Studies of Chrysanthemic Acid Derivatives: Catalysed Reactions of 3-(2-Hydroxymethyl-3,3-dimethylcyclopropyl)-2-methylpropanol and Formation of a Novel Eight-membered Cyclic Sulphite†

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Acid catalysed reaction of the cyclopropanediol (3) derived from *cis*-chrysanthemic acid *cis*-(1) afforded, depending on the reaction conditions, 3-vinyl-2,2,5,5-tetramethyltetrahydrofuran (4) and 4,4,7,7-tetramethyl-3-oxabicyclo[4.1.0]heptane (5). On treatment with thionyl chloride–pyridine complex there was obtained in addition the eight-membered cyclic sulphite, 6,6,9,9-tetramethyl-3,5-dioxa-4-thiabicyclo[6.1.0]nonane 4-oxide (6). X-Ray analysis confirms a boat-chair conformation with the S=O group *trans* to the cyclopropane ring and in an equatorial situation. Thermal reaction of (6) gave either (4) or a mixture of (5), *cis*-chrysanthemol (7), and *cis*-isochrysanthemol (8).

The (+)-*trans*-chrysanthemic acid *trans*-(1), an essential component of naturally occurring pyrethrin esters and its synthetic analogues such as allethrin and bioresmethrin are known for their high insecticidal activity with low mammalian toxicity.[1] Some synthetic *cis*-chrysanthemic acid esters such as cismethrin also have excellent insecticidal activity.[2]
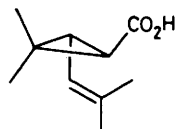

(1)-*trans*

The *trans*-chrysanthemic acid is readily separated from the commercially available racemic *cis/trans* mixture of ethyl chrysanthemate by lactonising the *cis*-chrysanthemic acid (1)-*cis* in the presence of a Lewis acid to dihydrochrysanthemolactone (2).[3]

During our investigation of the biological properties of (2) and its reduced derivative, the *cis*-cyclopropanediol (3), there was obtained a 10% impurity which was found to be 3-vinyl-2,2,5,5-tetramethyltetrahydrofuran (4) and was apparently formed from the acid catalysed rearrangement of (3). It was of interest to investigate some chemical reactions of the cyclopropanediol (3) in acidic and basic conditions.

Results and Discussion

Reaction of a hexane mixture of (3) with 50% aqueous sulphuric acid gave only (4) on inspection by g.l.c. analysis. The i.r. spectrum showed the presence of a vinyl group ($\nu_{max.}$ 3 080, 1 640, 990, and 910 cm^{-1}) and a cyclic ether band at $\nu_{max.}$ 1 110 cm^{-1}. The n.m.r. spectrum of the tetrahydrofuran gave an eight-line signal (ddd, vinylic hydrogen) centred at δ 5.72 (*J* 17.2, 10.2, and 8.3 Hz), two split doublets at δ 5.14 and 5.04 (CH$_2$), and a broad doublet of triplets centred at δ 2.70 (*J* 9.5 and 8.1 Hz) (allylic hydrogen). The geminal ring hydrogens appear as a doublet at δ 1.91 (*J* 9.5 Hz) which on decoupling gave a doublet at δ 2.70 (*J* 8.3 Hz). These spectral data confirm the
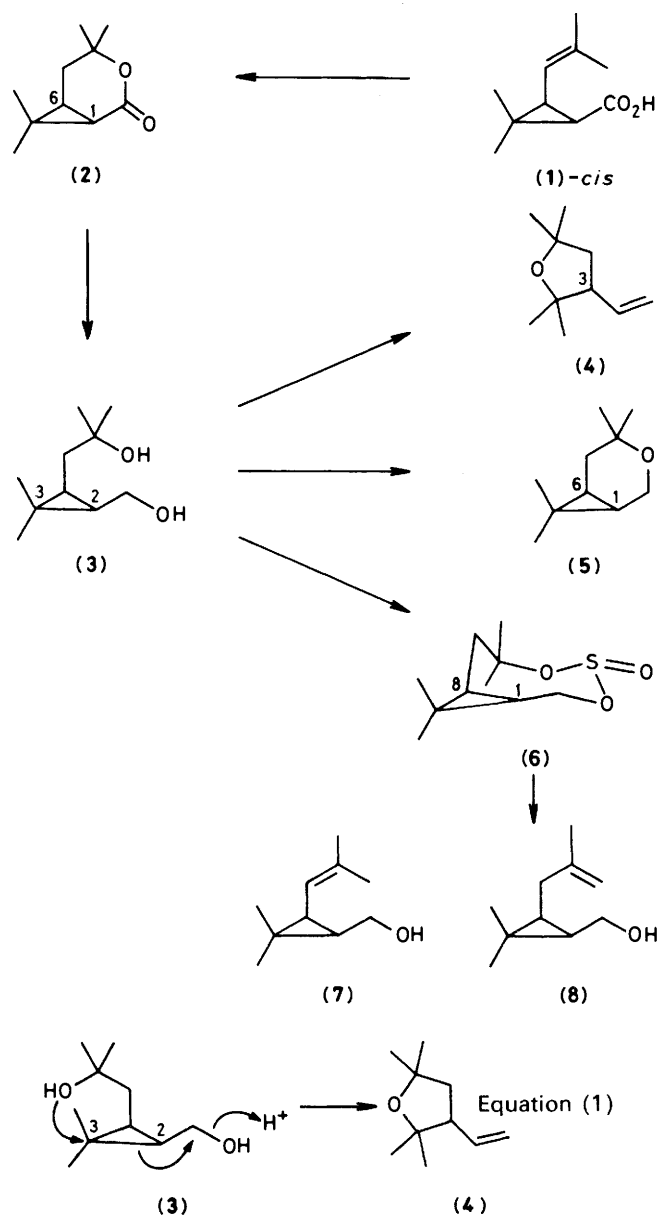
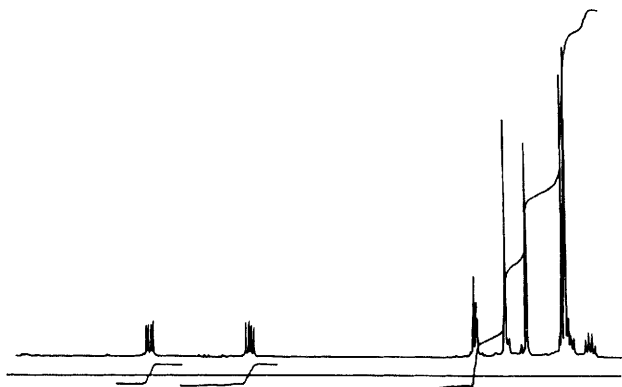Figure 1. ¹H N.m.r. spectrum of the cyclic sulphite (6)

Figure 2. The molecular structure of the cyclic sulphite (6)

vinyltetrahydrofuran (4) obtained by the acid catalysed rearrangement of the *cis*-cyclopropanediol (3) presumably *via* a mechanism involving ring cleavage of the 2,3 bond of the cyclopropane ring as shown in equation (1).[4]

On the other hand, reaction of the disodium salt of (3) with thionyl chloride gave a 90% yield of the isomeric cyclic ether of (4) which, on the evidence of spectral data, was the 3-oxabicyclo[4.1.0]heptane (5). The n.m.r. spectrum showed the two cyclopropane protons centred at δ 0.84 and 0.43 (*J* 9.5 Hz) verifying that under basic conditions the cyclopropane ring had not ruptured but, instead, the expected cyclisation of the diol to the pyran had occurred. Furthermore, reaction of the *cis*-cyclopropanediol (3) with pyridine–thionyl chloride complex gave two products: an oil (70% yield) the spectral data of which indicated that it was the 3-oxabicyclo[4.1.0]heptane (5) and a 20% yield of a pure crystalline product (m.p. 103.5 °C). Analytical and spectral data showed that the latter was an eight-membered cyclic sulphite (6). The i.r. spectrum of (6) shows intense absorption at $v_{max.}$ 1 192 cm⁻¹ (Nujol) and $v_{max.}$ 1 200 cm⁻¹ (KBr) which is characteristic of the S=O stretching vibration.[5] Hellier and Webb had investigated six-membered cyclic sulphites which may exist in a rigid chair conformation with either an axial or equatorial S=O group; the intense absorption at *ca.* $v_{max.}$ 1 230 cm⁻¹ is characteristic of an equatorial S=O group.[6] Petit, Lenstra, and Geise[7] confirmed by *X*-ray analysis that the S=O was equatorial in *cis*,*cis*-4,6-dimethyltrimethylene sulphite, a compound previously synthesised by Hellier and Webb who also assigned the S=O group conformation. The only known seven-membered cyclic sulphites were assigned for the S=O bond stretching vibration according to the results for six-membered cyclic sulphites. Thus, Faucher *et al.*[8] concluded from dynamic n.m.r. and i.r. spectroscopy that the seven-membered cyclic sulphite, 2-oxo-1,3,2-dioxathiepine consists of a mixture of a twist-boat and axially ($v_{max.}$ 1 184 cm⁻¹) orientated S=O bond. It was assumed that only slight changes take place in the S=O stretching frequency in going from a six- to a seven-membered ring (Δv ~10 cm⁻¹). If the same analogy is applied, then it can be assumed from the i.r. spectral data for the eight-membered cyclic sulphite (6) that the S=O bond is axial (*vide infra*).

The ¹H n.m.r. spectrum (Figure 1) shows signals at δ 4.78 (dd) and 3.88 (dd) indicative of the magnetic nonequivalence of the α-methylene protons adjacent to the oxygen atom. The magnitude of the coupling constant, J_{gem} 13.4 Hz, is very close to that of the known seven-membered cyclic sulphites (J_{gem} 14 Hz)[9] but higher than that of six-membered cyclic sulphites (J_{gem} 11—12.5 Hz).[10] At highfield the two-proton signals centred at δ 1.04 and 0.85 were assigned to the two *cis*-hydrogens of the cyclopropane ring (*J* 8.9 Hz). The ¹³C n.m.r. spectrum gives a clearly decoupled spectrum showing ten lines. The lines at δ
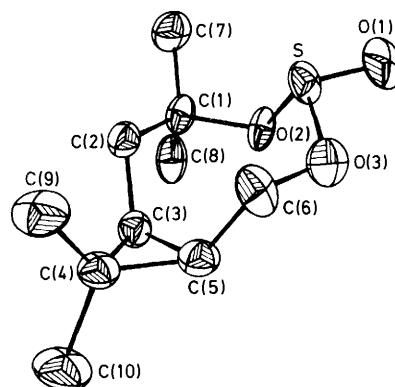
82.86 and 60.09 each adjacent to an oxygen atom arise from C-6 and C-2 of the ring. Hellier and Phillips suggested that for the six-membered cyclic sulphite, 4,4-dimethyl-1,3,2-dioxathiane 2-oxide[11] (C-4 δ 80.3 and C-6 δ 55.6), the S=O group is axial. Of particular interest is the structure of the novel eight-membered ring sulphite (6). In principle, two geometrical isomers are conceivable; a *cis*-isomer where the cyclopropane ring and the S=O group are on the same face of the cyclo-octane ring and the *trans*-isomer in which the two groups are on opposite sides of the cyclo-octane ring. Furthermore, it was of interest to determine, for the isomer obtained, which is the favoured conformation and unequivocally determine whether the S=O group is axial or equatorial.

Thus, crystals of the sulphite (6) were prepared, by slow evaporation of a pentane solution at room temperature, for *X*-ray analysis.

Crystallographic Measurements.—*X*-Ray analysis data were collected on a PW 1100/20 Philips four-circle computer controlled diffractometer. Mo-K_α (λ = 0.710 69 Å) radiation with a graphite crystal monochromator in the incident beam was used. The unit cell dimensions were obtained by a least-squares fit of 22 centred reflections. Intensity data were measured applying the ω–2θ technique to 2θ < 50°. The scan width, $\triangle w$ for each reflection was 1° with a scan time of 20 s. Background measurements were made at both limits of each scan. Intensities were corrected for Lorentz and polarization effects. All non-hydrogen atoms were found by using the results of the MULTAN[12] direct method analysis. After several cycles of refinement* the positions of the hydrogen atoms were calculated and introduced with a constant isotropic temperature factor of 0.5 Å². Refinement proceeded to convergence by minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, where the weight *w* is $\sigma(F_o)^{-2}$. The discrepancy indices $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$, and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ are presented with other crystal data.

Crystal Data.—$C_{10}H_{18}O_3S$, *M* = 218, m.p. 103.5 °C, monoclinic, *a* = 7.385(1), *b* = 8.756(1), *c* = 18.169(2) Å, β = 97.63(2)°, *U* = 1164.5 Å³, *Z* = 4, D_c = 1.25 g cm⁻³, *F*(000) 472, space group $P2_1/C$, *R*-factor 0.041, weighted *R*-factor 0.066. Crystal dimensions 0.4 × 0.4 × 0.5 mm. 1 680 Reflections having *I* > 3σ(*I*) were used in the final refinement cycles. Atomic co-ordinates are listed in Table 1 and bond lengths and angles in Table 2. Observed and calculated structure amplitudes

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* All crystallographic computing was carried out on a CYBER 74 Computer at the Hebrew University of Jerusalem, using the SHELX 1977 structure determination package.

Table 1. Fractional atomic co-ordinates

Atom	x	y	z
S	0.553 58(7)	0.561 03(7)	0.789 98(3)
O(1)	0.6859(2)	0.4615(2)	0.7624(1)
O(2)	0.4173(2)	0.4471(2)	0.824 34(9)
O(3)	0.6670(2)	0.6259(2)	0.865 67(9)
C(1)	0.2174(3)	0.4814(3)	0.8140(1)
C(2)	0.1821(3)	0.6337(3)	0.8517(1)
C(3)	0.2659(3)	0.6455(3)	0.9321(1)
C(4)	0.2993(3)	0.7956(3)	0.9724(1)
C(5)	0.4604(3)	0.7011(3)	0.9545(1)
C(6)	0.5787(3)	0.7533(3)	0.8993(1)
C(7)	0.1477(3)	0.4883(3)	0.7312(1)
C(8)	0.1382(3)	0.3447(3)	0.8498(2)
C(9)	0.2506(4)	0.9452(3)	0.9325(1)
C(10)	0.2686(4)	0.7984(3)	1.0534(1)

Table 2. Bond lengths (Å) and angles (°) for the cyclic sulphite (6)

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S–O(1)	1.448(2)	C(2)–C(3)	1.513(2)
S–O(2)	1.602(1)	C(3)–C(4)	1.508(3)
S–O(3)	1.615(1)	C(3)–C(5)	1.520(2)
O(2)–C(1)	1.493(2)	C(4)–C(5)	1.519(3)
O(3)–C(6)	1.467(3)	C(4)–C(9)	1.517(3)
C(1)–C(2)	1.538(3)	C(4)–C(10)	1.520(3)
C(1)–C(7)	1.524(3)	C(5)–C(6)	1.487(3)
C(1)–C(8)	1.517(3)		
O(1)–S–O(2)	104.34(2)	C(2)–C(3)–C(5)	122.1(2)
O(1)–S–O(3)	102.0(1)	C(4)–C(3)–C(5)	60.2(1)
O(2)–S–O(3)	99.71(9)	C(3)–C(4)–C(5)	60.3(1)
S–O(2)–C(1)	119.1(1)	C(3)–C(4)–C(9)	120.5(2)
S–O(3)–C(6)	114.4(1)	C(3)–C(4)–C(10)	116.6(2)
O(2)–C(1)–C(2)	110.0(2)	C(5)–C(4)–C(9)	120.7(2)
O(2)–C(1)–C(7)	109.3(2)	C(5)–C(4)–C(10)	116.0(2)
O(2)–C(1)–C(8)	102.6(2)	C(9)–C(4)–C(10)	113.1(2)
C(2)–C(1)–C(7)	110.5(2)	C(3)–C(5)–C(4)	59.4(1)
C(2)–C(1)–C(8)	113.3(2)	C(3)–C(5)–C(6)	122.5(2)
C(7)–C(1)–C(8)	110.8(2)	C(4)–C(5)–C(6)	121.6(2)
C(1)–C(2)–C(3)	114.7(2)	O(3)–C(6)–C(5)	112.4(2)
C(2)–C(3)–C(4)	123.2(2)		

and thermal parameters are listed in a Supplementary Publication (SUP No. 23854, 12 pages).†

Conformation of the Cyclic Sulphite.—The X-ray analysis of the sulphite (6) (see Figure 2) reveals an approximate boat-chair (BC) conformation with the S=O group in the *trans equatorial* position. It is known that cyclo-octane and its derivatives exist predominantly in the BC conformation.[13] The condensed cyclopropane ring causes a distortion of the conformation of the sulphite ring in such a way that it better resembles *cis*-cyclo-octene (9) whose low energy conformation was deduced from n.m.r. and conformational calculation studies[13,14] to be a slightly twisted BC conformation. This is also confirmed from the X-ray structure of 9,9-dimethyl-9-azoniabicyclo[6.1.0]-nonane iodide (10)[15] which also has a similar BC conformation to (6). If one or more carbons of the eight-membered ring is interrupted by a heteroatom such as nitrogen, phosphorus, or sulphur it is found that the BC conformation of the ring is still retained. This is verified by X-ray analyses of a cyclic phosphate,[16] a cyclic sulphoxide,[17] and more recently an imidosulphite.[18] These eight-membered heterocyclic structures all possess the BC ring conformation which enables 1,5-interactions between the heteroatoms phosphorus or sulphur and nitrogen. Clearly, these transannular interactions do not exist in the sulphite (6). The position of the

† For details of the Supplementary publications scheme see Instructions for Authors (1984), *J. Chem. Soc., Perkin Trans 1*, 1984, Issue 1.
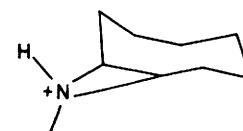
(9)   (10)

heteroatoms is stereocontrolled by the cyclopropane ring condensed through the C(1)–C(8) bond and its plane equatorial. Furthermore it appears that the steric requirements of the cyclopropane ring are also responsible for the fact that only one stereoisomeric sulphite was isolated, namely that with the *trans* configuration which, in turn, has the cyclopropane and S=O groups in the most stable equatorial conformation.

To our knowledge no eight-membered cyclic sulphites with an axial S=O bond have been prepared. The preferential equatorial direction of the S=O group in (6) is in contradistinction to the normally observed axial conformation found in six- and seven-membered cyclic sulphites;[9] it is also the reverse of that predicted by the observation of an equatorial S=O vibration in the i.r. spectrum ($v_{max.}$ 1 230 cm^{-1}).[5,6]

Clearly the axial–equatorial i.r. frequency rule for six-[5,6] and seven-membered[9] ring sulphites is not applicable to the eight-membered ring counterparts.

Geometry around the Sulphur Atom.—The sum of the angles around the sulphur atom of (6) is 306° indicating a pyramidal structure which is more pronounced than that for the imidosulphite (310°)[18] and the trimethylene sulphites (308—314°).[7,19] A variation of 4.7° is observed between the two S–O–C angles and is probably due to the dissymetry of the BC conformation of (6). This phenomenon occurs in the BC conformers of eight-membered rings. The S–O bonds (1.60 and 1.62 Å) are very close to the accepted bond lengths of sulphites (1.60 Å). The C–O distances (1.467 and 1.493 Å) are higher than the accepted values for C–O bonds in ethers and alcohols (1.43—1.44 Å) but the deviation is not significant. The valency angles of the chair side of the sulphite are close to the average valence angle of 116° of the BC conformer of cyclo-octane. As expected, the cyclopropane ring distorts to a greater extent the boat side of the sulphite as observed by the higher valence angles.

Thermal Reactions of the Sulphite (6).—When the cyclic sulphite (6) was heated in a sealed tube at 160 °C for 30 min it was found that only the vinyltetrahydrofuran (4) and sulphur dioxide were obtained (100% by g.l.c. and structure confirmed by n.m.r.) On the other hand if a solution of (6) in methylene chloride was injected into a Carbowax column, programmed from 40—205 °C it was found that two distinct peaks were obtained on the chromatogram. The first compound (35% by g.l.c.) was the 3-oxabicyclo[4.1.0]heptane (5) which was confirmed by n.m.r. spectroscopy. The other peak was found to be a mixture of two isomeric alcohols as observed from the i.r. and n.m.r. spectra. The i.r. spectrum reveals a primary hydroxy group at *ca.* $v_{max.}$ 3 300 and 1 020 cm^{-1} and strong vibrations at $v_{max.}$ 1 650 and 885 cm^{-1} which are characteristic of the vinyl group. The n.m.r. spectrum suggests the presence of two isomeric alcohols, *cis*-chrysanthemol (7) (60%) and *cis*-iso-chrysanthemol (8) (40%). The alcohols were quantitatively estimated from the intensity of the methyl singlets attached to the cyclopropane ring. The ¹H n.m.r. spectral data for (7) reveal a vinylic hydrogen doublet at δ 4.98 (*J* 8.4 Hz) coupled with an allylic cyclopropane hydrogen which appears as a triplet at δ 1.40 (*J* 8.4 and 9.0 Hz). The singlets at δ 1.74 and 1.71 correspond to the two methyls of the cyclopropane ring. The *cis*-isochrysanthemol (8) was inferred from the two broad methylene singlets at δ 4.83 and at 4.78, the vinylic methyl group

at δ 1.78, the allylic methylene triplet at δ 2.07 (*J* 6.7 Hz) and the two methyls of the cyclopropane ring at δ 1.12 and δ 1.03. The multiplet at δ 3.63 corresponds to the carbinol methylene hydrogens of both isomers (7) and (8).

Summary.—It was found that the reactions of the *cis*-cyclopropanediol (3) gave specific products under controlled conditions. In acidic media the cyclopropane ring is ruptured and rearrangement to the vinyltetrahydrofuran (4) occurs whereas under basic conditions the cyclopropane ring is unaffected and the pyran (5) is formed instead. In the presence of pyridine–thionyl chloride complex the crystalline eight-membered cyclic sulphite is obtained as the *trans*-isomer only. *X*-Ray analysis confirms a BC conformation with the S=O group in the equatorial position. Thermal reactions of the cyclic sulphite (6), depending upon the reaction conditions, results in either the vinyltetrahydrofuran (4) or a mixture of the pyran (5) and two isomeric *cis*-chrysanthemols (7) and (8).

Experimental

General.—^{1}H N.m.r. spectra were recorded on a Brucker WX 300 spectrometer using 5 μl of the sample per 300 μl of [^{2}H]-chloroform solution. Deuterium lock was provided by the solvent (CDCl$_3$) and tetramethylsilane (TMS) as the internal standard. Splittings (*J*) are given in Hz. I.r. spectra were measured with a Perkin-Elmer Model 157G. Preparative g.l.c. separations were carried out on a F & M Model 720 dual column programmed temperature gas chromatograph (equipped with both thermal conductivity and flame ionization detectors). The separations were achieved on a 2 m 10% OV 17 on Chromosorb W. The conditions were: detector temperature 300 °C, inlet temperature 245 °C, rate 4 °C/min, programmed from 60 to 210 °C. Molecular weights were determined from mass spectra measured on a Finnigan Model 4021 Gas Chromatograph Mass Spectrometer with data system. The conditions used for the g.c./mass spec. were an XE-60 column, programmed 50—180 °C at 5 °C/min. Elemental analyses were carried out at the analytical laboratories of the Hebrew University of Jerusalem.

Melting points were determined on a Thomas-Hoover apparatus and were uncorrected.

4,4,7,7-Tetramethyl-3-oxabicyclo[4.1.0]heptan-2-one (2).—Ethyl chrysanthemate used was commercially available (Aldrich) and contains a racemic mixture of *trans*:*cis* isomers (6 : 4). *cis*/*trans*-Chrysanthemic acid (obtained from alkaline hydrolysis of *cis*/*trans*-ethyl chrysanthemate) (79.5 g, 0.47 mol) and anhydrous zinc chloride (11 g) in ethylene dichloride (190 ml) were stirred for 19 h at 80 °C. The cooled mixture was stirred with saturated ammonium chloride solution (100 ml) for 10 min. The organic layer was separated and extracted with three portions (100 ml, 2 × 50 ml) 10% aqueous potassium hydroxide to remove the *trans*-chrysanthemic acid. The ethylene dichloride was removed to afford the crude *cis* δ-lactone (2) (32.5 g, 41%) which was distilled as a colourless oil, b.p. 84.5—85 °C (1.5 mmHg); it crystallised with time, m.p. 50—51 °C, (lit.,[3] 52—53°C) (Found: C, 71.7; H, 9.8. Calc. for C$_{10}$H$_{16}$O$_2$: C, 71.39; H, 9.58%); ν$_{max.}$(KBr)1 720 (CO), 1 385, 1 370, 1 100, and 1 010 cm^{-1} (cyclopropyl); the ^{1}H n.m.r. spectrum of the product was identical with that in the literature,[20] δ$_C$(CDCl$_3$) 173.38, 85.8, 32.83, 31.55, 30.06, 29.76, 28.74, 27.09, 25.44, and 18.67 p.p.m.; *m*/*z* 168 (*M*$^+$, 0.44%), 153 (8.2%, *M* − *CH*$_3$), 124 (14.8%, *M* − CO$_2$), 109 (67.5%, *M* − CO$_2$ − CH$_3$), 95 (54.5%), 81 (21.1%), 67 (67.1%), 55 (18.6%), and 43 (100%).

3-(2-Hydroxymethyl-3,3-dimethylcyclopropyl)-2-methyl-propan-2-ol (3).—The δ-lactone (2) (56 g, 0.33 mol) in anhyd-

rous ether (200 ml) was added dropwise to an ice-cooled solution of lithium aluminium hydride (12.5 g, 0.33 mol) in anhydrous ether (600 ml) under nitrogen for 2 h. The mixture was further stirred at room temperature for 24 h and ethyl acetate (100 ml) was slowly added to destroy excess of hydride. The resulting mixture was filtered over Celite and the ether removed to afford a semi-crystalline solid of the dilithium salt of (3); 20% aqueous hydrochloric acid (100 ml) and pentane (150 ml) were added and the mixture was stirred for 30 min. The pentane layer was dried and decolourised over a mixture of anhydrous magnesium sulphate and Nurite. Removal of the solvent gave a colourless oil which crystallised to the cyclopropane diol (3)[21] (40 g, 70%), m.p. 49 °C (Found: C, 69.45; H, 11.4. Calc. for C$_{10}$H$_{20}$O$_2$: C, 69.72; H, 11.70); ν$_{max.}$(KBr) 3 270 cm^{-1}, δ$_H$ 3.80 (1 H, dd, *J* 11.7 and 5.4 Hz), 3.47 (1 H, dd, *J* 11.7 and 10.5 Hz), 2.40 (2 H, br s), 1.63 (1 H, dd, *J* 14.7 and 3.9 Hz), 1.45 (1 H, dd, *J* 14.7 and 9.9 Hz), 1.31 (3 H, s), 1.28 (3 H, s), 1.08 (3 H, s), 0.96 (3 H, s), 0.92 (1 H, m, obscured), and 0.70 (1 H, dt, *J* 9.9, 8.7, and 3.9 Hz); δ$_C$(CDCl$_3$) 70.69, 58.78 (2 × C–OH), 37.35 (CH$_2$), 31.72, 29.21, 28.44, 27.92 (4 × CH$_3$), 22.16, 17.02, and 15.22 p.p.m. (3 × C-cyclopropane).

2,2,5,5-Tetramethyl-3-vinyltetrahydrofuran (4).—The cyclopropanediol (3) (2.54 g) in hexane (25 ml) was stirred with 50% aqueous sulphuric acid (5 ml) at 5 °C for 1 h. Work-up and removal of the solvent gave the pure tetrahydrofuran (4) (1.8 g, 77%), b.p. 43 °C at 20 mmHg; ν$_{max.}$(neat) 3 085, 1 838, 1 645 (CH=CH$_2$), 1 380, 1 370, 995, and 915 cm^{-1} (THF); δ$_H$ 5.72 (1 H, ddd, *J* 17.2, 10.2, and 8.3 Hz), 5.14 (1 H, split d, *J* 17.2 Hz), 5.04 (1 H, split d, *J* 10.2 Hz), 2.70 (1 H, br dt, *J* 9.5 and 8.3 Hz), 1.91 (2 H, d, *J* 9.5 Hz), 1.32 (3 H, s), 1.25 (3 H, s), 1.21 (3 H, s), and 1.03 (3 H, s); *m*/*z* 154 (*M*$^+$, 0.27%) 139 (8%, *M* − CH$_3$) 124 (4.1%, *M* − 2CH$_3$), 109 (6.5%, *M* − CH$_3$), 96 (59.6%), and 81 (100%). An acceptable microanalysis was not obtainable since the compound was too volatile; purity confirmed by g.l.c. (1 peak) and n.m.r. spectroscopy.

4,4,7,7-Tetramethyl-3-oxabicyclo[4.1.0]heptane. (5)—Freshly distilled t-pentyl alcohol (2.8 g, 31 mmol) in anhydrous toluene (17 ml) was added dropwise to a stirred solution of NaH (1.08 g, 55% oil dispersion) and anhydrous toluene (11 ml) under nitrogen. The mixture was heated to 70 °C for 30 min after which the solvents were removed to give sodium t-pentoxide (2.7 g). The cyclopropanediol (3) (2 g, 12 mmol) in toluene (10 ml) was added to the sodium t-pentoxide and the mixture refluxed for 3 h. After distilling off the toluene and t-pentyl alcohol the residual salt of (3) in toluene (10 ml) was cooled in an ice–water bath and thionyl chloride (1.4 g, 11 mmol) in toluene (20 ml) was added dropwise. The mixture was further stirred for 2 h and the solvents were removed by slow distillation. Chloroform (25 ml) was added to the residual brown-white solid and the mixture stirred for 10 min, filtered, and the chloroform removed to yield a yellow oil of (5) (1.5 g, 83%) (Found: C, 78.1; H, 11.7. Calc. for C$_{10}$H$_{18}$O: C, 77.87, H, 11.67%); ν$_{max.}$(neat) 1 380, 1 370, 1 220, 1 200, 1 100 (THP), 1 014, 940, and 815 cm^{-1} (THP); δ$_H$ 4.02 (1 H, dd, *J* 12.1 and 5.1 Hz), 3.77 (1 H, d, *J* 12.1 Hz), 1.61 (1 H, dd, *J* 14.3 and 10.2 Hz), 1.29 (1 H, dd, *J* 14.3 and 3.8 Hz), 1.20 (3 H, s), 1.10 (3 H, s), 1.05 (3 H, s), 1.01 (3 H, s), 0.84 (1 H, dt, *J* 10.2, 9.5, and 3.8 Hz), and 0.43 (1 H, dd, *J* 9.5 and 5.1 Hz).

6,6,9,9-Tetramethyl-3,5-dioxa-4-thiabicyclo[6.1.0]nonane 4-Oxide (6).—Thionyl chloride (2.4 g, 21 mmol) in pentane (10 ml) was added dropwise to a stirred ice-cold solution of pyridine (5 ml) and pentane (15 ml). To the resulting complex there was added, dropwise, a solution of the *cis*-cyclopropanediol (3) (3.5 g, 20 mmol) in pentane (50 ml) and pyridine (10 ml). The resulting mixture was stirred for 90 min. Pentane (50 ml) was added and the pentane mixture was washed with saturated

saline (2 × 30 ml), dried over anhydrous magnesium sulphate, and the pentane removed to yield a colourless oil. The pyridine was removed under reduced pressure and the residual semi-crystalline oil was triturated in pentane (5 ml). The resulting solution was cooled and filtered to afford pure crystalline (6) (0.92 g, 21%), m.p. 103.5 °C (Found: C, 55.3; H, 8.0; S, 14.5. Calc. for $C_{10}H_{18}O_3S$: C, 55.02; H, 8.31; S, 14.69%), $\nu_{max.}$(KBr) 1 200 (sulphite), 1 025 (cyclopropyl), 940, 930, 760, and 710 (S–O–C), and 683 cm^{-1} (SO); δ_H 4.78 (1 H, dd, J 13.4 and 5.4 Hz), 3.88 (1 H, dd, J 13.4 and 7.6 Hz), 1.87 (2 H, m), 1.61 (3 H, s), 1.42 (3 H, s), 1.10 (3 H, s), 1.07 (3 H, s), 1.04 (1 H, m, obscured), and 0.85 (1 H, dt, J 8.9, 8.9, and 7.0 Hz); δ_C(CDCl$_3$) 82.86 (C-6), 60.09 (C-2), 36.07 (C-7), 29.30 (CH$_3$), 28.82 (CH$_3$), 27.32 (CH$_3$), 25.40 (C-1), 22.08 (C-8), 18.00 (C-9), and 15.07 p.p.m. (CH$_3$); m/z (CI) 218 (M^+, 0.17%), 137 (100%, $M - SO_3H$), and 81 (16.5%, SO$_3$H). Removal of the pentane from the filtrate afforded (5) (2 g, 64%).

Thermal Rearrangements of the Cyclic Sulphite (6).—(a) The sulphite (6) (37.2 mg) was heated at 160 °C in a sealed tube for 30 min. On opening the tube, SO$_2$ was detected and the residual oil was found to be pure (4) (g.l.c. and n.m.r.).

(b) A 70% solution of the cyclic sulphite (6) (100 μl) in methylene chloride was injected into a column (2.5 m × 0.75 in diam.) containing 10% Carbowax 20M on Chromosorb W, programmed at 40—205 °C at a rate 7.5 °C/min. Inlet temperature 210 °C, detector temperature 300 °C. Two products were obtained: (a) 35% of (5) and (b) 65% of an isomeric mixture of *cis*-chrysanthemol (7) (60%) and *cis*-isochrysanthemol (8) (40%). These two alcohols could not be separated on the column. They were identified by i.r. and n.m.r. spectroscopy (see text).

Acknowledgements

References

1 'Synthetic Pyrethroids', ACS Symposium Series No. 42, ed. M. Elliott, American Chemical Society, Washington, D.C., 1977.

2 M. Elliott and N. F. Janes, *Chem. Soc. Rev.*, 1978, **7**, 473.
3 L. Crombie, S. H. Harper, and R. A. Thompson, *J. Sci. Food Agric.*, 1951, **2**, 421.
4 H. Hart and P. A. Law, *J. Am. Chem. Soc.*, 1962, **84**, 2462; N. C. Deno, H. G. Richey, Jr., J. S. Liu, J. D. Hodge, J. J. Houser, and M. J. Wisotsky, *J. Am. Chem. Soc.*, 1962, **84**, 2016.
5 C. H. Green and D. G. Hellier, *J. Chem. Soc., Perkin Trans. 2*, 1972, 458.
6 D. G. Hellier and F. J. Webb, *J. Chem. Soc., Perkin Trans. 2*, 1977, 613.
7 G. Petit, A. T. H. Lenstra, and H. J. Geise, *Bull. Soc. Chim. Belg.*, 1978, **87**, 659.
8 H. Faucher, A. C. Guimaraes, J. B. Robert, F. Sauriol, and M. St-Jacques, *Tetrahedron*, 1981, **37**, 689.
9 H. Faucher, A. C. Guimaraes, and J. B. Robert, *Tetrahedron Lett.*, 1977, 1743.
10 P. Albriktsen, *Acta Chem. Scand.*, 1972, **26**, 1783; 3687; T. Virtanen, H. Nikander, K. Pihlaja, and E. Rahkamaa, *Tetrahedron*, 1982, **38**, 2821.
11 D. G. Hellier and A. M. Phillips, *Org. Magn. Reson.*, 1982, **18**, 178.
12 P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, 'MULTAN 78. A system of Computer Programs for the automatic solution of Crystal Structures from X-ray Diffraction Data,' Universities of York, England and Louvain, Belgium, 1978.
13 F. A. L. Anet, 'Conformational Analysis,' ed. G. Chiurdoglu, Academic Press, New York, 1971, p. 15, R. W. Miller and A. T. McPhail, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1527.
14 G. Favini, G. Beumi, and M. Raimondi, *J. Mol. Struct.*, 1968, **2**, 137.
15 L. M. Trefonas and R. Majeste, *Tetrahedron*, 1963, **19**, 929.
16 J. Devillers, D. Houalla, J. J. Bonnet, and R. Wolf, *Nouv. J. Chim.*, 1980, **4**, 179.
17 I. C. Paul and Kuan Tee Go, *J. Chem. Soc. B*, 1969, 33.
18 C. Picard and L. Cazaux, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1554.
19 J. W. L. van Oyen, R. C. D. E. Hasekamp, G. C. Verschoor, and C. Romers, *Acta Crystallogr., Sect. B*, 1968, **24**, 1471; P. A. C. Carbonnelle, Y. Jeannin, and F. Robert, *Acta Crystallogr., Sect B*, 1978, **34**, 1631.
20 J. d'Angelo and G. Revial, *Tetrahedron Lett.*, 1983, 2103.
21 R. Sobti and S. Dev, *Tetrahedron*, 1974, **30**, 2927; Y. Gopichand, A. S. Khanra, R. B. Mitra, and K. K. Chakravarti, *Indian J. Chem.*, 1975, **13**, 433.