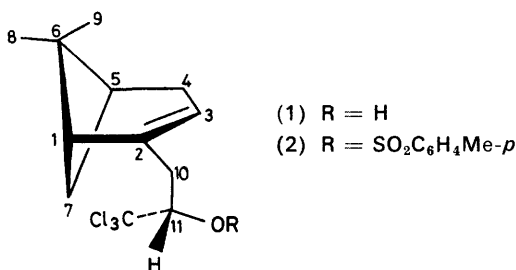


X-Ray Structure Analysis of the Tosylate Ester of (1*S*,5*S*)-6,6-Dimethyl-2-[(2*S*)-3,3,3-trichloro-2-hydroxypropyl]bicyclo[3.1.1]hept-2-ene, the Major Product of the Iron(III) Chloride-catalysed Ene Addition of Chloral to (–)-(1*S*,5*S*)-Pin-2(10)-ene

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The crystal structure of the title compound (2) was determined by X-ray diffraction from diffractometer data by direct methods. Crystals are orthorhombic, space group $P2_12_12_1$, with $Z = 4$ in a unit cell of dimensions: $a = 13.076(4)$, $b = 9.858(3)$, $c = 16.234(4)$ Å; the structure was refined by full-matrix least-squares to R 0.0447, without recourse to weighting analysis, for 1 547 independent reflections. The correlation of the conformation of the pinene skeleton in (2) with the published crystallographic data for *cis*-pinocarvyl *p*-nitrobenzoate is good. Data are used for comment upon a published analysis of the ^1H n.m.r. spectra of pinenes.

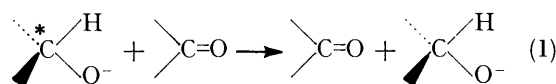
We have reported¹ that the ene addition of chloral to (–)-(1*S*,5*S*)-pin-2(10)-ene is highly stereoselective when catalysed by a bulky Lewis acid. With iron(III) chloride a 97 : 3 ratio of the two diastereoisomeric ene adducts was obtained. On the basis of steric arguments, the major reaction product was assigned the (*S*)-configuration at the new asymmetric centre formed in the side chain, as indicated in (1). This paper provides the proof for the correctness of that assignment.



Initially it was intended that X-ray methods would be used to prove absolute configuration by the heavy-atom anomalous dispersion procedure. The mixture of the *p*-bromobenzoate esters of (1) and its diastereoisomer were prepared for this purpose, but unfortunately could not be induced to crystallise. Since, however, the structural integrity of the pinene skeleton is retained in the formation of the ene adduct, the absolute stereochemistry at the new chiral centre can be assigned relative to the known absolute stereochemistry about the chiral bridgehead carbon atoms of the hydrocarbon moiety. The crystalline tosylate derivatives of the mixture of alcohols could not be prepared by the usual derivatisation procedure, which employs toluene-*p*-sulphonyl chloride and pyridine, for the reason that ester formation was very slow. It seemed likely, therefore, that electron withdrawal by the Cl₃C group sufficiently deactivated the nucleophilic hydroxy-function in (1) and its isomer as to make attack on the sulphonyl chloride electronically difficult. Accordingly, the alcohol mixture was converted into the corresponding sodium alkoxides by heating under reflux with sodium hydride

in diethyl ether, thereby facilitating the subsequent reaction with tosyl chloride. The ester of the minor alcohol component in the ene adduct mixture was readily removed by fractional crystallisation of the mixture of tosylates from ethanol, to give pure tosyl ester (2) of constant m.p. and specific rotation.

Since tosylate formation does not involve alkyl oxygen fission in the alcohol, the ester will have the same absolute stereochemistry about the chiral carbon atom as the alkoxide ion from which it is derived. Nevertheless, it is necessary to ensure that alkoxide formation from the parent alcohol does not result in configurational change, which could arise by hydride transfer from the alkoxide to the corresponding ketone [reaction (1)] if the ketone is present as an adventitious impurity. The diastereoisomeric alcohol mixture was subjected to the



reaction conditions as for the tosyl ester preparation, but without the addition of toluene-*p*-sulphonyl chloride, and quenched with water to regenerate the hydroxy-compounds from the alkoxide salts. Analysis of the 100 MHz n.m.r. spectrum of the recovered alcohols, using Eu(fod)₃ shift reagent to separate the resonances of the two components in the mixture,¹ showed there to be no change in the original ratio of diastereoisomers as a consequence of salt formation.

EXPERIMENTAL

Tosyl Ester (2).—A magnetically stirred suspension of sodium hydride (0.06 g, 0.0025 mol) in dry diethyl ether (3 ml) was warmed by an i.r. lamp to near the reflux temperature, and a solution of the (–)-pin-2(10)-ene-chloral adduct obtained from an iron(III) chloride (1 mole %) catalysed ene reaction¹ (0.56 g, 0.002 mol) in dry ether (5 ml) was added dropwise at a rate sufficient to maintain a gentle reflux. After completion of the addition (*ca.* 10 min) the boiling mixture was stirred for 0.5 h. A solution of recrystallised toluene-*p*-sulphonyl chloride (0.42 g,

¹ G. B. Gill and B. Wallace, *J.C.S. Chem. Comm.*, 1977, 380, 382.

0.0022 mol) in dry ether (5 ml) was added to the warm suspension at a rate sufficient to cause the ether to reflux gently, and the mixture then stirred for 0.5 h, allowed to cool, and diluted with ether (25 ml). Conventional work-up of the reaction mixture afforded a pale yellow oil (0.9 g, 100%) which, on treatment with an equal volume of warm ethanol, deposited white crystals. Recrystallisation from ethanol readily removed the impurity of the tosyl ester of the minor alcohol component in the mixture to give *ester* (2), m.p. 79—79.5 °C, $[\alpha]_D^{23} - 69$ °C (CHCl₃, *c* 0.173) (Found: C, 52.0; H, 5.3. C₁₉H₂₃Cl₃O₃S requires C, 52.2; H, 5.3%); *m/e* 436.0430 (*M*⁺; C₁₉H₂₃³⁵Cl₃O₃S⁺ requires 436.0433), and 265 (*M*⁺ - TsOH); t.l.c. (benzene, on silica) *R_F* 0.58; i.r. ν_{\max} (KBr): 2 900, 1 925, 1 600, 1 375, 1 190, and 820 cm⁻¹; 100 MHz n.m.r. τ (CDCl₃)² 2.16 (2 H, d, *J* 8 Hz), 2.66 (2 H, d, *J* 8 Hz), 4.59 (1 H, br s, olefinic H), 4.82 (1 H, t, line separation 5 Hz, C-11 proton), 7.10 (1 H, m, C-10 proton), 7.52 (1 H, m, C-10 proton), 7.56 (3 H, s, aromatic CH₃), 7.65 (1 H, m, C-7 *exo*-proton H-7A), 7.76 (2 H, m, C-4 protons), 7.94 (2 H, m, C-1 and C-5 protons), 8.72 (3 H, s, C-8 CH₃), 8.92 (1 H, d, line separation 8 Hz, C-7 *endo*-proton H-7B), and 9.17 (3 H, s, C-9 CH₃).

This procedure was repeated for the preparation of the sodium alkoxides, and the suspended salts stirred under reflux for 1 h. Careful addition of wet ether (20 ml) to the cooled mixture was followed by the slow addition of water (5 ml), and the ethereal solution was then washed with water (10 ml) and the organic layer dried (Na₂SO₄). Removal of the solvent gave a yellow oil (0.45 g, 80.4% recovery) shown by spectral data to be the original alcohol. Analysis of the 100 MHz n.m.r. spectrum recorded in the presence of the lanthanide shift reagent Eu(fod)₃ showed that the ratio of diastereoisomers was identical to the ratio obtained for the original mixture of alcohols isolated from the ene reaction.¹ Hence, alkoxide formation caused no detectable epimerisation of the exocyclic chiral carbon atom.

Crystallography.—Oscillation and Weissenberg photographs were taken about the *a* axis of a colourless crystal of ester (2) measuring *ca.* 0.2 × 0.3 × 0.5 mm, and *X*-ray intensity data were obtained for the crystal similarly mounted on a Hilger and Watts Y290 automatic four-circle diffractometer by use of Mo-*K α* radiation. A 2 θ - ω scan up to the value θ 25° was employed. Background was measured at the ends of each scan and reflections with a net count < 3 σ were considered unobserved. A total of 1 547 reflections were thus obtained, and intensities were corrected for Lorentz polarisation factors.

Crystal Data.—C₁₉H₂₃Cl₃O₃S, *M* = 437.8. Orthorhombic, *a* = 13.076(4), *b* = 9.858(3), *c* = 16.234(4) Å, *U* = 2 093 Å, *D_c* = 1.389 g cm⁻³, *Z* = 4, *F*(000) = 912. Space group *P*2₁2₁2₁. Mo-*K α* radiation, λ = 0.7107 Å; μ (Mo-*K α*) = 3.40 cm⁻¹.

Structure Analysis.—The multiresolution program MULTAN³ yielded two results with high figures-of-merit, respectively 1.274 and 1.275. The first solution was used in the *E* map calculation, and from the 31 strongest peaks were located the sulphur and chlorine, two of the oxygen, and eleven of the carbon atoms. The co-ordinates of the strongest peak in the map proved to be those of the sulphur atom, and those of the next three corresponded to the positions of the chlorine atoms. Following the first cycle

² For an analysis of the ¹H n.m.r. spectra of pinenes see R. J. Abraham, M. A. Cooper, J. R. Salmon, and D. Whittaker, *Org. Magn. Resonance*, 1972, **4**, 489.

of full-matrix least-squares refinement on the above seventeen atomic positions, with isotropic temperature factors, a subsequent Fourier-difference map enabled location of the remaining non-hydrogen atoms. Four further refinement cycles led to convergence at *R* 0.103. In subsequent refinement atomic temperature factors were allowed to vary anisotropically, and after two such

TABLE I

Atom co-ordinates (× 10⁴), with standard deviations in parentheses

(a) Non-hydrogen atoms			
	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
C(1)	3 599(6)	10 879(8)	533(5)
C(2)	2 881(6)	10 301(7)	1 164(5)
C(3)	1 918(6)	10 681(8)	1 154(5)
C(4)	1 590(6)	11 713(9)	520(5)
C(5)	2 487(7)	12 162(8)	9(5)
C(6)	3 076(6)	10 936(7)	-335(5)
C(7)	3 403(7)	12 447(8)	580(5)
C(8)	3 828(7)	11 370(10)	-991(6)
C(9)	2 529(7)	9 706(8)	-633(5)
C(10)	3 298(7)	9 346(7)	1 824(4)
C(11)	3 400(5)	7 854(7)	1 518(4)
C(12)	4 286(6)	7 109(7)	1 937(4)
C(13)	626(5)	7 311(7)	1 243(4)
C(14)	91(6)	7 207(8)	1 990(4)
C(15)	-803(6)	7 931(9)	2 095(4)
C(16)	-1 192(5)	8 764(8)	1 465(4)
C(17)	-672(5)	8 810(8)	725(4)
C(18)	235(5)	8 113(8)	610(4)
C(19)	-2 143(5)	9 558(9)	1 589(5)
O(1)	2 485(3)	7 176(5)	1 747(3)
O(2)	1 621(4)	5 098(5)	1 422(3)
O(3)	2 144(3)	6 598(5)	299(3)
S(1)	1 754(1)	6 405(2)	1 108(1)
Cl(1)	4 306(2)	5 404(2)	1 598(1)
Cl(2)	4 179(2)	7 147(2)	3 010(1)
Cl(3)	5 442(2)	7 868(3)	1 631(1)
(b) Hydrogen atoms			
	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
H(1)	4 387	10 650	611
H(3)	1 385	10 367	1 643
H(4A)	1 002	11 619	143
H(4B)	1 017	12 217	959
H(5)	2 193	12 975	-301
H(7A)	3 995	12 983	346
H(7B)	3 209	12 761	1 127
H(8A)	4 188	10 543	-1 093
H(8B)	3 793	11 286	-1 529
H(8C)	4 404	11 852	-864
H(9A)	1 995	9 922	-1 111
H(9B)	1 813	9 416	-379
H(9C)	3 002	8 762	-530
H(10A)	2 799	9 315	2 336
H(10B)	4 195	9 895	1 854
H(11)	3 585	7 760	806
H(14)	388	6 556	2 443
H(15)	-1 199	7 860	2 659
H(17)	-1 185	9 471	213
H(18)	596	8 212	8
H(19A)	-2 597	9 043	2 118
H(19B)	-1 816	10 404	1 915
H(19C)	-2 602	9 601	1 220

cycles the agreement factor had converged to *R* 0.0632. A Fourier-difference synthesis revealed the presence of 34 peaks of intensity > 0.2 eÅ⁻³. Eleven of these were in the vicinity of the sulphur, chlorine, oxygen, or certain of the carbon atoms, the most intense such peak (0.28 eÅ⁻³) being

³ G. Germain, P. Main, and M. M. Wolfson, *Acta Cryst.*, 1971, **A27**, 368.

in the region of the aryl-sulphur bond. The remaining 23 peaks were assigned to the hydrogen atom positions, and four further cycles of full-matrix refinement (fixed coordinates and isotropic temperature factor U_{iso} 0.05 for hydrogen atoms; temperature factors of other atoms allowed to vary anisotropically) reduced R to 0.0447.

TABLE 2

Molecular geometry, with standard deviations in parentheses

(a) Interatomic distances (Å)			
C(1)–C(2)	1.502(10)	C(12)–Cl(1)	1.769(7)
C(1)–C(6)	1.566(10)	C(12)–Cl(2)	1.748(7)
C(1)–C(7)	1.569(10)	C(12)–Cl(3)	1.759(8)
C(2)–C(3)	1.313(10)	O(1)–S(2)	1.602(5)
C(2)–C(10)	1.527(10)	S(1)–O(2)	1.404(5)
C(3)–C(4)	1.510(11)	S(1)–O(3)	1.422(5)
C(4)–C(5)	1.503(11)	S(1)–C(13)	1.739(7)
C(5)–C(6)	1.538(10)	C(13)–C(14)	1.404(9)
C(5)–C(7)	1.541(11)	C(13)–C(18)	1.393(9)
C(6)–C(8)	1.510(11)	C(14)–C(15)	1.380(10)
C(6)–C(9)	1.489(10)	C(15)–C(16)	1.407(10)
C(10)–C(11)	1.558(10)	C(16)–C(17)	1.381(9)
C(11)–C(12)	1.531(9)	C(16)–C(19)	1.483(9)
C(11)–O(1)	1.420(8)	C(17)–C(18)	1.383(10)

(b) Interatomic angles (°)			
C(1)–C(2)–C(3)	118.9(7)	C(11)–C(12)–Cl(3)	108.7(5)
C(1)–C(2)–C(10)	119.3(7)	C(11)–O(1)–S(1)	123.8(4)
C(1)–C(6)–C(5)	85.5(6)	Cl(1)–C(12)–Cl(2)	109.4(4)
C(1)–C(6)–C(8)	111.2(7)	Cl(1)–C(12)–Cl(3)	107.7(4)
C(1)–C(6)–C(9)	118.2(6)	Cl(2)–C(12)–Cl(3)	110.0(4)
C(1)–C(7)–C(5)	85.3(6)	C(12)–C(11)–O(1)	107.2(5)
C(2)–C(1)–C(6)	110.8(6)	O(1)–S(1)–O(2)	106.1(3)
C(2)–C(1)–C(7)	103.8(7)	O(1)–S(1)–O(3)	108.7(3)
C(2)–C(3)–C(4)	118.2(8)	O(1)–S(1)–C(13)	100.4(3)
C(2)–C(10)–C(11)	112.9(6)	O(2)–S(1)–O(3)	120.2(3)
C(3)–C(2)–C(10)	121.8(8)	O(2)–S(1)–C(13)	108.9(3)
C(3)–C(4)–C(5)	110.7(6)	O(3)–S(1)–C(13)	110.6(3)
C(4)–C(5)–C(6)	111.1(7)	S(1)–C(13)–C(14)	119.6(5)
C(4)–C(5)–C(7)	109.2(7)	S(1)–C(13)–C(18)	120.7(5)
C(5)–C(6)–C(8)	111.2(7)	C(13)–C(14)–C(15)	119.4(7)
C(5)–C(6)–C(9)	121.2(7)	C(13)–C(18)–C(17)	119.8(6)
C(6)–C(1)–C(7)	86.4(6)	C(14)–C(13)–C(18)	119.7(6)
C(6)–C(5)–C(7)	88.4(6)	C(14)–C(15)–C(16)	121.3(7)
C(8)–C(6)–C(9)	108.1(7)	C(15)–C(16)–C(17)	118.2(6)
C(10)–C(11)–C(12)	112.1(6)	C(15)–C(16)–C(19)	120.8(7)
C(10)–C(11)–O(1)	106.8(6)	C(16)–C(17)–C(18)	121.6(6)
C(11)–C(12)–Cl(1)	109.2(5)	C(17)–C(16)–C(19)	120.9(7)
C(11)–C(12)–Cl(2)	111.8(5)		

Analysis of the agreement between $|F_c|$ and $|F_o|$ over ranges of $|F_o|$ and $\sin\theta/\lambda$ indicated that unit weights were satisfactory. The largest parameter shifts were $<0.1\sigma$, showing that refinement had converged.

Final atomic positions are listed in Table 1. Observed and calculated structure factors and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 22149 (18 pp.).*

Computation was achieved with the aid of the program CRYSTALS,⁴ and the molecular structure diagrams utilised the plotting program PLUTO.⁵

DISCUSSION

Bond lengths and angles of the main atoms in the atomic skeleton of the ester (2) are listed in Table 2. The atom numbering convention adopted here is given in Figure 1. No one diagram could be drawn to illus-

* See Notice to Authors No. 7, in *J.C.S. Perkin I*, 1976, Index issue.

trate all the conformational features in (2); the pinene residue is shown to better advantage in a partial structure diagram (Figure 2). Hydrogen atoms (Table 1) are numbered according to the carbon atoms to which they are attached. The arrangement of the molecules in the unit cell is shown in Figure 3.

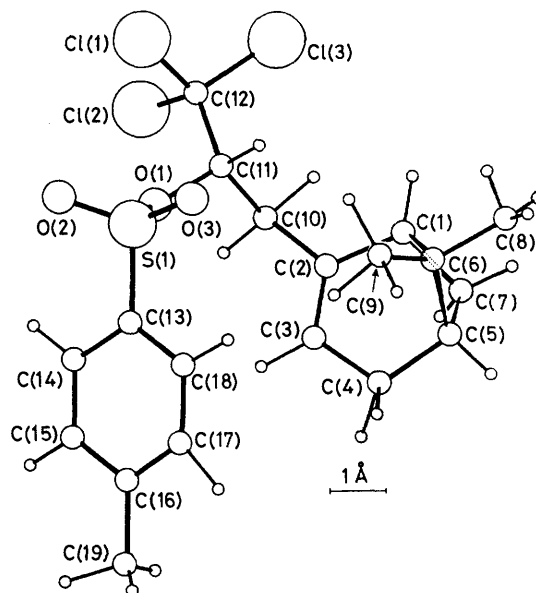


FIGURE 1 The molecular structure of ester (2)

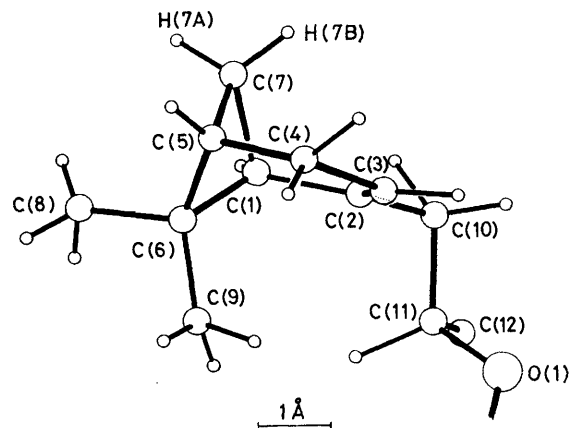


FIGURE 2 A perspective view of the pinene unit in (2)

Inspection of Figure 1, which was constructed on the basis of the known (1*S*,5*S*)-configuration of the pinene skeleton, reveals that C(11) has the (*S*)-configuration, thereby vindicating our conclusion that the preferred geometry of approach of the enophile (chloral) to the ene component (β -pinene) during reaction is that which minimised the non-bonded interactions between the two reacting molecules.¹ Since (1) was the major product of the iron(III) chloride-catalysed ene addition of chloral

⁴ W. R. Carruthers, personal communication to T. J. King, Nottingham University.

⁵ Cambridge Data Centre, W. D. S. Motherwell, personal communication to T. J. King, Nottingham University.

to (-)-pin-2(10)-ene, and the catalysed reaction is very much faster than the uncatalysed (thermal) addition, it is clear that the effective enophile is a $\text{Cl}_3\text{CCHO}\cdot\text{FeCl}_3$

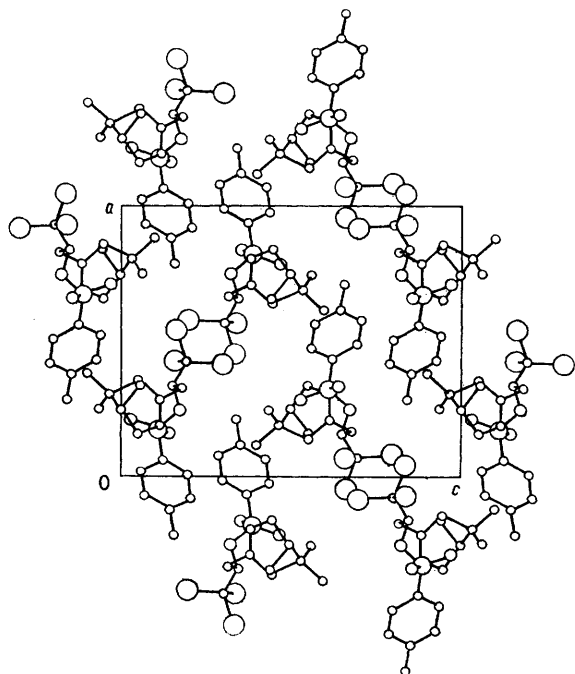
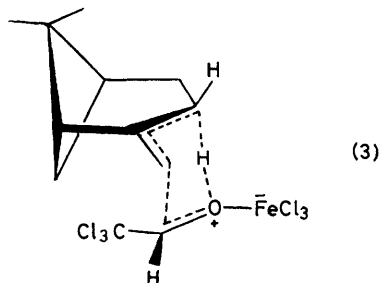


FIGURE 3 Arrangement of molecules in the unit cell

complex. It may reasonably be expected that complex formation by the oxygen atom in chloral will occur, so as to place the FeCl_3 moiety in an *anti* geometrical relationship to the bulky Cl_3C group. Thus, steric interactions during the ene addition are minimised if the larger FeCl_3 grouping is aligned *exo* relative to the pin-2(10)-ene skeleton, thereby placing the Cl_3C group in the *endo*-geometry, such that the *si*-face of the chloral molecule is offered to the allylic system of the ene component. The approach of the enophile occurs from the side remote from the C(8) and C(9) methyl groups of the pinene; it is well documented that only the *endo*-allylic hydrogen atom of pin-2(10)-ene is transferred in ene reactions.⁶ Development of the carbon-carbon bond thus leads to the formation mainly of (1), which possesses the (*S*)-configuration at C(11), by way of the kinetically preferred transition state (3).



The converse arguments apply in the thermally initiated ene addition since now the Cl_3C group should

mainly adopt the *exo*-alignment, so that the *re*-face of the uncomplexed chloral molecule is offered to the least-hindered face of the allylic system in the olefin. Indeed, we have shown¹ that the other diastereoisomer, which therefore possesses the (*R*)-configuration at C(11), is the major product of the thermal process (isomer ratio 75:25). We are currently examining possible extensions of these procedures for the purpose of the synthesis of optically active molecules by employing chiral olefinic systems as templates for ensuring asymmetric induction during ene reactions.

Examination of the bond length, bond angle, and dihedral angle data (Tables 2 and 3) reveals marked,

TABLE 3
Torsion angles ($^\circ$) for the alcohol portion (1) of tosyl ester (2)

C(1)-C(2)-C(3)-C(4)	-1.7
C(1)-C(2)-C(10)-C(11)	-82.5
C(1)-C(6)-C(5)-C(4)	-81.5
C(1)-C(6)-C(5)-C(7)	28.5
C(1)-C(7)-C(5)-C(4)	83.3
C(1)-C(7)-C(5)-C(6)	-28.4
C(2)-C(1)-C(6)-C(5)	75.4
C(2)-C(1)-C(6)-C(8)	-173.6
C(2)-C(1)-C(6)-C(9)	-47.7
C(2)-C(1)-C(7)-C(5)	-82.6
C(2)-C(3)-C(4)-C(5)	-1.8
C(2)-C(10)-C(11)-C(12)	149.0
C(2)-C(10)-C(11)-O(1)	-93.9
C(3)-C(2)-C(1)-C(6)	-41.8
C(3)-C(2)-C(1)-C(7)	49.6
C(3)-C(2)-C(10)-C(11)	100.5
C(3)-C(4)-C(5)-C(6)	50.9
C(3)-C(4)-C(5)-C(7)	-45.0
C(4)-C(3)-C(2)-C(10)	175.3
C(4)-C(5)-C(6)-C(8)	167.6
C(4)-C(5)-C(6)-C(9)	38.9
C(5)-C(6)-C(1)-C(7)	-28.0
C(5)-C(7)-C(1)-C(6)	27.9
C(6)-C(1)-C(2)-C(10)	141.2
C(7)-C(1)-C(2)-C(10)	-127.5
C(7)-C(1)-C(6)-C(8)	83.1
C(7)-C(1)-C(6)-C(9)	-151.1
C(7)-C(5)-C(6)-C(8)	-82.5
C(7)-C(5)-C(6)-C(9)	148.8
C(10)-C(11)-C(12)-Cl(1)	176.9
C(10)-C(11)-C(12)-Cl(2)	55.7
C(10)-C(11)-C(12)-Cl(3)	-65.9
O(1)-C(11)-C(12)-Cl(1)	60.0
O(1)-C(11)-C(12)-Cl(2)	-61.1
O(1)-C(11)-C(12)-Cl(3)	177.3

but expected, distortion of the four-membered ring C(1),C(6),C(5),C(7) of the pinene moiety. Particularly noticeable features are the puckering of this ring, and the appreciable lengthening of the C(1)-C(6) and C(1)-C(7) bonds relative to C(5)-C(6) and C(5)-C(7). The angles formed by the bridgehead atoms C(1) and C(5) are therefore slightly larger than the angles formed by the other two atoms of the ring, C(6) and C(7). The distortion of this part of the molecule is undoubtedly enhanced by the effects of unsaturation at C(2)-C(3). The very low values of dihedral angles C(1)-C(2)-C(3)-C(4) (-1.7°) and C(2)-C(3)-C(4)-C(5) (-1.8°) indicates

⁶ V. Garsky, D. F. Koster, and R. T. Arnold, *J. Amer. Chem. Soc.*, 1974, **96**, 4207; R. K. Hill, J. W. Morgan, R. V. Shetty, and M. E. Synerholm, *ibid.*, p. 4201.

the near-coplanarity of the atoms within these units. The computed distances of the five ring atoms C(1)—(5) from the least-squares plane through this molecular fragment (atoms weighted equally in the calculation) are, respectively, 0.023, -0.019, -0.002, 0.022, and -0.024 Å. The angle between the planes containing C(1), C(6), C(5) and C(1), C(7), C(5) is 140.1°, and the angles between each of these planes and the least-squares plane through C(1)—(5) are, respectively, 66.8 and 73.3°. Hence, the pinene unit of (2) when viewed along the C(1) ··· C(5) axis approximates remarkably well to a Y-shaped molecule.

Other notable features are the appreciable widening of the C(5)-C(6)-C(9) and C(1)-C(6)-C(9) bond angles from the tetrahedral value of 109.5°. These are a consequence of the strained four-membered ring; whereas the C(8)-C(6)-C(9) bond angle is near the tetrahedral value, the angle C(1)-C(6)-C(5) is, of course, less than 90°. Contrary to expectation, bonds C(1)-C(2) and C(3)-C(4) are not shorter than C(4)-C(5) but are all of equal length, even though the first two bonds involve the trigonal ring atoms C(2) and C(3). This feature again illustrates the distortion created by the double bond C(2)-C(3), and the tendency toward the equalisation of strain throughout the molecule.

The mean C-C bond length within the benzene ring is 1.391 Å, and all bonds are equivalent within experimental error. The average distance of the aromatic carbon atoms from the least-squares plane through the ring (all atoms weighted equally) was 0.010 Å, the largest distance being 0.016 Å. The atom C(19) was 0.048 Å from this mean plane, whilst S(1) lay 0.006 Å from it. The mean bond angle within the benzene ring was 120.0°, with no angle deviating significantly from this mean value.

Few crystallographic or other physical studies have been concerned with the details of the molecular structure of the pinene skeleton, and it is worthwhile drawing such comparisons as are possible.* One is that between the crystal and molecular structure of *cis*-pinocarvyl *p*-nitrobenzoate (*cis*-PNB),⁷ a molecule based on the pin-2(10)-ene skeleton [exocyclic double bond at C(2)] and of (2) which is a derivative of α -pinene [endocyclic double bond between C(2) and C(3)]. Excluding therefore comparisons at, or including, C(2) and C(3) in the two systems, bond-length agreements are within ± 0.025 Å except for the C(6)-C(9) bond which is 0.03 Å shorter in (2); hence, all differences lie within the range of experimental error. Bond-angle agreements are all within $\pm 2^\circ$ except for C(5)-C(6)-C(9) which is 2.9° larger in (2), and C(2)-C(1)-C(7) which is 7.1° smaller in (2). This last case, however, includes C(2), an atom which is not strictly comparable in its two different situations. The exclusion of C(2) and C(3) disqualified

comparison of eight of the fourteen ring torsion angles; the remaining six agree to within $\pm 1.5^\circ$ in the two systems. The angles between plane C(1), C(6), and C(5) and plane C(1), C(7), C(5) agree to within 1°. The correlation between the relevant portions of (2) and *cis*-PNB is therefore extremely good.

The assignment of the ¹H n.m.r. spectrum of (2) (see Experimental section) relies on comparison with literature data,² which itself depends upon assumed or deduced bond angles and dihedral angles and upon the applicability of the Karplus equation to such strained-ring systems. In the case of pin-2-ene (the most direct comparison) several of the assumptions are broadly justified, for example the planarity of the C(1)—(5) unit and a C(5)-C(7)-C(1) angle of *ca.* 87°. However, an assigned dihedral angle of the cyclobutane part of *ca.* 150° is seen to be *ca.* 9–10° too large; as a consequence, the deduction that the H-C-H angle in the cyclobutane is much smaller than tetrahedral is incorrect, the angle H(7A)-C(7)-H(7B) is 112.0(8)°. The lack of observable ¹H couplings $J_{1,7A}$ and $J_{5,7B}$ was rationalised in terms of the Karplus $\cos^2\phi$ relationship by assuming the torsion angles H(7B)-C(7)-C(1)-H(1) and H(7B)-C(7)-C(5)-H(5) to be close to 85°; in fact these values are, respectively, -94.4 and 84.4°, making the reason for the lack of coupling a little clearer. The ¹H coupling constants $J_{1,7A}$ and $J_{5,7A}$ of *ca.* 5.5 Hz were thought reasonable for the assumed dihedral angles of *ca.* 40°. However, in (2) the torsion angles H(1)-C(1)-C(7)-H(7A) and H(5)-C(5)-C(7)-H(7A) are, respectively, 33.6 and -49.6°. Thus, the fact that $J_{5,7A} \geq J_{1,7A}$ in the pinene series can be explained in terms of the larger dihedral angle for H(5)-C(5)-C(7)-H(7A) rather than in terms of differences in electronegativity [*i.e.* C(1) is usually attached to a more electronegative sp^2 hybridised carbon atom].

The structural analysis of (1) by means of this study of its tosylate ester serves a second purpose. Reaction of the chloral-olefin ene adducts with excess of sodium ethoxide in dry ethanol affords, after aqueous acid work-up, the α -ethoxy-carboxylic acids [reaction (2)]



in nearly quantitative yield.¹ Various features of this reaction are puzzling, but the availability of an ene adduct of known absolute configuration at the chiral centre will considerably assist in the study of the stereochemistry and mechanism of reaction (2).

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* We thank a referee for suggestions concerning this section.

⁷ G. F. Richards, R. A. Moran, J. A. Heitmann, and W. E. Scott, *J. Org. Chem.*, 1974, **39**, 86.