3) at −78 °C was added DIBAL (0.98 cm^3, 0.98 mmol; 1 mol dm^{-3} in toluene). The temperature was allowed to rise gradually to ambient. After being stirred for 12 h the mixture was treated with cold 1 mol dm^{-3} hydrochloric acid (8 cm^3) and the aq. layer was extracted with $CHCl_3$ (3 × 8 cm^3). The organic phase was washed with brine, dried and concentrated. The residual solid (94 mg) was chromatographed on silica gel with hexane–AcOEt (3:1) to give *compound* **17** (52 mg, 61%), m.p. 224–225 °C (from hexane–AcOEt) (Found: C, 65.1; H, 7.5. $C_{19}H_{26}O_4S$ requires C, 65.09; H, 7.53%); $[\alpha]_D^{25}$ +44.2° (*c* 1.0); $\nu_{max}(CHCl_3)/cm^{-1}$ 3450, 2950, 1750 and 1035; δ_H 0.89 (3 H, s, Me), 1.16 (3 H, s, Me), 1.1–2.0 (8 H, m), 2.17 (1 H, d, *J* 9, 7-H), 3.07 (1 H, d, *J* 13, SC*H*H), 3.21 (1 H, br, 4-H), 3.33 (1 H, dt, *J* 9, 3, 3-H), 3.40 (1 H, d, *J* 13, SCH*H*), 3.66 (1 H, d, *J* 3, OH), 3.76 (1 H, br, 1-H), 3.91 (1 H, dd, *J* 10, 3, OCH), 4.04 (1 H, dt, *J* 8, 3, C*H*OH), 4.38 (1 H, dd, *J* 10, 9, OCH), 6.43 (1 H, dd, *J* 6, 3, CH=) and 6.55 (1 H, dd, *J* 6, 3, CH=).

* Systematic name: (1S)-(+)-2-*Methyl Hydrogen Bicyclo*[2.2.1]*hepta*-2,5-*diene*-2,3-*dicarboxylate*.

† Systematic name: (1*S*)-2-*Methyl Hydrogen* 5-exo,6-exo- (*Isopropylidenedioxy*)*bicyclo*[2.2.1]*hept*-2-ene-2,3-*dicarboxylate*.

(+)-(2S,3R)-3-endo-(*Hydroxymethyl*)*bicyclo*[2.2.1]*hept*-5-*ene*-2-endo-*carboxylic Acid Lactone* **20**.—To a solution of compound **17** (100 mg, 0.29 mmol) in degassed, dry t-butyl alcohol (0.11 cm^3, 1.14 mmol) was added SmI_2 (18 cm^3, 1.4 mmol; 0.08 mol dm^{-3} in THF) under stream of argon. After 10 min, cold 1 mol dm^{-3} hydrochloric acid (30 cm^3) was added to the mixture. The aq. layer was extracted with $CHCl_3$ (3 × 20 cm^3). The organic phase was washed with brine, dried and evaporated to give a solid (104 mg), which was chromatographed with hexane–AcOEt (3:1) on silica gel (8 g) to give a mixture of 10-mercaptoisoborneol and the disulphide **19** in the ratio 81:19, and then compound (+)-**20** (42 mg, 98%). The ratio of the thiol to disulphide was estimated by integration in the ^1H NMR spectrum. One of the methylene protons (C-10) in compound **19** resonated at δ 3.14 as a doublet (J 13 Hz), whereas one of the methylene protons in the thiol appeared at δ 2.56 as a doublet of doublets (J 13, 5 Hz).

Compound **19**. Prisms; m.p. 226–229 °C (from hexane) (Found: C, 64.9; H, 9.5. $C_{20}H_{34}O_2S_2$: C, 64.84; H, 9.25%); $[\alpha]_D^{23}$ +128.6° (c 1.0). The spectroscopic data were in good agreement with those reported earlier.[27]

Compound (+)-**20**. M.p. 122–124 °C (from hexane–AcOEt) (lit.,[22] 120–122 °C); $[\alpha]_D^{25}$ +143.9° (c 1.0) {lit.,[22] $[\alpha]_D^{25}$ +143.2° (c 5.2, $CHCl_3$)}; $\nu_{max}(CHCl_3)/cm^{-1}$ 1755, 1380, 1080 and 1000; δ_H 1.47 (1 H, d, J 9, 7-H), 1.65 (1 H, dt, J 9, 1.5, 7-H), 3.1–3.2 (2 H, m), 3.26 (1 H, dd, J 9.5, 4.5, 2-H), 3.34 (1 H, br, 1- or 4-H), 3.80 (1 H, dd, J 10, 3, OC*H*H), 4.29 (1 H, dd, J 10, 8, OCH*H*) and 6.3–6.4 (2 H, m, 2 × CH=).

(+)-(2S,3R)-3-endo-(*Hydroxymethyl*)*bicyclo*[2.2.1]*heptane*-2-endo-*carboxylic Acid Lactone* **21**.—A mixture of compound **20** (38 mg, 0.25 mmol) and 5% Pd–C (280 mg) in ethanol (8 cm^3) was degassed and then covered with hydrogen. The mixture was stirred vigorously at 1 atmosphere pressure for 2 h and filtered. The precipitate was washed with a small amount of hot ethanol. The filtrate was concentrated and the residue was filtered through a short pad of silica gel with AcOEt. The fraction was concentrated to give compound (+)-**21** (38 mg, 100%), m.p. 146–147 °C (from hexane) (lit.,[23] 145–146 °C; $[\alpha]_D^{25}$ +150.4° (c 1.0) {lit.,[23] $[\alpha]_D^{26}$ +153.28° (c 1.01, $CHCl_3$)}; $\nu_{max}(CHCl_3)/cm^{-1}$ 2950, 1755, 1170 and 1000; δ_H 1.45–1.65 (6 H, m), 2.37 (1 H, br), 2.67 (1 H, br), 2.88 (1 H, m, 3-H), 2.98 (1 H, dd, J 11, 5, 2-H), 4.24 (1 H, dd, J 10, 3, OCH) and 4.30 (1 H, dd, J 10, 8, OCH).

(−)-(2R,3S)-3-endo-(*Hydroxymethyl*)*bicyclo*[2.2.1]*heptane*-2-endo-*carboxylic Acid Lactone* **21**.—In a similar manner, compounds **22**, (−)-**20** and (−)-**21** were obtained from compound **9**.

Compound **22**. Prisms, m.p. 179–180 °C (from hexane–AcOEt) (Found: C, 65.4; H, 7.2. $C_{19}H_{26}O_4S$ requires C, 65.12; H, 7.48%); $[\alpha]_D^{25}$ −47.6° (c 1.0); $\nu_{max}(CHCl_3)/cm^{-1}$ 3450, 2950, 1750 and 1030; δ_H 0.85 (3 H, s, Me), 1.10 (3 H, s, Me), 1.1–2.1 (9 H, m), 2.55 (1 H, d, J 13, SC*H*H), 3.25 (1 H, br, 1- or 4-H), 3.29 (1 H, br, 4- or 1-H), 3.45 (1 H, d, J 13, SCH*H*), 3.56 (1 H, dt, J 9, 3, 3-H), 3.62 (1 H, d, J 4, OH), 3.95 (1 H, dd, J 10, 3, OC*H*H), 4.02 (1 H, dt, J 8, 4, *H*COH), 4.36 (1 H, dd, J 10, 9, OCH*H*), 6.41 (1 H, dd, J 5.5, 3, CH=) and 6.49 (1 H, dd, J 5.5, 3, CH=).

Compound (−)-**20**. A powder, m.p. 122–124 °C (from hexane); $[\alpha]_D^{25}$ −135.9° (c 1.0); the IR and ^1H NMR spectra were in good agreement with those of the (+)-isomer.

Compound (−)-**21**. Needles, m.p. 149–150 °C (from hexane); $[\alpha]_D^{25}$ −151.0° (c 0.95) {lit.,[23] $[\alpha]_D^{26}$ −156.21° (c 0.81, $CHCl_3$)}. The IR and ^1H NMR spectra were in good agreement with those of the (+)-isomer.

X-Ray Structure Determination of Compound **7**[8a].—$C_{21}H_{30}O_6S$, M, 410.5, monoclinic, space group $P2_1$, a = 21.650(7), b = 7.027(2), c = 6.918(3) Å, β = 98.74(3)°, V = 1040.2(6) $Å^3$, Z = 2, D_c = 1.311 g cm^{-3}, μ = 16.4 cm^{-1}. Single crystals (plates) were prepared by recrystallisation from hexane–ethyl acetate. The 1559 independent reflections were read on a Rigaku AFC-5 diffractometer in the ω-scan mode to 2θ = 120° using Cu-Kα radiation (λ = 1.541 78 Å). Of 1559 unique reflections, 1298 with $|F_o| > 3\sigma|F_o|$ were considered as observed, with a final R = 0.088. The structure was solved with direct methods, using the MULTAN84 program,[29] and was refined by block-diagonal least-squares methods with non-hydrogen-atom anisotropic thermal parameter.

Acknowledgements

We are grateful for financial support from the Research Foundation for Pharmaceutical Sciences and the Yamada Science Foundation. We thank Professor M. Ohno (The University of Tokyo) for suggesting the method of determination of the optical purity of compound **12**.

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Paper 1/00597I
Received 7*th February* 1991
Accepted 26*th February* 1991